INTRINSIC DIFFUSION SIMULATION FOR SINGLE-PHASE MULTICOMPONENT SYSTEMS AND ITS APPLICATION FOR THE ANALYSIS OF THE DARKEN-MANNING AND JUMP FREQUENCY FORMALISMS

By

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2004
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Nagraj Sheshgiri Kulkarni
DEDICATED

This dissertation is dedicated to my father, the late Dr. S. N. Kulkarni, himself a scientist and advisor to many aspiring organic chemists. The unwavering support of my mother (Amma) and brothers, Anurag and Nandkishore, was deeply felt during the course of this quest for which I am eternally grateful.
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INTRINSIC DIFFUSION SIMULATION FOR SINGLE-PHASE MULTICOMPONENT
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By

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A multicomponent, single-phase, diffusion simulation based on Darken’s
treatment of intrinsic diffusion has been developed, which provides all the information
available from an intrinsic diffusion experiment, including composition profiles and
diffusion paths, lattice shifts and velocities, intrinsic and interdiffusion fluxes, as well as
fluxes and mean velocities in different frames of reference. The various steps involved in
the simulation are discussed and the self-consistency of the simulation is tested with the
aid of model systems having constant and variable molar volumes.

After an examination of the historical development of the Darken-Manning
theories and a brief discussion of previous tests in the literature, a systematic procedure
for the comprehensive assessment of these theories is proposed in which the intrinsic
diffusion simulation developed in this work occupies a central role. This procedure is
then utilized to perform an assessment of the Darken-Manning relations for four binary
systems: Ag-Cd, Au-Ni, Cu-Zn and Cu-Ni. It is shown that the Darken-Manning
relations that provide the connection between the tracer, intrinsic and interdiffusion coefficients, are unsatisfactory. Hence, it is suggested that the development of multicomponent diffusion databases, which often use the Darken relations for the evaluation of the phenomenological coefficients, may be compromised.

As an alternative to the traditional phenomenological formalism of multicomponent diffusion, a kinetic formalism based on atom jump frequencies is proposed. An expression for the intrinsic flux in terms of an unbiased and a biased component is derived. It is demonstrated with the aid of the simulation for the Cu-Zn system, that the biased flux may be evaluated from the experimental intrinsic flux and the unbiased flux (obtained from the tracer jump frequency). An unbiased jump frequency formalism that utilizes effective rather than tracer jump frequencies and avoids the complexities associated with bias effects has shown some success in modeling diffusion in ternary systems such as Fe-Ni-Co and the Fe-C-X systems, using simple jump frequency models obtained through an informed trial and error approach. A procedure to compute the effective jump frequency at every composition in a diffusion couple from the experimental intrinsic flux is discussed. It is suggested that the effective jump frequency approach, if validated through intrinsic diffusion measurements in ternary systems, offers the potential for building physically meaningful diffusion databases in multicomponent systems.
CHAPTER 1
INTRODUCTION

The study of diffusion and diffusion related processes in solid-state materials encompasses a broad spectrum of modern technologies. Semiconductors, precipitation hardened superalloys, metal and ceramic matrix composites, corrosion resistant coatings and alloys are all subject to complex diffusion processes that are dependent on a variety of operational parameters. The ability to analyze and model diffusion processes so as to be able to predict the variation in the relevant properties of such advanced materials assumes even greater significance today given the ever-increasing demands that are being placed on them. Global competition and budgetary constraints have reduced the time and finances available for significant experimental investigations due to which modeling efforts in fundamental areas such as diffusion are being increasingly emphasized. The present work is an effort in this direction.

Most of the present diffusion modeling efforts owe their origin to the phenomenological formalism first proposed by Adolf Fick [Fic55] in 1855 for the description of diffusion in binary electrolytes, which relates diffusion fluxes to driving forces which in his case were the concentration gradients. Since that time, significant progress has been made especially in the adaptation of the phenomenological formalism to multicomponent systems and the associated developments in the field of irreversible thermodynamics [Ons31, Ons32a, Pri55, Lec53, Gro62, How64, Man68, Haa69, Phi91, All93]. Typical studies in diffusion examine the diffusion of components with respect to
a fixed frame of reference, the so-called laboratory frame. This description of diffusion behavior known as *interdiffusion* has proven to be rather inadequate for the description of diffusion in solid state crystalline materials (indeed in liquids and gases as well) since variations in the movements of the individual components are not explicitly considered. For example in a single-phase binary system, there exists only a single independent interdiffusion flux and a single interdiffusion coefficient, which effectively means that differences in the actual movements of the two components are not accessible in the description.

That these differences are quite important was first suggested by Smigelskas and Kirkendall [Smi47] in their description of the “Kirkendall Effect,” a phenomenon in which imbalances in atom flows caused the appearance of porosity in their α Cu-Zn diffusion annealed couples. To explain their observations, Kirkendall proposed an atom-vacancy exchange mechanism as the primary diffusion mechanism for their system rather than the direct exchange mechanism [Zen50] that was prevalent at the time. Later, Darken [Dar48] in his seminal paper of 1948 provided a formal treatment that helped explain Kirkendall’s observations by describing the *intrinsic diffusion* of each atom species with respect to a frame of reference that effectively moves with the lattice on which the atoms reside, the so-called lattice frame of reference. In Darken’s treatment of binary single-phase diffusion, for example, in case of α Cu-Zn, differences in diffusion behavior are explicitly considered by defining intrinsic diffusion coefficients and intrinsic diffusion fluxes for each component that are related to their respective concentration gradients. Darken’s purely macroscopic formalism was followed by the work by Seitz [Sei50, Sei53] who provided an atomic interpretation of the Kirkendall
effect and thus firmly established the vacancy diffusion mechanism as the primary diffusion mechanism in metals.

Darken was also able to relate the diffusion behavior of atoms in a homogenous system to that in a flowing system in the form of relations commonly referred to as the Darken relations. This led him to suggest a more suitable formalism for diffusion in multicomponent systems in which the driving forces for diffusion are the chemical potential gradients rather than the concentration gradients as embodied in the Fickian formalism. He was able to demonstrate the utility of this formalism by providing an explanation for the phenomenon of “uphill diffusion” (i.e., diffusion of a component in a direction opposite to its concentration gradient) of carbon in the presence of silicon in $\gamma$ iron [Dar49, Dar51]. Darken’s analysis of diffusion in solid state systems was based primarily on earlier treatments for aqueous systems by Onsager and Fuoss [Ons32b], and Hartley [Har31]. These and other efforts led to the development of the field of irreversible thermodynamics of which solid state diffusion is an important component.

Unfortunately, the determination of the kinetic descriptors (e.g., intrinsic diffusion, interdiffusion coefficients or mobilities) of diffusion in the various phenomenological formalisms has turned out to be a rather non-trivial endeavor, especially for multicomponent systems. The difficulty stems primarily from the fact that the kinetic descriptors of diffusion in multicomponent systems are in the form of a matrix, the evaluation of which is extraordinarily difficult. Furthermore this matrix cannot be determined for systems containing more than three components without simplifying assumptions. More worrisome is the fact that the actual values of the terms
of the matrix are dependent on the choice of independent concentration variables\textsuperscript{1} used in the description of the diffusion fluxes, and can even be negative. Indeed phenomenological coefficients by their very definition do not have a direct relation to the actual physics of the diffusion process, i.e., the jumping of individual atoms in a multicomponent system. As a result, efforts geared towards the systematic development of diffusion databases [Cam02, Bor00] in multicomponent systems have not been easy without some simplifying assumptions. These assumptions usually involve ignoring the cross-terms in the matrix of phenomenological coefficients (i.e., $L_{ij} = 0$, $i \neq j$), and relating the on-diagonal terms to the tracer diffusion coefficients using the Darken theory. Thus, the Darken relations that connect tracer diffusion measurements in homogenous systems, with the phenomenological coefficients in gradient systems, still occupy a central role in current diffusion applications.

In spite of the fact that the Darken theory [Dark48] has been around for more than fifty years, it was felt that a critical assessment was lacking. It was found that many of the earlier tests of the theory were incomplete in several respects. Particularly lacking was the ability to compare the experimental diffusion data (e.g., concentration profiles and lattice shifts) with those predicted by the Darken theory. Since an \emph{intrinsic diffusion simulation} is necessary to perform such a comparison, an important goal of the present work was the development of such a simulation, and its utilization for the assessment of

\textsuperscript{1} In an $n$ component system, there are $n$ concentration variables; however only ($n-1$) of these are independent since there exists a relation between them. If $c_k$ is the concentration and $X_k$ the mole fraction of component $k$, then since the sum of the mole fractions is one, $\sum_{k=1}^{n} c_k = \frac{1}{V} \sum_{k=1}^{n} X_k = \frac{1}{V}$, where $V$ is the molar volume.
the Darken relations in a number of binary systems. The Manning corrections [Man68, Man70] to the Darken relations, which take into account correlation and vacancy wind effects during diffusion, are usually too small to be of major consequence; nevertheless, these were also considered in the present endeavor.

A kinetic approach that is based on the effective atom jump frequencies was previously proposed by Iswaran [Isw93] and DeHoff [Deh02] as an alternative to the traditional phenomenological formalism. Although kinetic formalisms based on atom jump frequencies had been discussed earlier in the literature by Manning [Man68], LeClaire [Lec58] and Seitz [Sei50], they are usually too complicated or impractical to be utilized for the analysis of diffusion in practical multicomponent systems. Iswaran and DeHoff were able to devise a rather simple yet efficient kinetic diffusion formalism that could be easily utilized for the analysis of diffusion in practical multicomponent systems with the aid of an intrinsic diffusion simulation that they also developed. Suitable jump frequency models were concocted using an “informed trial and error” approach to describe diffusion in several isomorphous ternary systems with the aid of the simulation [Isw93, Deh02]. In spite of the reasonable success achieved, this approach was incomplete in several respects. Firstly, their kinetic flux expression did not explicitly take into account so-called “bias” effects that are considered in the Darken formalism [Dar48, Dar49] as well as in the previous kinetic formalisms of Manning [Man67, Man70, Man71, Man89] and others [Sei50, Lec58, How64, All93]. Secondly, although the simulation modeled intrinsic diffusion using the atom jump frequency formalism, Iswaran and DeHoff did not extend its application for the purpose of examining other intrinsic formalisms in the literature, most notably the Darken intrinsic
diffusion formalism. Thirdly, the Darken-Manning relations that provide a connection
between diffusion in homogenous and flowing systems and are an integral part of the
prevalent diffusion theory were not critically examined with the aid of the simulation,
even though that was not the focus at the time. A fourth point of weakness was in the
development of jump frequency models using an “informed trial and error” approach that
obviously could not be replicated by an individual not knowledgeable in the field.
Lastly, the simulation itself was developed in a now rarely used programming
language—TurboPascal, which again requires some expertise and is not very user-
friendly. These and other issues in diffusion modeling and analysis are considered in the
present dissertation.

In Chapter 2 of this dissertation, some of the more traditional phenomenological
formalisms including those proposed by Fick, Darken and Onsager are considered. The
trouble with these formalisms is highlighted. Simplifications employed so as to make the
formalisms more tractable are discussed.

The development of an intrinsic diffusion simulation in MathCad [Mat01] is the
focus of Chapter 3. The details of the simulation are discussed in some length with the
aid of a flow-chart. Model systems with constant and variable molar volumes, and a
practical system (Fe-Ni) are used to illustrate the special features of the simulation.

Chapter 4, the main focus of this dissertation, discusses the utilization of the
simulation for the analysis of the Darken-Manning relations, which are of great
importance in present diffusion theory. Previous tests of the Darken-Manning relations
in the literature are first briefly examined. A systematic procedure for the assessment of
these relations with the aid of the simulation is presented. Using this procedure, the
Darken-Manning relations are critically examined for four well-characterized binary systems (Ag-Cd, Au-Ni, Cu-Zn and Cu-Ni) and important conclusions are reached on these assessments.

The jump frequency formalism is the main theme of Chapter 5. An expression for the intrinsic diffusion flux of a component in a multicomponent system is first derived. The significance of the biased and unbiased terms in the flux expression is then considered. Even though the physical content of the bias term in this formalism is unknown at the present time, a novel application of the simulation for computing the bias terms, using the experimental intrinsic diffusion data in the Cu-Zn system, is demonstrated. A simplified version of the jump frequency formalism based on the unbiased version is suggested as a practical way of avoiding the complications associated with bias effects. The construction of effective jump frequency models in this formalism is explored with the aid of a few ternary systems including Darken’s “uphill diffusion” system. Rather than using an informed trial and error approach for the development of jump frequency models, an alternate procedure for the direct computation of the jump frequencies from the intrinsic diffusion fluxes is proposed. It is shown that the lattice velocities needed for the determination of the intrinsic fluxes can be obtained using an oblique marker technique, the construction of which is examined in Appendix E.

Chapter 7 summarizes the findings from the present work regarding the Darken-Manning relations. The utility of the simulation developed in this work is highlighted. Some important advantages of the jump frequency approach for the potential development of diffusion databases are presented. A number of recommendations for further research in the field of solid state diffusion are also suggested. Several rather
detailed appendices are provided at the end of the dissertation as an aid to the discussions in various chapters.
CHAPTER 2
PHENOMENOLOGICAL DIFFUSION FORMALISMS

2.1 Diffusion Formalisms: An Overview

Diffusion must occur in any process that requires a change in local chemistry. In crystalline systems this requires that single atoms change their position on the crystal lattice. The average frequency with which this event occurs in a local volume element is different for each chemical component in the system, and varies with the composition and temperature of the volume element. The pattern of these events ultimately determines the evolution of the spatial distribution of the elements in a single phase crystal. Prediction and control of this chemical evolution require an understanding of the diffusion process.

To achieve this understanding it is first necessary to be able to describe the diffusion process, i.e., to develop a formalism that relates how the atoms move to the current condition of the system. The phenomenological equations of irreversible thermodynamics [Haa69, Kir87, She89, Phi91] define fluxes as measures of the atom motions and relate them to forces defined in terms of gradients of the properties of the system calculated from the current condition of the system. These equations have been widely accepted as the basis for the description of the diffusion process.

Application of the phenomenological formalism to the description of interdiffusion of the elements in binary systems is straightforward and requires modest experimental effort. However, for three component systems, the formalism becomes
cumbersome and the level of experimental effort required to evaluate the matrix of four interdiffusion coefficients defined for the system is significant. As the number of components in the system increases beyond three, the number of diffusion coefficients needed to describe behavior increases rapidly. Further, values for the matrix of diffusivities in quaternary and higher order systems cannot be determined experimentally.

Evidently a practical description of diffusion behavior in multicomponent systems would require an ability to understand the physical content of these diffusion coefficients so that their values could be computed or at least estimated from more fundamental information. Tracer diffusion experiments, which report the penetration of a radioactive tracer of an element into a chemically homogeneous alloy, provide fundamental information about the frequency with which atoms of a component make a jump between adjacent sites on a crystal lattice. If the physical content of interdiffusion coefficients is to be understood, their values must be related to this fundamental information about the pattern of atom jump frequencies in the system.

Kirkendall’s classic observation that the crystal lattice moves during diffusion first complicated, then clarified this situation. Tracer information describes atom motion relative to the crystal lattice, but the Kirkendall observation showed that the crystal lattice moves in interdiffusion. Darken solved this problem by introducing the concept of intrinsic diffusion, describing motion of atoms in the non-uniform flowing system relative to the moving lattice.

The stage was set for what became the central theoretical problem in multicomponent diffusion: the determination of the connection between the fundamental
tracer diffusion information, through the intrinsic diffusion coefficients to the practical interdiffusion coefficients. Without this theoretical connection the description of diffusion in multicomponent systems would remain impractical.

Subsequent sections in this chapter review the experimental observables for each of the three kinds of diffusion experiments: tracer, intrinsic and interdiffusion. The formalisms devised to describe each of these kinds of experimental results are then recalled briefly. Problems with the formalisms themselves are discussed. The established theoretical connection between the three kinds of information and experimental tests is briefly discussed; a detailed presentation of this theory and the experimental results that illuminate the inadequacies of the theory connecting these kinds observations are the focus of Chapter 4. These deliberations support the thesis that the traditional phenomenological description of diffusion does not provide a useful or practical basis for collecting and organizing information about diffusion in a multicomponent system. Alternate approaches to this problem are needed.

One strategy for overcoming some of these problems is based on the simplified version of the phenomenological formalism in the lattice frame of reference, which ignores the off-diagonal terms in the matrix of phenomenological coefficients [Kir87, Agr82, And92]. With this assumption, the on-diagonal terms can then be determined either directly from intrinsic diffusion experiments, or more frequently, by invoking the Darken theory that establishes the connection between tracer diffusion coefficients and the on-diagonal phenomenological coefficients or mobilities. Unfortunately, it does not appear that this approach has been examined with the necessary rigor in multicomponent systems. Given the problems with the Darken relations even in binary systems, it appears
questionable whether the Darken relations in multicomponent systems can be reliably utilized in this simplified version of the phenomenological formalism.

Another, perhaps more preferable, alternative considered in Chapter 5 is a kinetic approach. This is based upon a kinetically derived flux equation which avoids the problems associated with the phenomenological approach. In its rigorous version, it has a potential for providing new insights into influences that operate in diffusion that bias the jumps of components relative to the diffusion direction. A simplified version has been shown to provide relatively simple models for diffusion behavior that successfully describe the experimental observables in a number of ternary systems. The latter has the potential to make the description of diffusion in multicomponent systems practical. The derivation and application of this kinetic formalism is the focus of Chapter 5.

2.2 Experimental Observables in Diffusion

2.2.1 Interdiffusion Experiments

Diffusion produces changes in the distribution of chemical elements with time. The primary experiment designed to yield an understanding of diffusion behavior in an alloy system is based on the diffusion couple. Blocks of two alloys, P and Q, are bonded at a temperature that is low enough so that the components in the alloys cannot intermix (Fig. 2-1). The distribution of each component is initially a step function (Fig. 2-1a). The couple is then taken to a high temperature and isothermally annealed for many hours or perhaps days. The components interpenetrate; each develops its composition profile after some time, $t$ (Fig. 2-1b). The couple is cooled, sectioned and chemically analyzed to yield the functions $c_k(x, t), (k = 1, 2, \ldots, n)$ where $c_k$ is the molar concentration (moles/cc) of component $k$. The design of the couple guarantees that the flow of all of the
Figure 2-1. Composition distribution in a diffusion couple: (a) before and (b) after the isothermal anneal. An error function was employed to generate the composition profile where the interdiffusion coefficient, $D^0 = 10^{-9}$ cm$^2$/s, and the time for the diffusion anneal, $t = 6$ hours.
\[ \text{dn}_k = C_k \, \text{dV} = C_k \, \text{dA} \, \text{dx} \]

\[ \text{dx} = v_k \, \text{dt} \]

\[ \text{dn}_k = C_k \, \text{dA} \, v_k \, \text{dt} \]

\[ J_k = \frac{\text{dn}_k}{\text{dA} \, \text{dt}} = C_k \, v_k \]

Figure 2-2. Interdiffusion flux in a flowing system.

components will be one dimensional (call it the \( x \) direction, perpendicular to the original bond interface). Generally the size of the two blocks is large compared to the diffusion zone (the zone of composition change) so that the boundary conditions for the diffusion process is “semi-infinite”; this simply means that for sufficiently large values of \( x \) the composition profiles after the anneal remain at the original concentration values on each side of the couple.

The motion of the atoms of a component in such flowing systems is described by the concept of the interdiffusion flux of component \( k \). Focus upon a volume element \( dV \) in the couple (Fig. 2-2). Atoms of component \( k \) form a subset of all of the atoms in this volume. Define \( v_k \) to be the average velocity of \( k \) atoms in \( dV \) during some small time
interval. Focus further upon the area element $dA$ bounding the right side of $dV$. The number of atoms of $k$ that flow across $dA$ reported per unit area and per unit time is defined to be the flux of component $k$ at $dA$. The area element is viewed as being at a fixed position in the couple relative to a coordinate system that is external to the couple. The flux of atoms relative to a value of $x$ that is fixed in the laboratory is called the interdiffusion flux of $k$ (see Appendix A), and can be shown to be

$$J_k^o = c_k^o v_k^o \quad (k = 1, 2, \ldots, n) \quad (2-1)$$

The superscript ($^o$) in this and subsequent equations is used to describe properties associated with the interdiffusion process, i.e., with the motion of atoms in a fixed external (laboratory) reference frame. Note also that $c_k$ represents the concentration (mol/cc) and $n$ the number of components in the systems. $X_k$ is the atom fraction of component $k$ in the volume element $dV$. It can be shown (Appendix A) that this definition of the interdiffusion flux yields the relationship

$$\sum_{k=1}^{n} J_k^o = 0 \quad (2-2)$$

if the molar volume of the system is constant. That is, in a $n$ component system there are $(n - 1)$ independent interdiffusion fluxes. Dayananda [Day83] showed that these fluxes can be evaluated from the concentration profile measurements without additional information:

$$J_k^o(x) = \frac{1}{2t} \int_{c_k}^{c_k(x)} x \, dc_k \quad (k = 1, 2, \ldots, n) \quad (2-3)$$

where $t$ is the time of the diffusion anneal, $c_k$ is the far field concentration of component $k$ on the left side of the couple and $c_k(x)$ is the concentration of component $k$ at the
position \( x \) in the couple. The derivation of this result neglects variations in molar volume in the system, a common assumption in diffusion theory.\(^1\) A sample result of this calculation is shown in Fig. 2-3. The concentration profiles for this demonstration were generated using ternary error function solutions given by Kirkaldy [Kir87].

The typical interdiffusion experiment yields a pattern of composition profiles for all of the \( n \) components in the system. The pattern of interdiffusion fluxes in that couple can be computed from this information for each of the components. Because these fluxes sum to zero, there are \((n - 1)\) independent interdiffusion fluxes in an \( n \) component system.

### 2.2.2 Intrinsic Diffusion Experiments

In 1947 Smigelskas and Kirkendall [Smi47] placed thin molybdenum wires at the original interface between two alloys P (pure Cu) and Q (\( \alpha \) brass, Cu 70\% Zn 30\%) and annealed the resulting couple. The wires moved during the experiment (Fig. 2-4). Kirkendall concluded that the wires moved with the crystal lattice in the couple. Subsequent investigations established that this behavior is pervasive. The fundamental diffusion process in crystals is the motion of atoms from one lattice site to an adjacent vacant site, i.e., motion relative to the crystal lattice. Kirkendall’s experiment established that the crystal lattice is moving in the external fixed reference frame that is used to describe interdiffusion. Thus, in order to follow the fundamental diffusion process, it is necessary to define the diffusion flux relative to the moving crystal lattice:

\[
J_k = c_k^v (v_k^o - v_L)
\]  

\( 2-4 \)

\(^1\) Appendices A to D discuss various issues related to molar volume effects and diffusion fluxes in non-laboratory reference frames.
where $v_L$ (or $v^k$) is the local lattice velocity. Darken [Dar48] defined this measure of atom motion relative to the moving lattice to be *intrinsic diffusion*. (In the notation of the discussion in this chapter, intrinsic diffusion fluxes and other intrinsic properties have no superscript ($^\circ$) in order to distinguish from the analogous interdiffusion properties.) The intrinsic and interdiffusion fluxes are related by [Dar48]

$$J_k = J_k^\circ - c_k v_L$$

Unlike the interdiffusion fluxes (Eq. (2-3)), all $n$ intrinsic fluxes are independent. They sum, not to zero, but to the local value of the vacancy flux $J_v$:

$$\sum_{k=1}^{n} J_k = - J_v$$

The original Kirkendall experiment and its successors could only provide the lattice velocity at the marker plane inherited from the original bond plane. Thus information on intrinsic diffusion could be obtained from a single composition in a given couple. In later years couples have been constructed with markers distributed through the diffusion zone, see Appendix E. Fig. 2-5 shows one couple design that incorporates a marker plane that is oblique to the direction of diffusion. Upon sectioning after diffusion, the markers have displaced forming a curve that may be described by a function, $g(x)$. Philibert [Phi91] has devised an analysis that permits the determination of the lattice velocity distribution $v_L(x)$ from the marker pattern $g(x)$ without simplifying assumptions. Thus, both terms in Eq. (2-6) are experimentally accessible and the intrinsic diffusion fluxes of all $n$ components can be computed from experimental composition profiles and marker displacements without simplifying assumptions.
Figure 2-3. Calculation of the interdiffusion flux directly from the concentration profiles using Dayananda’s equation [Day83]. (a) concentration profiles (b) interdiffusion fluxes.
Figure 2-4. Displacement of wires in an interdiffusion experiment for the Cu-Zn system, a phenomenon known as the Kirkendall effect [Smi47].

Figure 2-5. Oblique marker plane for the determination of lattice velocities for the entire diffusion zone before and after the interdiffusion anneal.
2.2.3 Tracer Diffusion Experiments

The classic tracer diffusion experiment begins with a block of an alloy of a desired composition. A thin layer containing the desired radioactive element is dispersed on one face of the block. The sample is annealed at a predetermined temperature for a predetermined time. The radioactive isotope permits measurement of the concentration of tracer as a function of depth of penetration even though the tracer element is present in very small quantity. Thus the experiment monitors the motion of one of the components into an alloy that is essentially chemically uniform. A straightforward analysis of the tracer profile yields the tracer diffusion coefficient, $D_k^*$, for that element in that alloy. A physical argument that describes the tracer flux in terms of the mean effective jump frequency of component, $\Gamma_k^*$, yields the relation [She89, Phi91]

$$D_k^* = \frac{1}{6} \lambda^2 \Gamma_k^*$$  \hspace{1cm} (2-7)

where $\lambda$ is the diffusion jump distance. The jump frequency for each component in a given system is found to depend upon the composition of the alloy and the temperature of the anneal. The number of jumps an atom makes per second between sites is the central physical descriptor of the diffusion process. In principle it would seem that, given the jump frequencies of each of the components as a function of composition one could predict the other experimental observables, i.e., the composition distribution function, $c_k(x,t)$, for $k = 1, 2, ..., n$, and the lattice velocity distribution, $v_L(x,t)$, in a chemically evolving system. This connection between tracer, intrinsic and interdiffusion behavior is the focus of the physical theory of diffusion.
2.3 Diffusion Formalisms

The information obtained from the diffusion experiments described above is explicit to that experiment. It is desirable to use that information for predicting diffusion behavior in other situations in the same alloy system. This has been achieved by devising a formalism that provides a general description of diffusion phenomena. The experimental results are then used to evaluate parameters introduced in the formal description. With the parameters evaluated for an alloy system, the general, formal equations may be used to predict diffusion behavior in that alloy system for any set of initial and boundary conditions.

The time evolution of the distribution of the compositions in a chemically evolving system is formally described by the phenomenological equations adapted from the thermodynamics of irreversible processes [Haa69, Kir87, All93]. These equations are qualitatively based upon the notion that flow rates increase as a system gets farther from equilibrium. Flow rates are defined in terms of the fluxes of the things that move (quantity per m² - sec) as in Eq. (2-1). The conditions for equilibrium specify that, in the absence of externally applied fields, gradients of certain local intensive thermodynamic properties are zero at equilibrium, specifically,

\[ \text{grad} T = 0 \]
\[ \text{grad} \mu_k = 0 \quad (k = 1, 2, ..., n) \] (2-8)

where \( \mu_k \) is the chemical potential of component \( k \). In the absence of external fields in an isothermal system the chemical potential is an algebraic function of composition, so that the condition \( \text{grad} \mu_k = 0 \) implies \( \text{grad} c_k = 0 \) \( (k = 1, 2, ..., n) \). When the gradients vanish, the corresponding flows are zero. It is natural to write the flow equation based on
the assumption that each flux is proportional to all of the independent gradients in a non-equilibrium system.

2.3.1 Interdiffusion Formalism

For isothermal interdiffusion in a system with $n$ components the phenomenological equations may be written

$$ J_k^i = - \sum_{i=1}^{n-1} L_{ki}^{o,n} \text{grad} \mu_i \quad (k = 1, 2, ..., n-1) \quad (2-9) $$

The matrix of phenomenological coefficients, $L_{ki}^{o,n}$, must be evaluated from diffusion couple experiments. If they are determined as a function of composition and temperature then Eq. (2-9) permits prediction of the evolution of composition distribution in the system. Recall that, in an $n$-component system there are $(n - 1)$ independent interdiffusion fluxes, Eq. (2-3).

An alternate, and more traditional formalism for describing the interdiffusion fluxes in a multicomponent system is a generalization of Fick’s law for binary systems:

$$ J_k^o = - \sum_{j=1}^{n-1} D_{kj}^{o,n} \text{grad} c_j \quad (k = 1, 2, ..., n-1) \quad (2-10) $$

where $D_{kj}^{o,n}$ is a matrix of interdiffusion coefficients. The suffix superscript “$n$” for the phenomenological or interdiffusion coefficient is used to denote the dependent variable.

Note that in either formalism there are $(n - 1)$ independent fluxes in the system (because the interdiffusion fluxes sum to zero, Eq. (2-3)) and $(n - 1)$ terms in each equation. There are $(n - 1)$ independent chemical potential gradients in Eq. (2-9) because the chemical potentials of the $n$ components are related by the Gibbs-Duhem equation in thermodynamics [Haa69, DeH93]. There are $(n - 1)$ independent concentration gradients...
in Eqs. (2-10) because the atom fractions sum to 1. There are thus \((n - 1)^2\) coefficients in the description of an \(n\) component system. In the thermodynamics of irreversible processes the principle or microscopic reversibility devised by Onsager [Ons31, Ons32a] shows that the square matrix of mobility coefficients is symmetrical, i.e., corresponding off-diagonal terms are equal. This reduces the number of independent phenomenological coefficients in a \(n\)-component system to \(\frac{1}{2} n (n - 1)\). The two descriptions in Eqs. (2-9) and (2-10) are interconvertible since the chemical potentials are functions of composition. Accordingly, the matrix of diffusion coefficients, \(D_{ij}^o\), or, alternatively, the matrix of phenomenological coefficients, \(L_{ij}^o\), can be computed from one another [Kir87, Phi91]. The analyses of experimental penetration profiles yields the matrix of diffusivities [Kir87, Tho86]. If desired the matrix of phenomenological coefficients can then be computed by combining the diffusivity results with a thermodynamic solution model that permits calculation of the chemical potentials from the concentrations.

2.3.2 Intrinsic Diffusion Formalism

Phenomenological equations used to describe intrinsic diffusion behavior appear to be very similar to Eqs. (2-9) and (2-10) with two important differences:

a. The fluxes and diffusivities are “intrinsic” properties of the process, in the sense that this word is used in diffusion theory (indicated by dropping the superscript \(o\) in the notation. Sometimes the superscript \(K\) for the Kirkendall or lattice frame is added for clarification), and

b. The fluxes do not sum to zero, see Eq. (2-6).

For intrinsic diffusion:
\[ J_k = - \sum_{i=1}^{n-1} L_{ki}^{n} \text{grad} \mu_i \quad (k = 1, 2, ..., n) \quad (2-11) \]

\[ J_k = - \sum_{j=1}^{n-1} D_{kj}^{n} \text{grad} c_j \quad (k = 1, 2, ..., n) \quad (2-12) \]

As before, the suffix \( n \) superscript “n” in these equations is used to denote the dependent variable. There remain \((n - 1)\) terms in each flux equation (since there remain \((n - 1)\) independent composition variables) but now there are \(n\) independent fluxes. The matrix of diffusion coefficients is thus not a square matrix, but contains \(n (n - 1)\) elements.

In principle the matrix of intrinsic diffusivities for a multicomponent system can be evaluated by combining experiments that report concentration evolution data and lattice marker displacement measurements. The corresponding matrix of phenomenological coefficients can be computed from this information and a thermodynamic solution model to compute the chemical potentials.

2.4 Problems with the Phenomenological Formalism and its Implementation

Unfortunately, both the interdiffusion and intrinsic diffusion formalisms have their own share of problems besides the obvious difficulties associated with the measurement of the matrix of phenomenological coefficients in multicomponent systems.

2.4.1 Interdiffusion Problems

The interdiffusion equations provide a basis for incorporating results of diffusion couple experiments into a framework that permits prediction of the evolution of concentration patterns for that system for any set of initial and boundary conditions.

Given \(c(x, t)\) for a full range diffusion couple in a binary system, \(D^*(c)\) can be computed from the classic Boltzman [Bol94] - Matano [Mat33] analysis, a procedure that has been
in introductory textbooks for more than half a century [She89]. Then, given $D^o(c)$ an appropriate simulation of the governing flux equation can be used to predict the chemical evolution for any other situation involving that binary alloy system.

The trouble begins when this analysis is extended to three component systems and beyond. In a three component system there are only two independent compositional variables and two independent interdiffusion fluxes. Thus, a variety of flux equations can be written for the same system, depending upon which component is chosen to be the dependent variable. E.g.,

**Component 3 as dependent variable:** \[ J_2^o = - D_{21}^o \, \text{grad} \, c_1 - D_{22}^o \, \text{grad} \, c_2 \] \tag{2-13}  

**Component 1 as dependent variable:** \[ J_2^o = - D_{22}^o \, \text{grad} \, c_2 - D_{23}^o \, \text{grad} \, c_3 \]

It becomes necessary to add a superscript to the notation to make explicit the choice of dependent variable made in writing the equation. It is evident that the coefficients $D_{22}^o$ and $D_{22}^o$, both of which report the effect of the gradient of component 2 on the flux of component 2, are not equal.

In general, the values of the phenomenological coefficients depend upon the choice of the dependent variable made in setting up the problem. In the light of this observation, it is unlikely that these coefficients will convey much physical understanding of how the atoms move in the system. This approach may be used to describe the composition evolution, but not to explain or understand it.

The analysis can be significantly simplified if it is assumed that “off-diagonal terms”, $D_{kj}^o$, which describe the contribution of the gradient of component $j$ to the flux of component $k$, may be neglected as small in comparison with “on-diagonal terms”, $D_{kk}^o$, which describes the contribution of gradient of component $k$ upon its own flux, $J_k$. This
is a convenient and intuitive assumption because it decouples the flux equations and greatly simplifies the mathematics of the description. This is a dangerous assumption. Analysis of relations between coefficients defined for two different choices of dependent variable, as illustrated in Eq. (2-13) for example, shows that some off-diagonal terms in one description contain an on-diagonal term in the other description. For example, it can be shown that $D_{32}^3 = D_{32}^1 - D_{33}^1$. In addition one can always find local situations in the patterns that develop in which the concentration gradient for the on diagonal term is small so that the local flux is primarily determined by the off-diagonal term.

In order to determine the matrix of four diffusion coefficients in a three component system, it is necessary to prepare and analyze two diffusion couples with composition paths that cross in the Gibbs triangle. At the position of the crossing point both couples will have the same composition (and hence the same set of values for the $D_{kj}^o$ matrix) but different values of the fluxes and gradients. The two flux equations (2-10) for each couple yield four equations in four unknowns (the $D_{kj}^o$ matrix), and may be solved for their values at that specific composition. To obtain the pattern of composition dependent functions for the diffusivities, $D_{kj}^o(c_2, c_3)$ for the whole system, it is necessary to construct and anneal a series of diffusion couples with composition paths that criss-cross each other in the Gibbs triangle. Values of the each of the four diffusivities are computed at crossing points. These isolated values may be analyzed statistically to deduce best fit functions, - four surfaces over the Gibbs triangle -, that complete the database for interdiffusion in the system for the temperature chosen for the diffusion anneals. A complete data base would require that this process be repeated at other temperatures.
Because of the level of effort required to obtain these data there have been relatively few determinations of this matrix in the five decades since the procedures were first outlined [Kir87]. In their text, Kirkaldy and Young [Kir87] list 26 references reporting such analyses where “the data is sufficiently accurate and comprehensive that a closure with theory can be illustrated.” Only four of these cover the full composition range or even an entire phase field. Evidently the level of effort required to generate interdiffusion data bases for three component alloys is difficult to justify. This situation is not helped by the fact that the interdiffusion coefficients do not convey a physical understanding of how the atoms move in the system as discussed above. The data do not contribute to a physical understanding of the processes going on in diffusion so that patterns might be divined or predictions hypothesized.

Determination of the matrix of nine diffusivities for a single composition point in a quaternary system requires an experiment involving a set of three diffusion couples with composition paths that intersect at a point in the three dimensional composition space of the Gibbs tetrahedron. Unfortunately the probability that three space curves intersect in three dimensional space constitutes a set of points of measure zero. Accordingly, this matrix has never been measured for any quaternary system.\(^2\) Experimental methods for measuring interdiffusion coefficients in quaternary and higher order systems are evidently impractical.

\(^2\) The nine diffusivities have been estimated at a single quaternary composition in the Ni-Cr-Al-Mo system by constructing three incremental couples (i.e., with small composition differences) with crossing diffusion vectors and applying the approximation that the nine diffusion coefficients may be treated as constants in this small composition interval [Sta92].
2.4.2 Intrinsic Diffusion Problems

Because the intrinsic diffusion fluxes are independent, the description of the intrinsic behavior of an \( n \) component system requires an additional flux equation requiring addition of \((n - 1)\) diffusion coefficients. Darken analyzed the problem of determining intrinsic diffusion coefficients in a binary system [Dark48]. He derived the result

\[
D_1 = D^o - (1 - X_2)\left(\frac{\partial x}{\partial X_2}\right) v_L
\]

\[
D_2 = D^o + X_2\left(\frac{\partial x}{\partial X_2}\right) v_L
\]  

(2-14)

In a binary system, the interdiffusion coefficient can be obtained by applying the Boltzmann-Matano analysis to composition profiles, and the lattice velocity can be obtained from marker displacements during diffusion. \( D_1 \) and \( D_2 \) may then be evaluated at any composition for which \( v_L \) is measured. The original Kirkendall experiment placed a marker at a single point, the original interface, and measured its displacement. Thus, \( v_L \), and hence \( D_1 \) and \( D_2 \), could be determined at a single composition in this experiment. That composition was not known a-priori; it was determined as the composition at the marker plane after the experiment. To generate a database for a range of compositions requires the preparation of a number of diffusion couples with initial composition pairs that produced marker plane compositions that spanned the range. If the oblique marker plane experiment (Fig. 2-5) is implemented, \( v_L \) can be determined at each composition in the couple. Combination with \( D^o \) values for the couple will permit computation of the two intrinsic diffusivities at all compositions that exist in the couple. The values of \( D_1 \) and \( D_2 \) are indicative of the relative rates of motions of the two components on the lattice.
Darken and others extended his analysis to ternary systems [Dar51, Guy65, Kir87, Man70]. Implementation of the analysis requires determination of the matrix of interdiffusion coefficients, $D_{kj}^o$, in the system using a pair of couples with intersecting composition paths with the attendant difficulties described above. In addition, the lattice velocity must be determined in both couples at their common composition. Evidently this cannot be achieved with traditional, single marker couples because the compositions at the marker planes in each couple, where $v_L$ may be determined, will not in general coincide with the composition at the intersection point of their composition paths. The oblique marker plane experiment permits determination of $v_L$ at all points in the compositions that exist in the couple, including that of the point of intersection of the composition paths. The resulting six equations (three flux equations in each couple) may be solved simultaneously to determine the matrix of six intrinsic diffusion coefficients at the composition of the intersection point.

Given the level of effort involved it is not surprising that intrinsic diffusivities have been estimated at but a few points in a few ternary systems [Guy65, Day68, Car72, Car73, Che75]. There has been no systematic study attempting to map this matrix, $D_{kj}$, as a function of composition in any ternary system.

The extra effort might be justified in the light of the fact that intrinsic fluxes provide a more direct view of how the components move with respect to one another, since they report independent motions of the components relative to the crystal lattice. However this insight is not supplied by the numerical values of the elements of the diffusivity matrix, $D_{kj}$. These properties suffer from the same problem cited for the interdiffusion coefficients: their values depend upon the choice of independent
compositional variable in the analysis. $D_{22}^1$ and $D_{22}^3$ are different numbers, though both purport to describe the effect of the concentration gradient of component 2 on the intrinsic flux of component 2. Evidently the numerical values of the elements in the diffusivity matrix is not a useful basis for understanding these atom flows in the system.

The intrinsic fluxes themselves have the potential to provide a level of physical understanding of the real motion of the components in the system. Eq. (2-5) provides the relationship between intrinsic fluxes and the interdiffusion fluxes and lattice velocities. On the right side of this equation, Dayananda’s analysis permits determination of the interdiffusion flux $J_{k}^o(x)$ for each component by applying Eq. (2-3) to the measured composition distribution. The lattice velocity distribution $v_i(x)$ can be determined from a couple with an oblique marker plane, using Philibert’s analysis. Thus the pattern of the intrinsic fluxes in a couple can be determined experimentally from the composition profiles and marker shift pattern in that couple. These relationships make no simplifying assumptions. Unfortunately, the oblique marker plane experiment has only been applied to a few binary systems (see Appendix E). It has never been applied to ternary or higher order systems, though the methodology makes such an application relatively straightforward.

2.5 Connection Between Tracer, Intrinsic and Interdiffusion Information

The phenomenological formalism was devised so that information extracted from diffusion couple experiments could be used to make more general calculations. In its complete form, it has proven to be a cumbersome basis for developing a diffusion database. Perhaps if a physical understanding of the content of the diffusivities could be developed, patterns could be recognized and correlations evoked that would foster the
generation of a more useful diffusion database. Tracer diffusion data provides the most
direct link to a physical understanding of atom motions in binary and multicomponent
systems. Darken recognized this in his initial paper on the subject [Dar48, Dar51]. He
set out to establish the connection between tracer diffusion information and intrinsic and
interdiffusion behavior. Since a detailed discussion of Darken’s theory is the subject of
Chapter 4, only the final Darken relations are presented here. The Darken relations
between tracer diffusivities and intrinsic diffusivities are

\[ D_k^* = D_k^* \left( 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln X_k} \right) \right) \quad (k = 1, 2) \tag{2-15} \]

where \( \gamma_k \) is the activity coefficient of component \( k \) in the alloy system. The Darken
relation between interdiffusion and tracer diffusion coefficients is

\[ D^o = (X_2 D_1^* + X_1 D_2^*) \left( 1 + \left( \frac{\partial \ln \gamma_k}{\partial \ln X_k} \right) \right) \tag{2-16} \]

In order to test the Darken relations, it is necessary to carry out all three kinds of
diffusion experiments (tracer profiles, marker displacement and composition profile) over
a composition range in a binary system. There are a few examples of binary systems in
the literature for which this information exists. The definitive test combines tracer
diffusion coefficients, thermodynamic information and intrinsic diffusivity measurements
to test Eqs. (2-15, 2-16). Analyses for a number of these systems have been reported in
the literature and are discussed in Chapter 4. It has been found in some cases that if the
two components have similar tracer behavior, then the tests support Darken’s hypothesis
within experimental error at least for the interdiffusion coefficient. However if the tracer
behavior is significantly different, then the results show that the theory is inadequate to
explain the differences between tracer and intrinsic diffusivities. Examples of tests for such systems are given in Chapter 4. Assessments of the data with the aid of an intrinsic diffusion simulation have shown that the disagreement in the intrinsic diffusion coefficients and hence the lattice shifts, are well outside the experimental error in these systems. It must be concluded from these results that Darken’s hypothesis yields a theory that is inadequate to explain the connection between tracer and intrinsic diffusion coefficients.

Manning [Man68, Man70, Man71] and others [Bar51, How64, Heu79, All93] have analyzed this connection at a more sophisticated level, introducing concepts such as correlation and vacancy wind effects. Examples of the predictions of Manning’s more detailed analysis are also discussed in Chapter 4. In some cases, the additional term produces a small correction to Darken’s prediction, within the range of experimental error in most cases. In other cases, Manning’s correction is in the wrong direction.

Darken’s treatment, and Manning’s corrections, have been expanded to describe three component systems [Man70, Kir87, Phi91, All93]. Experimental studies in a few ternary systems would provide a truly definitive test of this explanation of the phenomenological coefficients. The effort involved to make such a series of tests appears daunting. There is but one ternary system for which tracer data exists for all three components over a significant composition range: Cu-Ni-Zn [Anu72]. Interdiffusion data exists for the same system in the same composition range. There is anecdotal information about marker displacements for couples in this system, but no systematic study exists that would permit determination of the intrinsic diffusion coefficients. It is possible that, with the use of a suitable simulation of intrinsic diffusion,
one could arrive at an intrinsic diffusion model, that provides a satisfactory description of
the available marker data, but this has not been reported. Thus, the generalization of
Darken’s theory to ternary systems has not been tested systematically.

2.6 Simplifications to the Phenomenological Formalism

Because of the experimental difficulties involved in the determination of the
matrix of phenomenological coefficients (even though their meaning is abstruse), an
often used simplification is to ignore the cross-terms in this matrix. With this
assumption, the simplified version of the formalism for the intrinsic flux can be stated:

\[
J_k = - \sum_{i=1}^{n} L_{ki} \frac{\partial \mu_j}{\partial x} = - L_{kk} \frac{\partial \mu_k}{\partial x} = - c_k M_k \frac{\partial \mu_k}{\partial x} \quad (L_{ki} = 0, k \neq i) \quad (k = 1,2,...,n) \tag{2-17}
\]

\(M_k\) in this equation is known as the mobility and its evaluation is the focus in this version
of the formalism that has been adapted by the DICTRA software [Agr82, And92, Bor00].

Note that in Eq. (2-17), \(M_k\) is related to \(L_{kk}\) by

\[
L_{kk} = c_k M_k \tag{2-18}
\]

The term “mobility” was first used by Darken [Dar48] for deriving the relations between
tracer, interdiffusion and intrinsic diffusion (Chapter 4). From the Darken theory, the
connection between \(L_{kk}\) or \(M_k\) and the tracer diffusion coefficient of component \(k\) is

\[
L_{kk} = c_k M_k = \frac{c_k D_k^*}{RT} \tag{2-19}
\]

Originally, the relation between the mobility and the tracer diffusion coefficient was
proposed by Darken for binary systems; in this formalism it has been extended to
multicomponent systems as well.
2.6.1 Intrinsic Diffusion Coefficients

In order to relate \( L_{ki} \) or \( M_k \) in this formalism to the intrinsic diffusion coefficients, Eq. (2-12) is rewritten in the following form:

\[
J_k = - \sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial x} \quad (k = 1, 2, \ldots, n)
\]  

(2-20)

The \( D_{kj} \) in this equation is related to \( D_{kj}^n \) in Eq. (2-12) by

\[
D_{kj}^n = D_{kj} - D_{kn}
\]

(2-21)

Eq. (2-17) can be rewritten using the chain rule of differentiation and noting that \( L_{ki} = 0 \) when \( k \neq i \):

\[
J_k = -\sum_{j=1}^{n} L_{ki} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial x} = -L_{kk} \sum_{j=1}^{n} \frac{\partial \mu_k}{\partial c_j} \frac{\partial c_j}{\partial x} \quad (k = 1, 2, \ldots, n)
\]

(2-22)

Comparing Eqs. (2-20) and (2-22), it is seen that

\[
D_{kj} = L_{kk} \frac{\partial \mu_k}{\partial c_j}
\]

(2-23)

Since \( L_{kk} \) is related to \( D_{k}^* \) by the Darken relation Eq. (2-19), relations between \( D_{kj}^n \) or \( D_{kj} \) and \( D_{k}^* \) may be similarly obtained.

2.6.2 Interdiffusion Coefficients

In order to compute the interdiffusion coefficients, which are defined in the laboratory frame of reference, from the \( L_{ki} \)'s, which are defined in the lattice frame of reference, a transformation of the intrinsic fluxes to the laboratory frame is necessary. The flux in the laboratory frame is related to the intrinsic flux by [Dark48]

\[
J_k^o = J_k^k - X_k \sum_{k-1}^{n} J_k^k
\]

(2-24)
This follows from Appendix A, Eqs. (A-45), (A-46), (A-51) and (A-52), noting that $v^N$ is zero if the molar volume is constant.

The phenomenological flux equation in the laboratory frame in a convenient form is

$$ J_k^o = - \sum_{i=1}^{n} L_{ki}^o \frac{\partial \mu_j}{\partial x} \quad (k = 1, 2, ..., n-1) \quad (2-25) $$

From Eqs. (2-17) and (2-25), and using Eq. (2-24), it may be shown that

$$ L_{ki}^o = \sum_{j=1}^{n} \left( \delta_{jk} - X_k \right) L_{ji} \quad (k = 1, 2, ..., n-1) \quad (2-26) $$

Eq. (2-25) may be rewritten as follows:

$$ J_k^o = - \sum_{i=1}^{n} L_{ki}^o \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial x} \quad (k = 1, 2, ..., n-1) \quad (2-27) $$

The interdiffusion flux can also be expressed as

$$ J_k^o = - \sum_{j=1}^{n} D_{kj}^o \frac{\partial c_j}{\partial x} \quad (k = 1, 2, ..., n-1) \quad (2-28) $$

Comparing Eqs. (2-27) and (2-28), the relation between $D_{kj}^o$ and $L_{ki}^o$ is obtained:

$$ D_{kj}^o = \sum_{i=1}^{n} L_{ki}^o \frac{\partial \mu_i}{\partial c_j} \quad (2-29) $$

The interdiffusion coefficient $D_{kj}^o$ in Eq. (2-29), and $D_{kj}^{o,n}$ in Eq. (2-10) are related by

$$ D_{kj}^{o,n} = D_{kj}^o - D_{kn}^o \quad (2-30) $$

where $n$ is the dependent species in Eq. (2-10).

Since the $L_{ki}^o$'s are related to the $L_{ki}$'s which are in turn related to the tracer diffusion coefficients, expressions relating the interdiffusion coefficients $D_{kj}^{o,n}$ or $D_{kj}^o$ to the tracer diffusion coefficients $D_k^*$ can be obtained. The expressions for ternary
systems have been given in the paper by Cserháti et al. [Cse01]. These authors determined the interdiffusion coefficients at crossing points in fcc Cu-Fe-Ni system and computed the tracer diffusion coefficients at these locations using the above formalism. The thermodynamic data needed for computing the chemical potentials, was also assessed by the research group [Rön96]. The computed tracer diffusion coefficients were found to be significantly different from the experimental values [Cse01]. In some cases, the authors reported that negative values were obtained, which is of course not possible with experimental tracer diffusion coefficients. This suggested to the authors that there were either problems with the experimental data and procedures or with the fundamental formalism.

2.6.3 Problems with the Simplified Version

The central question in the simplified version of the phenomenological formalism is whether the $L_{kk}$'s are a unique function of composition in multicomponent systems. This can be tested by measuring the intrinsic fluxes (using for example, the oblique interface technique (Appendix E)) in ternary systems for two or more independent diffusion couples that have crossing diffusion paths. If the $L_{kk}$'s are unique, the values at the compositions where the diffusion composition paths intersect, should be the same. Unfortunately, it does not appear that this test has been performed at the present time, although indirect tests such as the one by Cserháti et al. [Cse01], which were discussed in the previous section, also cast doubt on this simplified formalism. Nevertheless, the development of diffusion databases using this formalism has progressed [And02, Cam02] using the Darken relations that connect the mobilities or the $L_{kk}$'s with the tracer diffusion coefficients. In Chapter 4, the Darken relations are examined for several binary
systems with the aid of an intrinsic diffusion simulation developed in this work. Since these relations are not satisfactory even in binary systems, it appears unlikely that they will work in multicomponent systems as well.
The original diffusion experiments in the α Cu-Zn system by Kirkendall and Smigelskas [Smi47] demonstrated the need to consider the “intrinsic” motion of atoms in a crystalline lattice so as to explain the phenomenon of the Kirkendall Effect, a phenomenon in which an imbalance of atom flows on a crystalline lattice results in the displacement of the lattice, thus causing the movement of inert markers residing on the lattice. The intrinsic motion of atoms, i.e., the diffusion of atoms between lattice planes due to an atom-vacancy exchange mechanism, first recognized by Kirkendall, was given a firm foundation by Darken in his theory of intrinsic diffusion [Dar48, Dar51]. A discussion of Darken’s treatment of intrinsic diffusion is provided in Chapter 4. Although Darken’s treatment of intrinsic diffusion has withstood the test of time, there have been relatively few efforts devoted towards the simulation of intrinsic diffusion in the original classical form presented by Darken. The reason may be partly attributed to the lower number of intrinsic diffusion studies in the literature due to the inherent experimental difficulties involved in the measurement of lattice velocities. In Appendix E, a technique for the measurement of lattice velocities known using an “oblique interface technique” [Cor72, Cor74] is presented, which the author hopes should partly mitigate some of these difficulties and encourage more intrinsic diffusion measurements in the future. Indeed in the last decade, there has been an increasing emphasis on intrinsic diffusion in both single and multiphase systems [Dal00a, Dal00b, Loo90a,
Loo90b]. The development and application of an intrinsic diffusion simulation, which is the focus of this chapter, is expected to provide a valuable predictive tool for the diffusion specialist engaged in intrinsic diffusion studies.

### 3.1 The Need for an Intrinsic Diffusion Simulation

A variety of intrinsic diffusion formalisms have been discussed in the literature, in which the kinetic descriptors of intrinsic diffusion as well as the driving forces are different, even though the meaning and value of the intrinsic flux is still retained. Phenomenological treatments include, for example, Darken’s, which considers intrinsic diffusion coefficients as the kinetic descriptors and concentration gradients (in mol/cc) as driving forces while others, such as the diffusion software DICTRA¹ [Agr82, And92, Bor00] are coded in terms of mobilities and chemical potential gradients. Kinetic expressions for the intrinsic flux, such as the jump frequency approach (see Chapter 5) [Isw93], involve gradients in jump frequencies and concentrations. The test of any intrinsic formalism is a comparison with experimental observables, for example, concentration profiles and lattice shifts. An intrinsic diffusion simulation, such as the one developed here, has the potential of assessing a variety of formalisms and examining the underlying assumptions inherent in these approaches. For example, in the case of multicomponent systems, the assumption that the cross terms in the matrix of phenomenological coefficients can be ignored (such as in DICTRA) can be tested by utilizing the simulation to examine a number of composition paths and lattice shifts in the

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¹ Diffusion controlled transformations (DICTRA) for diffusion simulations in multicomponent alloys, Royal Institute of Technology, Stockholm, Sweden.
Similarly in the jump frequency approach, the assumption that the bias terms can be neglected can be assessed with the aid of the simulation.

The measurement of diffusion coefficients using conventional experiments involving semi-infinite diffusion couples is unfortunately not a very accurate process and can result in significant errors [Ior73, Kap90, Loo90a]. The advent and development of the electron microprobe [Zie64, Phi91, Gol02] and other modern techniques for the determination of concentration profiles in diffusion couples has resulted in improved measurement accuracies as compared to older techniques (e.g., wet chemical analysis). Similarly, the availability of the personal computer along with improved algorithms for data analysis has reduced the computational effort and improved the accuracy involved in the determination of diffusion coefficients from experimentally measured concentration profiles and lattice shifts. Nevertheless, errors in diffusion measurements and analysis cannot be eliminated and quite often the practitioner’s own expertise or lack of it may be an important contributor. As compared to interdiffusion coefficients, the measurement of intrinsic diffusion coefficients requires, in addition to the concentration distributions, the accurate measurement of lattice shifts. Thus it would be quite desirable for the diffusion researcher to have at his/her disposal a diffusion simulation that can rapidly ascertain the accuracy of the diffusion measurements.

The Darken-Manning theories have long been used to connect the diffusion of atoms in homogenous solid solutions (i.e., tracer diffusion) with those in gradient systems (i.e., interdiffusion). A discussion of the Darken-Manning theories is provided in Chapter 4. The Darken-Manning theories are usually tested by comparing the experimentally determined interdiffusion and intrinsic diffusion coefficients with those
predicted using these theories. Besides having the capability of assessing the quality of
the experimental data and analysis, the simulation developed in this work has the added
advantage of reproducing all the experimental information that is available from a
diffusion experiment using the intrinsic diffusion coefficients predicted from these
theories as an input. Thus the Darken-Manning theories that connect the intrinsic and
interdiffusion coefficients with the tracer diffusion coefficients, can be examined more
critically with the aid of the simulation. This is considered in some depth in Chapter 4.

An important contribution of the present effort is the introduction of bias effects
in the jump frequency approach, that has been developed for modeling intrinsic diffusion
in multicomponent systems. At the time of this writing, a theoretical approach for the
analysis of the bias factors in the jump frequency approach, is lacking. However, it has
been demonstrated in Chapter 5 with the aid of the simulation, that the bias factors can be
directly determined from the total and unbiased intrinsic fluxes. Thus for the first time, it
has been shown that the bias contributions of the individual components in the classical α
Cu-Zn system are not only unequal but in fact have opposite signs. This unexpected
development is expected to provide some critical insights into the origin of bias effects
in diffusion. Needless to say, this could not have been discovered without the benefit of
the simulation.

In principle, the simulation could have been developed using conventional
software packages such as C++ or Fortran. In fact, the previous version of the simulation
was developed in TurboPascal [Isw93]. Significant improvements, particularly on the
application side, have been made in the recent version that has been developed using the
math software, MathCad. The author’s preference in utilizing MathCad was primarily
influenced by its user friendliness, advanced math subroutines, simple programming syntax, and easy display of graphical output. A special advantage of MathCad is the ability to enter expressions and comments in the working document in a manner very similar to that utilized by an instructor teaching traditional topics in Materials Science & Engineering. The development of the simulation in MathCad has been a strong foundation that resulted in valuable educational and research benefits in many diverse fields within the materials sciences.

3.2 The Simulation

Given an initial concentration distribution of the components in a system, the goal of the intrinsic simulation is to predict the variation in the concentration of the components and the lattice velocity as a function of position and time. The simulation of multicomponent diffusion is based on a finite difference evaluation of the expression for the intrinsic flux for multicomponent systems. Various approaches for evaluating the intrinsic fluxes are available depending on the choice of the kinetic descriptors and the driving forces. The expression for the intrinsic flux in multicomponent systems based on the multicomponent version of the Darken equation for binary systems [Kir87] is

\[ J_i^K = -\sum_{j=1}^{n-1} D_{ij}^{K,n} \left( \frac{\partial c_j}{\partial x} \right)_{p,T,i,c_m} \quad (i = 1, 2, \ldots n) \]  (3-1)

This expression is similar to the multicomponent version of Fick’s law (see Chapter 2 or Appendix C), however unlike the fluxes in the other reference frames, the fluxes in the lattice or Kirkendall frame (i.e., the intrinsic fluxes) are all independent. The \( D_{ij}^{K,n} \) are the matrix of intrinsic diffusion coefficients in the \( n \) component system with the \( n^{th} \) component taken to be the dependent one. Unfortunately, as discussed in Chapter 2, the
determination of the matrix of intrinsic diffusion coefficients in ternary or higher order systems is a non-trivial task. Hence the evaluation of intrinsic fluxes using the Darken equation is usually restricted to binary systems. In the case of binary systems, the Darken equation [Dar48] is

\[
J_{k}^{K} = -D_{k}^{K} \frac{\partial c_{k}}{\partial X} \quad (k = 1, 2)
\]  

(3-2)

where \(D_{k}^{K}\) is now the binary intrinsic diffusion coefficient of component \(k\) in \(\text{cm}^{2}/\text{s}\) and \(c_{k}\) is the concentration of component \(k\) in \(\text{cc/mole}\).

The intrinsic flux expression utilized by DICTRA [Agr82, And92, Bor00] uses mobilities as the kinetic descriptors and chemical potential gradients as the driving forces (see Chapter 4). This is essentially obtained from the phenomenological intrinsic flux expression:

\[
J_{i}^{K} = -\sum_{j=1}^{n} L_{i,j}^{K} \left( \frac{\partial \mu_{j}}{\partial X} \right)_{p,T,\mu_{m}} \quad (i = 1, 2, \ldots n)
\]  

(3-3)

where the \(L_{ij}\)'s are the phenomenological coefficients in the lattice or Kirkendall frame and \(\mu_{j}\) is the chemical potential of component \(j\). In the case of substitutional solid solutions, based on Kirkaldy’s analysis [Kir87], the cross-terms in the matrix of the phenomenological coefficients are neglected (i.e., \(L_{ij} = 0\) if \(i \neq j\)) and the resultant expression is the one used by DICTRA:

\[
J_{i}^{K} = -L_{i,i}^{K} \frac{\partial \mu_{i}}{\partial X} = -c_{i} M_{i}^{K} \frac{\partial \mu_{i}}{\partial X}
\]  

(3-4)

where \(M_{i}^{K}\) is the mobility of component \(i\) as defined by DICTRA in the Kirkendall frame. It is evident from the above equation, that neglecting the cross-terms in the matrix
of phenomenological intrinsic coefficients significantly simplifies the effort involved in the determination of the $L_i$’s or the mobilities, $M_i$’s. Manning and Lidiard have vigorously objected to Kirkaldy’s assertion that the cross-terms in the matrix of phenomenological coefficients can be neglected (see [Kir85], discussions by Lidiard and Manning, and responses by Kirkaldy therein). In spite of this, the utilization of Eq. (3-4) has persisted primarily due to the experimental difficulties associated with the measurement of the non-diagonal terms in Eq. (3-3). The procedure for determining the mobilities in Eq. (3-4) is discussed by Agren et al. [Agr82, And92, Bor00].

The expression for the intrinsic flux based on intrinsic jump frequencies for multicomponent systems proposed by DeHoff and Iswaran [Isw93, Deh02] is

$$J_k^\lambda = \frac{1}{6} \lambda^2 \frac{\partial c_k \Gamma_k}{\partial x}$$  \hspace{1cm} (3-5)

where $\Gamma_k$ is the effective intrinsic jump frequency of component $k$ in # jumps/s ($\Gamma_k$ not equal to the tracer jump frequency $\Gamma_k^*$) and $\lambda$ is the jump distance between atomic planes. This expression ignores bias effects operating during the diffusion process, i.e., the fraction of the number of jumps in the $+x$ and $-x$ directions are assumed to be equal to $1/6$ (the isotropic value). A more rigorous expression that takes into account bias effects is discussed in Chapter 5. This expression is

$$J_k^\lambda = 2 \alpha_k \lambda c_k \Gamma_k^* - \frac{1}{6} \lambda^2 \frac{\partial c_k \Gamma_k^*}{\partial x}$$  \hspace{1cm} (3-6)

where $\alpha_k$ is the bias factor for component $k$, i.e., the difference between the fraction of the total number of jumps in the $+x$ direction and $1/6$, and $\Gamma_k^*$ is the tracer jump frequency of
component $k$. At the present time, the theoretical content for $\alpha_k$ is lacking, hence the unbiased version of the jump frequency formalism (Eq. (3-5)) has been utilized in the simulation for modeling diffusion in multicomponent systems (see Chapter 5). However, in Chapter 5 it is demonstrated, that the Darken flux expression, Eq. (3-2), and the rigorous jump frequency expression, Eq. (3-6), can be effectively combined to extract $\alpha_k$ with the aid of the simulation. This unique piece of information is expected to provide some critical insights into the physical origin of the bias factor and aid in the development of an analytical expression that can be utilized in the simulation.

3.2.1 Input for the Simulation

The current version of the simulation has been set up to model unidirectional, isothermal diffusion in a semi-infinite diffusion couple, a situation in which the initial compositions at the two ends of the diffusion couple remain unchanged during the course of the diffusion experiment. The input for the simulation are:

1. The initial concentration distribution for each component.

2. Depending upon the intrinsic flux formalism, a functional relationship for the kinetic descriptors as a function of composition. For example, the intrinsic diffusion coefficients for the Darken formalism, the mobilities for the DICTRA formalism or the jump frequencies in the jump frequency formalism.

3. The molar volume as a function of composition.

The measurement of concentration profiles using the electron microprobe requires knowledge of the molar volume (concentration (mol/cc) = atom fraction (from microprobe) / molar volume (cc/mol) or $c_k = X_k/V$). For a single phase, solid state crystalline system, the assumption that the molar volume is constant is commonly
employed. This assumption is a reasonable one in single phase systems where molar volumes usually do not vary appreciably (less than 30%), hence the errors involved in neglecting molar volume effects are usually within the experimental errors involved in the determination of the kinetic parameters (20% or higher reported by Kapoor and Eagar [Kap90], ± 10% reported by Dayananda for the Ag-Cd system [Ior73]). If it is still desired to take into account variations in molar volume, a reasonable approximation is to compute the molar volumes from the molar volumes of the pure components assuming ideal mixing [Loo90a], i.e., Vegard’s law. For e.g., it is shown in Chapter 4 for the Au-Ni system [Dal00a], that this approximation works rather well. For the jump frequency formalism, the jump distance, $\lambda$, is obtained from the molar volume and crystal structure assuming nearest neighbor jumps.

3.2.2 The Setup

A schematic of the setup for the simulation is shown in Figure 1. The diffusion zone is divided in the direction of the positional coordinate (the x-axis) into a number of slices or intervals having the same width $\delta$ and cross-sectional area $A$. 240 such intervals (or slices) has been found to give adequate resolution of composition variations in the diffusion zone, however additional intervals can be added if needed. The spacing between the points on the x-axis or the width of the slices $\delta$ is chosen to be commensurate with the order of magnitude of the jump frequencies or the intrinsic diffusion coefficients and the time interval chosen. For values of jump frequencies in the range of $10^5$-$10^7$ per second or diffusion coefficients in the range of $10^{-8}$-$10^{-10}$ cm$^2$/s, a time interval $\Delta t$ of 10 seconds and a spatial interval $\delta$ of 2-4 microns usually gave useful resolutions of the evolution of the composition distribution in both space and time. In
case the differences in the jump frequencies or intrinsic diffusion coefficients of the
various components were significant (3-4 orders in magnitude), the slice width was
increased up to 10 microns. It was found that on a Pentium 4 based PC, 128-256
iterations, taking less than a minute in real time, were sufficient to obtain sufficient
resolution, so as to examine and adjust the choice of the setup parameters.

The various slices are numbered from left to right (Fig. 3-1) along the positive x
axis with the position of the left end of the first slice \((i = 1)\) taken to be the origin. From
knowledge of the slice widths, which are initially equal for all slices \((\text{slicewidth}_i = \delta_i)\), the
position of the slices \(x_i\) are determined. Thus for example, the first slice has the position
\(x_i = 0\), while the center slice \((i = 121)\) that corresponds to the Kirkendall interface, is
located at \(x_i = 240\) for \(\delta = 2 \, \mu\text{m}\). The last slice \((i = 241)\) is taken to begin at the end of
the 240th interval and is located at \(x_i = 480\). Each of the positions \(x_i\) in the spatial grid,
that denotes the initial position of the slice, is assigned an initial value of concentration,
\(c_{k,i}\) (the first suffix “\(k\)” denotes the component, the second suffix “\(i\)” the slice number),
atom fraction, \(X_{k,i}\), and a molar volume, \(V_i\). The values of these variables at the midpoint
of the slice, are also computed for every slice. From knowledge of the mean
concentrations, the slice widths and the cross-sectional area, \(A_o\), the number of atoms of
each component in each slice is calculated, hence the total number of atoms in each slice
is known at the start of any iteration.

If chemical potentials are needed as in the DICTRA software, a thermodynamic
solution model for the Gibbs excess free energy as a function of composition is required.
Chemical potentials \(\mu_{k,i}\) and their gradients can then be easily computed from such a
model. If the jump frequency formalism is utilized, then the jump frequency of each
Figure 3-1. Setup for the intrinsic diffusion simulation: (a) The diffusion zone is initially divided into a number of equally spaced slices having a thickness $\delta$. $x_i$ is the position of the $i^{th}$ slice with respect to the origin taken to be the position of the first slice ($i = 1$). $c_{ki}$, $X_{ki}$ and $D_{ki}$ are the concentration, atom fraction and intrinsic diffusion coefficient respectively of component $k$ in slice $i$. $V_i$ is the molar volume of slice $i$ and $A_o$ is the cross-sectional area of each slice, here assumed to be constant at any time during the diffusion process. The diffusion direction is normal to $A_o$ as indicated in the figure. (b) After performing a number of iterations corresponding to a diffusion time $t_1$, the positions and widths of the slices as well as the concentrations have changed due to the accumulation or depletion of atoms within the individual slices. The schematic illustrates the movement of lattice planes due to the Kirkendall phenomenon.

The intrinsic diffusion coefficient of each component, $D_{ki}$, is computed from the composition dependent jump frequency model that is input for the system and is assigned to the position $x_i$. Similarly if the Darken intrinsic formalism is utilized, the intrinsic diffusion coefficient of each component, $D_{ki}^K$, is computed from the input model and assigned to $x_i$ and likewise for the mobilities, $M_{k,i}^K$, in the DICTRA approach.
Figure 3-2. Flow-chart depicting the various steps in the intrinsic diffusion simulation.
3.2.3 Run-Time Iterations

After the initialization procedure is completed, the main body of the program begins (Fig. 3-2). The fluxes at the first \(i = 1\) and last slice \(i = 241\) are set equal to zero at the beginning of each iteration. The intrinsic flux of component \(k\) at \(x_i\) is computed from a central finite difference formulation of the desired expression for the intrinsic flux, Eqs. (3-2), (3-4), (3-5):

\[
J_{k,i}^\text{K} = -D_{k,i}^\text{K} \frac{c_{k,i+1} - c_{k,i-1}}{x_{k,i+1} - x_{k,i-1}} \quad (3-7)
\]

\[
J_{k,i}^\text{K} = -c_{k,i}^\text{K} M_{k,i}^\text{K} \frac{\mu_{k,i+1} - \mu_{k,i-1}}{x_{k,i+1} - x_{k,i-1}} \quad (3-8)
\]

\[
J_{k,i}^\text{K} = -\frac{1}{6} \lambda^2 \frac{c_{k,i+1} \Gamma_{k,i+1} - c_{k,i-1} \Gamma_{k,i-1}}{x_{k,i+1} - x_{k,i-1}} \quad (3-9)
\]

The phenomenological flux expressions given in Eqs. (3-7) and (3-8) are applicable to multicomponent systems, if one neglects the cross terms in the matrix of intrinsic diffusion or phenomenological coefficients respectively. Otherwise, both are restricted to binary systems. If in the rare situation where multicomponent intrinsic diffusion coefficients become available, the expression for the intrinsic flux can be modified to include the cross-terms, see Eq. (3-1). In contrast, the kinetic expression represented by Eq. (3-9) is always valid for multicomponent systems. Since there exists a unique composition dependent jump frequency for each component, the question of neglecting cross-terms does not arise in the jump frequency formalism (Eq. (3-9)). However, as mentioned earlier with reference to Eqs. (3-5) and (3-6), bias effects are ignored in this equation but are discussed with some depth in Chapter 5.
The flux of each component is thus computed using one of the above equations at each position \( x_i \). The accumulation or change in the number of atoms of component \( k \) in the \( i^{th} \) slice or the interval \( (x_{i+1} - x_i) \) is given by

\[
dn_{k,i} = \left( J_{k,i}^K A_i \Delta t - J_{k,i+1}^K A_{i+1} \Delta t \right) N_o \tag{3-10}
\]

where \( N_o \) is Avagadro’s constant. Hence the total number of atoms that accumulate in the \( i^{th} \) interval can be computed. Note that the total number of atoms depends on the sign and magnitude of the fluxes in the adjacent slices, and hence can be either positive or negative in sign. By adding the accumulation of each component \( k \) to the number of atoms of component \( k \) existing in the \( i^{th} \) slice at the start of the current iteration \( n_{k,i}(t-\Delta t) \), the total number of atoms of each component \( k \) is obtained.

\[
n_{k,i}(t) = dn_{k,i}(t) + n_{k,i}(t - \Delta t) \tag{3-11}
\]

Hence the total number of atoms of all components \( (n_i^T = \sum_{k=1}^c n_{k,i}) \) in the \( i^{th} \) slice is computed and thus the mean atom fraction \( (\overline{X}_{k,i}) \) of component \( k \) in the \( i^{th} \) slice can be determined for the current iteration. If the molar volume is a function of composition, then knowledge of the mean atom fractions permits the computation of the new mean molar volume \( (\overline{V}_i) \) in each slice \( i \) and hence the mean concentration \( (\overline{c}_{k,i}) \) of slice \( i \) is determined. A net change in the total number of atoms in each slice requires that the total volume of the slice be adjusted so as to accommodate this net change. The newly computed molar volume can be used to compute the new slice width \( \delta_i \):

\[
\delta_i = \frac{\overline{V}_i n_i^T}{N_o A_i} \tag{3-12}
\]

In making this adjustment for the slice widths, it is assumed that sites are created or destroyed as needed. This is equivalent to the assumption of local equilibrium in the
concentration of vacancies. Intervals that have a net gain in atoms must expand to accommodate this accumulation, while those that experience a net loss must contract. In semi-infinite diffusion couples, it has been shown that this adjustment in volume occurs primarily along the diffusion directions, i.e. in the +x or -x directions. Balluffi’s [Bal52, Bal60] and Ruth’s [Rut97] experiments have demonstrated that contractions or expansions in directions normal to the diffusion direction are primarily restricted to regions very close to the surfaces of the specimens. Hence as long as the diffusion specimens are of sufficient dimensions and are not classified as “thin films”, volume changes normal to the diffusion direction can be neglected. This is equivalent to assuming that the cross-sectional area $A_i$ of each slice remains unchanged during the entire diffusion experiment.

From knowledge of the new slice widths, $\delta_i$, the new position of a slice, $x_i$, can then be determined for the current iteration:

$$x_{i+1} = x_i + \delta_i$$  \hspace{1cm} (3-13)

Note that the position of the first slice is always zero at all times ($x_1 = 0$). Eq. (3-13) has to be applied from the second slice onwards. Thus, the new position of any slice $x_i$ depends upon the cumulative sum of all the slice widths to the left of slice $i$. The difference between the position of a slice at time $t$ and $t + \Delta t$ is the instantaneous lattice shift. The sum over time of all the shifts for the $i^{th}$ plane is the distance that a marker originally placed at this plane would move during the time of the experiment (i.e., the lattice shift):

$$\Delta x_i(t) = x_i(t) - x_i(t=0)$$  \hspace{1cm} (3-14)
The instantaneous velocity of the \(ith\) plane or the local lattice velocity \(v_i^K\) may be calculated from the lattice position using Philibert’s (p. 218 in [Phi91] expression (see Appendix E):

\[
v_i^K = \frac{1}{2t} \left( (x_j - x_{o_{121}}) - (x_{o_i} - x_{o_{121}}) \frac{dx_j}{dx_{o_i}} \right) = \frac{1}{2t} \left( (x_j - x_{o_{121}}) - (x_{o_i} - x_{o_{121}}) \frac{x_{i+1} - x_{i-1}}{x_{o_{i+1}} - x_{o_{i-1}}} \right)
\]

(3-15)

where \(x_{o_i} = x_i(t=0)\)

Note that for the Kirkendall interface \((i = 121)\), the lattice velocity simplifies to the well-known expression \(\Delta x_{121}/2t\). Eq. (3-15) can also be expressed in terms of the lattice shift \(\Delta x_i\), Eq. (3-14):

\[
v_i^K = \frac{1}{2t} \left( \Delta x_i - (x_{o_i} - x_{o_{121}}) \frac{d\Delta x_i}{dx_{o_i}} \right)
\]

(3-16)

where the differential can be expressed in a finite difference form as in Eq. (3-15).

Alternatively, the lattice velocity may be directly computed from the instantaneous lattice shift:

\[
v_i^K = \frac{x_i(t+\Delta t) - x_i(t)}{\Delta t}
\]

(3-17)

The vacancy flux and the interdiffusion fluxes can be computed from the intrinsic fluxes and the lattice velocity (Appendix A):

\[
J_{v_i}^K = - \sum_{j=1}^{c} J_{k,i}^K
\]

(3-18)

\[
J_{k,i}^a = J_{k,i}^K + c_{k,i} v_i^K
\]

(3-19)
Note that the lattice velocity cannot be directly obtained from the vacancy flux, unless the reference velocity in the number frame $v^N$ is zero (Eq. (A-23)), which is only true if the molar volume is constant (Appendix D).

$$J_{v_i}^K = \frac{v_i^{KN}}{V_i} = \frac{v_i^K - v_i^N}{V_i} \quad (3-20)$$

The reference velocity $v^N$ as well as the flux $J_{k}^N$ in the number frame can also be obtained, see Eqs. (A-22) and (A-20):

$$v_i^N = V_i \sum_{k=1}^c J_{k,i}^o \quad (3-21)$$
$$J_{k,i}^N = J_{k,i}^o - c_{k,i} v_i^N \quad (3-22)$$

Similarly, mean velocities and fluxes in other reference frames can be computed if needed (see Appendix A).

The new molar volume $V_i$ and concentration $c_{k,i}$, which are then the starting values at position $x_i$ for the next iteration, are obtained by a linear interpolation of the mean values of these quantities in adjacent slices. For example, the updated concentration is given by

$$c_{k,i} = \bar{c}_{k,i} - \left( \frac{\bar{c}_{k,i} - \bar{c}_{k,i-1}}{1 + \frac{\delta_i}{\delta_{i-1}}} \right) \quad (3-23)$$

The updated values for the atom fractions $X_{k,i}$ are then obtained from $c_{k,i}$ and $V_i$ at $x_i$. Following this, the values for the kinetic descriptors ($D_{k,i}^K$, $\Gamma_{k,i}^K$, or $M_{k,i}^K$) are updated. The next iteration then commences.
The computation is repeated until the composition profiles stabilize and span a significant fraction of the full range of positions programmed into the simulation. It is found that in most cases, the concentration profiles plotted on normalized coordinates \((x/\sqrt{t})\) stabilize after about 128-256 iterations, and takes less than a minute of computer time on a normal PC. However for lattice velocity profiles, more iterations, usually 512-1024 (or more depending on the diffusion coefficients), are needed for stabilization.

3.3 Test of the Simulation for a Model System

An examination of the internal consistency of the simulation can be performed with the aid of model systems. The goal here is to compare the output from the simulation with those obtained using the analytical models. Two such model systems are considered here. The first is for a binary, semi-infinite diffusion couple having constant molar volume; the second is for a similar couple having variable molar volume, but with constant partial molal volumes.

3.3.1 Analytical Model System with Constant Molar Volume

The analytical model has to be capable of generating intrinsic diffusion information such as intrinsic fluxes and lattice velocity profiles, along with conventional interdiffusion information such as composition profiles. Such a simple model for a binary system is one in which the ratio \(R\) of the intrinsic diffusion coefficients is assumed to be constant over the range of compositions considered:

\[
R = \frac{D_A^K}{D_B^K}
\]  
(3-24)

where \(D_A^K\) and \(D_B^K\) are the intrinsic diffusion coefficients of components A and B respectively. A final simplification of the model assumes that the interdiffusion
coefficient $\tilde{D}$ for this system is constant for the range of compositions considered. It should be noted that since the molar volume is assumed to be constant, there exists a single, unique interdiffusion coefficient in this binary, single-phase system (see Eq. (C-15)), which is equal to the diffusion coefficient in the volume frame, $\tilde{D}^V$. Assuming a constant interdiffusion coefficient, the concentration profiles for the two components can be generated using error functions:

$$
X_B(x) = X_B^- + (X_B^+ - X_B^-) \text{cerf}\left(\frac{x}{2\sqrt{\tilde{D}t}}\right)
$$

$$
X_A(x) = 1 - X_B(x)
$$

$X_B^-$ and $X_B^+$ are the far field compositions of component B in the two binary alloys that comprise the diffusion couple. Cerf$(z)$ is the “complete error function” that is related to the normal error function $\text{erf}(z)$ by

$$
\text{cerf}(z) = \frac{1}{2}(1 + \text{erf}(z))
$$

The error function $\text{erf}(z)$ is defined as

$$
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} \exp(-u^2) du
$$

The concentration parameters $X_A$ and $X_B$ are the atom fractions of components A and B respectively. Usually, in the error function solution, Eq.(3-25), the concentrations have to be expressed in terms of $c_k$ (moles/cc), however since the molar volume is constant, concentrations in terms of atom fractions are valid (since $c_k = X_k/V$, the $V$ term cancels on both sides of the equation). In Eq. (3-25), $x$ is the diffusion distance parameter and $t$, the time for the diffusion experiment.
The Darken relation that relates the intrinsic and interdiffusion coefficients [Dar48] is

\[
\dot{D} = X_A D^K_B + X_B D^K_A
\]  

(3-28)

Using Eq. (3-28) and Eq. (3-24), expressions for the intrinsic coefficients in terms of the interdiffusion coefficient and \( R \) can be obtained:

\[
D^K_B(x) = \frac{\dot{D}(x)}{1 - X_B(x) + X_B(x)R}
\]  

(3-29)

\[
D^K_A(x) = RD^K_B(x) = R \left( \frac{\dot{D}(x)}{1 - X_B(x) + X_B(x)R} \right)
\]  

(3-30)

This variation of the intrinsic diffusion coefficients with composition is shown in Fig. 3-3 for the specified value of the interdiffusion coefficient and \( R \).

The lattice velocity is given by [Dar48]

\[
v^K(x) = \left[ D^K_B(x) - D^K_A(x) \right] \frac{dX_B(x)}{dx}
\]  

(3-31)

Substituting for the intrinsic coefficients given in Eqs. (3-29) and (3-30), in Eq. (3-31), an expression for the lattice velocity in terms of the interdiffusion coefficient and \( R \) is obtained:

\[
v^K(x) = (1 - R) \frac{\dot{D}(x)}{1 - X_B(x) + X_B(x)R} \frac{dX_B(x)}{dx}
\]  

(3-32)

An analytical expression for the differential on the R.H.S. of Eq. (3-32) can be obtained using Leibnitz’ rule:
Figure 3-3. Variation of the intrinsic diffusion coefficients with composition for the model system. The ratio of the intrinsic diffusion coefficients is given by: \( R = \frac{D_A^K}{D_B^K} = 5 \). The interdiffusion coefficient, \( D = 10^{-10} \text{ cm}^2/\text{s} \), is constant for all compositions.

\[
\frac{dX_B(x)}{dx} = \frac{(X_B^+ - X_B^-)}{\sqrt{\pi}} \frac{\exp\left(-\frac{x^2}{4Dt}\right)}{2\sqrt{Dt}}
\]

In order to obtain the original position \( x_0 \) of the markers or lattice planes at \( t = 0 \), the expression for the lattice velocity given in Eq. (3-15) is reproduced [Phi91]:

\[
v^K = \frac{1}{2t} \left(x - x_0 \frac{dx}{dx_0}\right)
\]

The distances \( x \) and \( x_o \) are assumed to be measured with respect to the origin at \( x = 0 \). The above equation (3-34) is a first order linear differential equation that can be solved for \( x_0 \) as a function of \( x \) for any given time \( t \). Rearranging Eq. (3-34) in a typical form,
This equation can be solved numerically using a math software such as MathCad (using the function “rkfixed”). The boundary conditions are known since at the far field compositions of the diffusion couple, the lattice velocity is zero, i.e., the lattice positions are unchanged. Since Eq. (3-35) has a singularity at the position corresponding to the Kirkendall interface \( x_K = v_K \cdot 2t \), the complete numerical solution \( x_0(x) \) was obtained for two separate intervals, from \( x = x^- \) to \( x_K \) and then from \( x = x^+ \) to \( x_K \). Once \( x_0 \) was obtained, the lattice shifts \( (x - x_0) \) could be also determined.

The intrinsic fluxes are given by

\[
J_A(x) = -\frac{D_A^K(x)}{V} \left( \frac{dX_A(x)}{dx} \right); \quad J_B(x) = -\frac{D_B^K(x)}{V} \left( \frac{dX_B(x)}{dx} \right)
\]

and the vacancy flux is

\[
J_v(x) = - \left[ J_A(x) + J_B(x) \right]
\]

Note that since the sum of the atom fractions is unity,

\[
\frac{dX_A(x)}{dx} = - \frac{dX_B(x)}{dx}
\]

Using Eqs. (3-30, 3-32, 3-36 and 3-38), the intrinsic fluxes given in Eq. (3-36) and the vacancy flux, Eq. (3-37), can be expressed in terms of the interdiffusion coefficient and \( R \). The interdiffusion fluxes are

\[
J_A^o(x) = -\frac{\tilde{D}(x)}{V} \left( \frac{dX_A(x)}{dx} \right); \quad J_B^o(x) = -\frac{\tilde{D}(x)}{V} \left( \frac{dX_B(x)}{dx} \right)
\]
Parameters. The following were the parameters for the model system:
interdiffusion coefficient $D = 10^{-10}$ cm$^2$/s, ratio of intrinsic coefficients $R = 5$, molar
volume $V = 9$ cc/mole, diffusion time $t = 12 \cdot 3600$ s for the error function solution. A
full-range diffusion couple, i.e., where the infinite compositions are the pure components,
was selected. The initial compositions at $t = 0$ were: $X_A^- = 0$, $X_B^- = 1$ and
$X_A^+ = 1$, $X_B^+ = 0$.

The initial setup conditions for the simulation are: spacing $\delta = 0.5$ µm, time step
for each iteration $\Delta t = 10$ s, # of slices = 240. A total of 512 iterations were performed to
obtain a high resolution output. This corresponds to a duration of the diffusion
experiment, $t_s = 5120$ s. In Figs. 3-4 to 3-7, the circles represent the output obtained
using the simulation and the solid lines those from the analytical error function solution.
If the output from the simulation were plotted for every slice position $x_i$, the distance
between any two points $x_i$ and $x_{i+1}$ in the figures would represent the slice width of slice $i$.
However in the present situation, the interval between the data points (every 10th data
point was plotted) was varied to permit sufficient resolution between the two outputs.

In Fig. 3-4a, the compositions profiles (in atom fractions, $X_k^+$'s) for the analytical
model and the simulation are plotted as a function of the distance. If $x$ is the distance
variable for the model system, the corresponding distance variable for the simulation is
$x_i - x_{0,121}$, where the initial position of the 121st slice, $x_{0,121}$, corresponds to the position $x$
= 0 (the Matano interface) for the analytical model solution. In Fig. 3-4b, the
compositions are plotted as a function of the normalized distance (or Boltzman)
parameter, $X/\sqrt{t_s}$ for the analytical solution, and $X/\sqrt{t_s}$ for the simulation. Although
the diffusion times in the simulation and the analytical solution are different, the resultant
profiles when plotted using the normalized parameter, are identical as predicted from Fick’s second law. The output from the simulation can be converted to any desired time by multiplying the normalized distance with the square root of the diffusion time. For example, in Fig. 3-4a, the composition profiles are plotted as a function of the distance $x$ for time $t = 12$ hrs.

Figs. 3-5a and 3-5b depict the variation in the lattice velocity and lattice shift with distance respectively. It is seen that the maximum value of the lattice shift and the lattice velocity both occur at the Kirkendall interface. Note that in general, this is not always true. Cornet and Calais [Cor72, Cor74] and van Dal et al. [Dal00b] have discussed models to prove this point. For example, instead of choosing a model where the ratio of the intrinsic diffusion coefficients is constant, a model where the difference between the coefficients is constant, can be shown to have different positions for the maximum in the lattice shift and lattice velocity profiles.

Figs. 3-6a and b show the lattice position $x$ and lattice shift $\Delta x$ as a function of the initial position $x_0$. An “oblique marker” experiment (Appendix E), that can provide the positions of lattice markers throughout the diffusion zone, results in a lattice position profile similar to that shown in Fig. 3-6b [Cor72, Cor74, Phi91]. The variation in the intrinsic fluxes and vacancy flux is depicted in Fig. 3-7a, while Fig. 3-7b shows the variation in the interdiffusion fluxes with position. Since the molar volume is constant for the present model system, the interdiffusion fluxes are equal and opposite in sign (see Appendix A).

It is clear from the figures that the simulation faithfully reproduces the analytical results for the model system considered.
Figure 3-4. Composition profile for the model system as a function of (a) distance from the origin (the initial interface) and (b) normalized distance. The solid lines denote the error function solution, the circles the output from the simulation. $x_K$ is the position of the Kirkendall interface. The parameters for this model system are: $\bar{D} = 10^{-10}$ cm$^2$/s, $R = D_A^K/D_B^K = 5$, $V = 9$ cc/mol, $t = 12\cdot3600$ s.
Figure 3-5. Variation of the lattice velocity and lattice shift as a function of position. (a) Lattice velocity; (b) lattice shift. The maximum for both the graphs is at the Kirkendall interface for the chosen model.
Figure 3-6. Dependence of the lattice shift and lattice position on the initial lattice position, i.e., at $t = 0$. (a) Lattice shift; (b) lattice position.
Figure 3-7. Diffusion fluxes for the model system. (a) Intrinsic fluxes of the components and the resultant vacancy flux for the model system and (b) interdiffusion fluxes. Since the intrinsic flux of A is greater than B, the resultant vacancy flux is positive. Hence the Kirkendall shift is also positive. The interdiffusion fluxes are equal and opposite in sign.
3.3.2 Analytical Model System with Variable Molar Volume

In this case, it is assumed that the molar volume of the system is a function of composition. A simple model for a composition dependent molar volume is one in which the partial molal volumes are equal to the molar volumes of the pure components but different from each other.

\[
\bar{V}_A = V_A^o ; \quad \bar{V}_B = V_B^o \quad (3-40)
\]

Hence the molar volume is obtained by ideal mixing of the pure components (Vegard’s law) and exhibits a linear variation with composition, \(X_B\) (Fig. 3-8a).

\[
V_{mix} = \bar{V}_A^o X_A + \bar{V}_B^o X_B = V_A^o X_A + V_B^o X_B \quad (3-41)
\]

As in the previous case, the ratio \(R\) of the intrinsic diffusion coefficients is assumed to be constant over the range of compositions considered. In Appendix D, it is shown that if the partial molal volumes are constant and equal to the molar volumes of the pure components, the volume averaged velocity, \(v^V\), is zero. Hence, as in the previous case, from Eq. (C-15), the interdiffusion coefficient, \(D^o\), for this system is constant for the range of compositions considered and equal to the diffusion coefficient in the volume frame, \(\tilde{D}^V = \tilde{D}\). Hence, the concentration profiles for the two components can be generated using error functions. However, since the molar volume is variable the concentration units have to be expressed in terms of \(c_k\) (moles/cc). The expressions are

\[
c_A(x) = c_A^- + (c_A^+ - c_A^-) \text{erf} \left( \frac{x}{2 \sqrt{D t}} \right)
\]

\[
c_B(x) = c_B^- + (c_B^+ - c_B^-) \text{erf} \left( \frac{x}{2 \sqrt{D t}} \right)
\]  

(3-42)
where \( c_A^- \) and \( c_A^+ \), and \( c_B^- \) and \( c_B^+ \) are respectively the far field concentrations of components A and B in the two binary alloys that comprise the diffusion couple, and are given by

\[
c_A^- = \frac{X_A^-}{V^-}; \quad c_B^- = \frac{X_B^-}{V^-} \quad \text{and} \quad c_A^+ = \frac{X_A^+}{V^+}; \quad c_B^+ = \frac{X_B^+}{V^+}
\]  

(3-43)

The far field molar volumes \( V^- \) and \( V^+ \) are obtained using Eq. (3-41):

\[
V^- = V_A^o X_A^- + V_B^o X_B^- \quad \text{and} \quad V^+ = V_A^o X_A^+ + V_B^o X_B^+
\]  

(3-44)

The variation of the molar volume with position is obtained from the concentrations that are provided by the error function solutions, Eq. (3-42):

\[
V_{\text{mix}}(x) = \frac{1}{c_A(x) + c_B(x)} = \frac{1}{C(x)}
\]  

(3-45)

where \( C \) is the total concentration in mol/cc. The atom fraction of component \( k \) is obtained from the product of the concentration and the molar volume:

\[
X_k(x) = c_k(x) V_{\text{mix}}(x)
\]  

(3-46)

The Darken relation that relates the intrinsic and interdiffusion coefficients is now modified (Eq. (C-50)).

\[
\tilde{D} = c_A \bar{V}_A D_A^K + c_B \bar{V}_B D_A^K = c_A V_A^o D_A^K + c_B V_B^o D_A^K
\]  

(3-47)

As in the previous case, expressions for the intrinsic coefficients in terms of the interdiffusion coefficient and \( R \) can be obtained:

\[
D_A^K(x) = \frac{\tilde{D}(x)}{c_A(x) V_A^o + c_B(x) V_B^o R}
\]  

(3-48)
Figure 3-8. Variation of the molar volume and intrinsic diffusion coefficients with composition for the model system with varying molar volume. (a) Molar volume and (b) intrinsic diffusion coefficients. The parameters are: $R = D_A^K / D_B^K = 5$, $V_A^o = 9$ and $V_B^o = 5$ cc/mol and $D = 10^{-10}$ cm$^2$/s.
\[ D_A^K(x) = RD_B^K(x) = R \left( \frac{\tilde{D}(x)}{c_A(x) V_A^o + c_B(x) V_B^o R} \right) \]  \hspace{1cm} (3-49)

The variation of the intrinsic diffusion coefficients with composition is shown in Fig. 3-8b.

The lattice velocity measured with respect to the volume frame (Eq. (C-48) and (B-9)) is given by

\[ v^{KV}(x) = \left[ D_B^K(x) - D_A^K(x) \right] V_B^o \frac{dc_B(x)}{dx} \]  \hspace{1cm} (3-50)

However, since \( v^V \) is zero,

\[ v^{KV}(x) = v^K(x) - v^V(x) = v^K(x) \]  \hspace{1cm} (3-51)

Substituting for the intrinsic coefficients given in Eqs. (3-48) and (3-49), in Eq. (3-51), an expression for the lattice velocity in terms of the interdiffusion coefficient and \( R \) is obtained:

\[ v^K(x) = (1 - R) \frac{\tilde{D}(x)}{c_A(x) V_A^o + c_B(x) V_B^o R} V_B^o \frac{dc_B(x)}{dx} \]  \hspace{1cm} (3-52)

The original position, \( x_0 \), of a marker or lattice plane at \( t = 0 \) and the lattice shift, \( (x - x_0) \), can be obtained from the lattice velocity in a manner similar to that for the previous model system, see Eqs. (3-34) and (3-35).

The intrinsic fluxes are given by

\[ J_A^K(x) = -D_A^K(x) \frac{dc_A(x)}{dx}; \quad J_B^K(x) = -D_B^K(x) \frac{dc_B(x)}{dx} \]  \hspace{1cm} (3-53)
and the vacancy flux is the negative sum of the intrinsic fluxes, see Eq. (3-37). As in the earlier case, the intrinsic fluxes and the vacancy flux can be expressed in terms of the interdiffusion coefficient and $R$. The interdiffusion fluxes are given by

$$J^o_A(x) = -\tilde{D}(x) \frac{dc_A(x)}{dx}; \quad J^o_B(x) = -\tilde{D}(x) \frac{dc_B(x)}{dx} \quad (3-54)$$

The number weighted velocity, $v^N$, is obtained using Eq. (A-22):

$$v^N(x) = V_{mix}(x) [J^o_A(x) + J^o_B(x)] \quad (3-55)$$

and the corresponding flux of component $k$ in the number-fixed frame, $J^N_k$, is (Eq. (A20))

$$J^N_k = J^o_k - c_k v^N \quad (3-56)$$

Parameters. The molar volumes of the two components for this model system were: $V_A^o = 5$ and $V_B^o = 9$ cc/mole. The other parameters for this model system were identical to the previous one: interdiffusion coefficient $\tilde{D} = 10^{-10}$ cm$^2$/s, ratio of intrinsic coefficients $R = 5$, diffusion time $t = 12,3600$ s for the error function solution. A full-range diffusion couple, i.e., where the infinite compositions are the pure components, was again selected. The initial compositions at $t = 0$ were: $X_A^- = 0, X_B^- = 1$ and $X_A^+ = 1, X_B^+ = 0$.

The initial setup conditions for the simulation were identical to the previous case. In Figs. 3-9 to 3-13, the circles represent the output obtained using the simulation and the solid lines those from the analytical error function solution.

In Fig. 3-9a, the concentration profiles, $c_k$ (mol/cc), are plotted as a function of distance, $x$, and in Fig. 3-9b as a function of the normalized distance (or Boltzman) parameter, $\frac{x}{\sqrt{t}}$. From knowledge of the concentrations and the molar volume, the
composition profiles in atom fractions, $X_k$, are plotted as a function of distance and normalized distance in Figs. 3-10a and b respectively.

In Fig. 3-11a, the variation in the lattice velocity, $v^K$ (Eq. (3-52)), and the number weighted velocity, $v^N$ (Eq. (3-55)), are shown. Since $v^N$ is non-zero only when the molar volume is variable, it is evident from Fig. 3-11a, that the contribution is quite significant. In Fig. 3-11b, a plot of the lattice shift as a function of distance again reveals that the maximum shift is for the Kirkendall plane. It is to be noted that in spite of choosing a model system with variable molar volume, the lattice velocity and lattice shift are identical to the previous case. This appears to be the case since the particular choice of parameters used for the model system (other than the varying molar volume) were identical to the previous case. A detailed analysis has however not been performed.

The variation in the intrinsic fluxes and vacancy flux is depicted in Fig. 3-12a. In Fig. 3-12b, the number fluxes (Eq. (3-56)), shown are equal in magnitude and opposite in sign as expected from Eq. (A-18). Since the molar volume is not constant, it is seen from Fig. 3-12c, that the partial molal volume weighted interdiffusion fluxes are equal in magnitude and opposite in sign, see Eq. (A-27). It is clear from these figures, that as in the previous case, the simulation again reproduces the analytical results for the model system with variable molar volume.

Rather than compare the output of the simulation with analytical results obtained for the model system, the true test of the simulation is in comparison with experimental information for a number of important systems. An application for the Fe-Ni system is discussed in the next section. More examples are provided in Chapter 4.
Figure 3-9. Concentration profile (in mol/cc) for the model system with variable molar volume as a function of (a) distance from the origin (the initial interface) and (b) normalized distance. The solid lines denote the error function solution, the circles the output from the simulation. $x_K$ is the position of the Kirkendall interface. The parameters for this model system are: $\bar{D} = 10^{-10}$ cm$^2$/s, $R = D_A^k / D_B^k = 5$, $V_A^\alpha = 9$ and $V_B^\alpha = 5$ cc/mol, $t = 123600$ s.
Figure 3-10. Composition profile (in atom fraction) for the model system as a function of (a) distance from the origin (the initial interface) and (b) normalized distance. Note that $X_k = c_k V_{\text{mix}}$. 
Figure 3-11. Mean and lattice velocities, and lattice shift as a function of position for the model system with variable molar volume. (a) Variation of the lattice velocity ($v^K$) and number averaged velocity ($v^N$), and (b) lattice shift.
Figure 3-12. Diffusion fluxes for the model system with variable molar volume. (a) Intrinsic fluxes of the components and the resultant vacancy flux, and (b) fluxes in the number frame. Note that the number fluxes are equal in magnitude and opposite in sign.
Figure 3-12. Continued. (c) Partial molal volume weighted interdiffusion flux as a function of distance. Since the molar volume of the system is varying, the partial molal volume weighted interdiffusion fluxes are equal in magnitude and opposite in sign.

3.4 Test of the Simulation for the Fe-Ni system

The intrinsic diffusion coefficients in the α Fe-Ni system at 1200°C were measured by Kohn et al. [Koh70] using a multi-foil technique [Heu57]. It is seen in Fig. 3-13a, that the intrinsic coefficient of Fe is much higher than Ni over the entire composition range. It is also noticed that the intrinsic coefficients of both components increase with increasing Ni (the slower diffuser). This is reflected in a deeper penetration depth on the Ni-rich side of the diffusion couple as shown in Fig. 3-13b. The Kirkendall shift (x_\text{K} in Fig. 3-13b) is significant for the duration of the experiment (48 h) due the large differences in the intrinsic fluxes of Fe and Ni (Fig. 3-14a). The lattice velocity distribution obtained from the simulation is compared with the experimental data in Fig. 3-14b. The agreement for all the graphs is reasonable given the fact that the authors
Fe-Ni, 1200°C

Atom Fraction Ni

0.0 0.2 0.4 0.6 0.8 1.0

Intrinsic Diffusion Coefficient (cm²/s)

1e-11

1e-10

1e-9

 DNi

DFe

Fe-Ni, 1200°C, 48 hrs

x (µm)

-400 -300 -200 -100 0 100 200

Atom Fraction Ni

0.0

0.2

0.4

0.6

0.8

1.0

xK

Figure 3-13. Application of the intrinsic diffusion simulation for the Fe-Ni system at 1200°C. (a) Intrinsic diffusion coefficients as a function of composition. (b) Concentration profile for a full-range Fe-Ni diffusion couple. The solid line represents the output of the simulation based on the intrinsic diffusion data in Table 1 of Kohn et al. [Koh70], that includes data from both full range and incremental couples. Circles indicate the data points obtained from the experimental concentration profile given in Fig. 4 of their paper. $x_K$ denotes the Kirkendall interface obtained from the simulation. The location of the Matano interface in their Figure 4 has been corrected by -15 microns to account for the porosity present on the Fe rich side of their diffusion couples.
Figure 3-14. Intrinsic fluxes and lattice velocity for the Fe-Ni system at 1200°C. (a) Intrinsic flux distribution as a function of composition. The intrinsic flux of Fe is much higher than Ni since the intrinsic diffusion coefficient of Fe is higher than Ni. (b) Lattice velocity profile. From Fig. 3-13(b), it is seen that the lattice shift is towards the Fe-rich side of the diffusion couple, i.e., in the +x direction. Hence, the lattice velocity is positive.
had to apply a correction in the measured lattice velocity profile to account for the
formation of Kirkendall porosity on the Fe-rich side of their diffusion couple. Vignes
and Badia [Vig69a] have demonstrated that the porosity formation can be attributed to
the low purity of the electrolytic Fe utilized in their experiments, the use of high-purity
zone-refined Fe prevented this problem. Nevertheless, the simulation demonstrates, that
the correction employed by the authors, results in reasonable agreement with the
experimental data. In upcoming chapters, the simulation is repeatedly applied to more
systems that include both binary and ternary systems.
CHAPTER 4
TESTS OF DARKEN-MANNING THEORIES USING THE INTRINSIC DIFFUSION SIMULATION

In the previous chapter, a simulation based on the Darken theory of intrinsic diffusion was introduced [Dar48] and its self-consistency was demonstrated with the aid of a model system. In this chapter, the Darken-Manning (D-M) theories [Dar48, Man68, Man70] that have long (about 50 yrs.) been used to connect diffusion behavior in homogenous and gradient systems, are analyzed with the aid of the simulation. Attempts to examine the D-M theories are not new, however most of these are based on comparisons between interdiffusion or intrinsic diffusion coefficients and tracer diffusion coefficients in binary systems. A more reliable method of assessing the D-M theories, is to compare the experimental observables in a diffusion experiment, e.g., concentration profiles and lattice shifts, with those predicted using these theories. Without the aid of a simulation capable of reproducing the experimental observables using the intrinsic diffusion coefficients predicted from the D-M theories as the input, such an endeavor could not be attempted in the past.

In this chapter, the relevance of the D-M theories to current diffusion theory is first considered. Some of the previous tests of these theories in the literature are critically examined. The Darken theory and the important assumptions involved in its development are then discussed. Since the Manning theory, although theoretically significant, results in relatively minor corrections to the Darken equations, only a brief
discussion is presented. A procedure for examining the D-M theories using the
simulation is discussed. This procedure is then utilized to test the D-M theories for four
systems: Ag-Cd, Au-Ni, Cu-Zn and Cu-Ni.

4.1 Importance of Darken-Manning Theories

There are many situations, where the kinetic parameters, e.g., the intrinsic
diffusion coefficients, that are needed as the input to the simulation, are either unreliable
or are impossible to determine due to the experimental difficulties involved in their
measurement. In thin films, composition gradients are very steep, due to which
measurement errors using a technique such as the electron microprobe [Gol02, Zie64],
can be rather inaccurate if adequate precautions are not taken [Loo90a]. Stress and
gradient energy effects [Ste88, Lar85, Hil69]; electric, magnetic and other external fields
[Man62, Man89, Hun75], can cause errors in the measured diffusion coefficients, if these
are not explicitly taken into consideration in formulating the diffusion equations in such
systems. Impurities can cause notable differences in the measured diffusion coefficients;
for e.g., in the Fe-Ni system, Vignes and Badia [Vig69a] have demonstrated, that the
utilization of low purity, electrolytic Fe causes the formation of Kirkendall porosity due
to which the measurements may be compromised. Similarly, Van Loo [Loo90] has
discussed a situation where the presence of oxygen impurities led to the formation of
oxide phases during the early stages of diffusion in the Ti-Al system. The microstructure
may also have an important effect on the experimental measurement of diffusion
coefficients. For example, in the case of diffusion in fine grained materials, it is
necessary to include a grain boundary diffusion contribution in addition to the usual
volume diffusion contribution. Furthermore, if there exists anisotropy in the
microstructure, the resultant diffusion coefficients may be quite different from those measured for isotropic microstructures. Even if the practitioner is aware of the many factors that may influence the measurement of the diffusion coefficients, quite often, it is too cumbersome and impractical for him/her to engage in deconvolution. As a result, the diffusion coefficients reported by different authors can vary appreciably.

Some of the more fundamental problems in the phenomenological theory of diffusion were considered in Chapter 2. For example, the values of the phenomenological diffusion coefficients are not unique, they depend on the choice of the independent composition variables. As the number of components in a system increases, the physical meaning of these coefficients and the connection with the actual jump frequency of atoms in the moving system, becomes increasingly abstruse. A more pressing problem is the well-known fact that in quaternary or higher order systems, the matrix of diffusion coefficients cannot be determined without simplifying assumptions, for e.g., the cross-terms in the matrix of diffusion coefficients are ignored (as in the software DICTRA), or the diffusion coefficients are assumed to be constant within a narrow composition range. While such assumptions may be adequate or justifiable in some cases, they fall short of providing a reliable methodology for developing robust multicomponent databases for diffusion, that can be utilized in a simple and effective manner by the average researcher.

In comparison to the phenomenological diffusion coefficients, tracer diffusion coefficients or tracer jump frequencies have unambiguous meaning, i.e., there is a unique value for each component regardless of the number of components. Ignoring the negligible difference in the atomic mass between a component and its isotope (tracer), the
tracer diffusion coefficient is practically identical to the diffusion coefficient of that component in a homogenous system (no composition gradients). The measurement of tracer diffusion coefficients is usually carried out on high-purity, homogeneous samples under well-controlled laboratory conditions. These measurements involve the use of radioactive tracers and are difficult to perform due to the obvious environmental and health concerns. Nevertheless, they are highly accurate if properly conducted and measurement errors within ±3 pct in tracer diffusion measurements from separately annealed specimens within the same laboratory are obtainable [Rot84]. Values of tracer diffusion coefficients from easy duplicable materials (e.g., Ag 99.999 pct) are found to be reproducible within ±10 pct between laboratories. This is to be compared to the 20 % or higher error usually reported for diffusion coefficients using diffusion couples [Kap90].

Modern thermodynamic databases based on CALPHAD techniques are being increasingly used in conjunction with calculations based on “first-principles” for the purpose of designing and comprehending complex multicomponent, multiphase systems [Kau70, Kat97]. The advantage of a first-principles approach is that the fundamental properties of the system, including the basic atom jump frequencies (practically equal to the tracer jump frequencies) of the components can be obtained, although such approaches are primarily restricted to unary and a few binary systems at the present time [Mur84]. Given the inherent difficulties associated with the measurement of diffusion coefficients in multicomponent systems (some of which may contain more than fifteen elements) and the ambiguous meaning of these coefficients, it appears that the best approach for developing modern diffusion databases and simulations for modeling evolutionary processes in multicomponent materials, should be based on the connection
between diffusion behavior in homogenous and gradient systems. Thus if the diffusion behavior of a component in a homogenous system can be accessed with the aid of a database, its behavior in a moving system can be predicted based on this connection. Alternatively if the diffusion coefficients have been measured in the moving system, their authenticity may be verified. The Darken-Manning theories that provide these connections are therefore of vital importance in such endeavors.

4.2 The Darken Theories

4.2.1 Darken A: Intrinsic Diffusion

The diffusion theory of Adolf Fick [Fic55], first proposed in 1855, is still regarded as the foundation behind modern diffusion theory, in spite of the numerous modifications that have occurred since that time. Darken’s theory of intrinsic diffusion [Dar48, Dar51], that was initially presented in 1948, was in response to the inherent limitations of Fick’s formalism in describing diffusion behavior in more complicated systems. Hence, a discussion of the historical context with which the Darken theories were originally formulated, appears necessary.

Fick’s first law states that the flux of a diffusing substance along the diffusion direction is proportional to the concentration gradient of the diffusing substance. In the case of unidirectional diffusion in a binary system, this can be written as

\[ J_k = -D \frac{\partial c_k}{\partial x} \]  

(4-1)

\( J_k \) is the flux of component \( k \) in mol/cm\(^2\)-s; the implied constant of proportionality in Eq. (4-1), \( D \), is the diffusion coefficient expressed in units of cm\(^2\)/s; \( c_k \) is the concentration of component \( k \) in mol/cc; and \( x \) is the distance in cm.
Fick’s second law is essentially a conservation statement for component $k$:

$$\frac{\partial c_k}{\partial t} = - \frac{\partial J_k}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial c_k}{\partial x} \right)$$

(4-2)

and if $D$ is independent of concentration, the second law simplifies to

$$\frac{\partial c_k}{\partial t} = D \frac{\partial^2 c_k}{\partial x^2}$$

(4-3)

At the time the laws were proposed, there existed little experimental information for validating whether the constant of proportionality in Fick’s first law, i.e., the diffusion coefficient, was indeed a constant as the law implied. Subsequently, experiments conducted (mostly in gaseous or dilute liquid solutions) found that variations in the diffusion coefficient with composition were relatively small (less than 8 %), thus appearing to validate the law [Dar48, Dar51]. It was not until considerably later, that diffusion studies in electrolytes and polymer systems and eventually in metallic systems, conclusively demonstrated that the diffusivity (or the diffusion coefficient) varied significantly with composition. In fact, it was found that the diffusion coefficient varied by several orders in magnitude in some systems (the Cu-Zn system discussed later in this chapter is an example). With these findings, Fick’s law evolved to a definition of the diffusion coefficient $D$ as a function of composition. Note that it is also implied in the Fickian formalism, that $D$ is not a function of the concentration gradient, but is only a function of state variables such as the temperature, pressure and composition. This definition of $D$ was facilitated by the works of Boltzmann [Bol94] and Matano [Mat33], who showed that by replacing the distance ($x$) and time ($t$) variables in Fick’s second law with a single variable, $\lambda = \frac{x}{\sqrt{t}}$, Fick’s second law (Eq. 4-2) in a semi-infinite system
could be transformed to an ordinary differential equation by virtue of which the
composition dependent diffusivity, $D$, could be easily computed. This expression is

$$D(c_k^i) = -\frac{1}{2} \left( \frac{d\lambda}{dc_k^i} \right) \frac{c_k^i}{c_k} \int \lambda dc_k = -\frac{1}{2t} \left( \frac{dx}{dc_k} \right) \frac{c_k^i}{c_k} \int x dc_k \tag{4-4}$$

where \( c_k^- \) is the concentration of component \( k \) at a far-field position \((x = \pm \infty)\), that is unchanged during the course of the diffusion process. In order to determine \( D \) in Eq. (4-4), it is necessary to determine the position of the origin from which \( x \) is measured. This choice of origin, first suggested by Matano [Mat33], is known as the “Matano interface,” and is obtained by dividing the two areas in Fig. 4-1, such that they are equal.

Mathematically, this can be stated as
Using an appropriate transformation of the distance axis, an equation similar to the Boltzman-Matano equation (Eq. (4-4)) can be derived for the case of variable molar volume [Sau62, Bro69, Loo70].

\[
\int_{c_k^-}^{c_k^+(x_M)} x dc_k + \int_{c_k(x_M)}^{c_k^-(x_0)} x dc_k = 0
\]

This implies that the change in the number of moles of component \( k \) on the two sides of the Matano interface \( (x_M = x_0) \) are equal (Fig. 4-1). It is assumed for the sake of this discussion, that the molar volume of the system is constant.\(^1\)

The selection of the origin required for the determination of the diffusivity using the Matano analysis determines the frame of reference, in this case the Matano frame of reference. Since the Matano interface is always at a fixed distance from one end of the sample, when the volume of the system is constant, the Matano frame of reference is identical to the “laboratory frame of reference (\( \mathbb{R}^n \))” (Appendix A). If the molar volume of the system is not constant, it becomes necessary to define various reference frames. The subject of reference frames is considered in Appendix A. The binary diffusion coefficient, \( D \), defined by Fick, is unique when measured in the volume frame of reference, even if the molar volume of the system is not constant (Appendix C). Hence, historically Fick’s law is written in the volume frame of reference to preserve the uniqueness of a single diffusion coefficient. The binary diffusion coefficient is not unique for other reference frames, unless the molar volume is constant, in which case the mean velocity weighted reference frames are all identical to each other (see Appendix C).

Thus for a system having a constant molar volume, Fick’s first law can be restated in the laboratory frame of reference as

\(^1\) Using an appropriate transformation of the distance axis, an equation similar to the Boltzman-Matano equation (Eq. (4-4)) can be derived for the case of variable molar volume [Sau62, Bro69, Loo70].
The fluxes defined in the lab frame are known as the interdiffusion fluxes and the diffusion coefficient, \( D^0 \), is known as the interdiffusion coefficient. The superscript \(^0\) in Eq. 4-6 indicates that the flux and the diffusion coefficient are measured in the lab frame of reference.

It was recognized by Darken, that there were many instances where the idea of a single diffusion coefficient was not very satisfactory in explaining the diffusion process. For e.g., in an ionic lattice, it was known that the migration velocity of the cation could be quite different from the anion; in a mixture of two inert gases having large differences in molecular weights, it could be expected that the velocity of the lighter molecules would be much greater than the heavier molecules. Thus it seemed necessary to define two diffusion coefficients, one for each component. There were other key experiments, that pointed in the same direction. Hartley and Crank [Har31, Har49] recorded the movement of inert markers of titanium dioxide during their study of diffusion of acetone in cellulose acetate. These authors reasoned, that the varying “intrinsic” motion of the two components resulted in a hydrostatic pressure buildup, that was subsequently released in the form of a “mass flow” of the entire system, thus causing the movement of the inert markers. This evidence of a mass flow in liquid systems, was suggested by Smigelskas and Kirkendall [Smi47] to be also applicable for solid state systems, although the mechanism proposed was different. They demonstrated that an inert molybdenum wire placed at the original interface in a Cu-Zn diffusion couple moved towards the zinc rich side during the diffusion process. This led the authors to conclude, that the marker
moved due to the movement of the lattice associated with the marker. They suggested that an unequal rate of atom-vacancy exchanges (the exchange rate of zinc being much higher than copper) caused a net vacancy flux and resulted in an accumulation (or depletion) of vacancies in different regions of their diffusion couple. The subsequent annihilation of these excess vacancies in order to maintain the equilibrium vacancy concentration, caused the motion of the lattice and the inert Mo marker associated with it, the authors reasoned. Kirkendall’s hypothesis was corroborated by the calculations of Huntington and Seitz [Hun49, Sei50, Sei53], who demonstrated on energetic grounds, that a vacancy mechanism was much more favorable as the preferred mode of diffusion as compared to the other mechanisms prevalent at the time.

Based on these experiments, Darken recognized that it was necessary to separate the diffusion of atoms relative to the bulk motion of the lattice (identical to the motion of inert markers) from the combined motion due to the two contributions. Thus he suggested that the flux of a component given by Fick’s first law be expressed in terms of two contributions: (1) the diffusion of atoms relative to the motion of the lattice on which they reside and (2) the bulk motion of the lattice itself. The expression he first suggested is

\[ J_k^0 = J_k^K + c_k v^K \]  \hspace{1cm} (4-7)

where \( J_k^K \) is the “intrinsic flux” of component \( k \) defined in the Kirkendall or lattice frame of reference (indicated by the superscript \( K \)), and \( v^K \) is the velocity of the lattice, which can be shown to be identical to that of an inert marker residing on the lattice (Appendix E). The intrinsic flux is
Based on the terminology first adopted by Hartley and Crank, $D_k$ is known as the “intrinsic diffusion coefficient” of component $k$. Eq. (4-7) can be used to write the intrinsic flux of component $k$ in the usual form used for defining fluxes in other reference frames (Appendix A):

$$J_k^K = J_k^o - c_k v^K$$

(4-9)

With this definition of the intrinsic diffusion coefficients and the intrinsic fluxes, Darken then proceeded to obtain a relation between the interdiffusion and intrinsic diffusion coefficients. He also derived an expression for the lattice velocity in terms of the intrinsic diffusion coefficients. The procedure that is adopted here is simpler than the one originally given by Darken, the results are the same. The molar volume is assumed to be constant throughout this development.

Let A and B denote the two components in a binary system. Fick’s first law that applies to the lab frame of reference is

$$J_A^o = -D_A^o \frac{\partial c_A}{\partial x}$$

$$J_B^o = -D_B^o \frac{\partial c_B}{\partial x}$$

(4-10)

The intrinsic fluxes of A and B are

$$J_A^K = -D_A \frac{\partial c_A}{\partial x}$$

$$J_B^K = -D_B \frac{\partial c_B}{\partial x}$$

(4-11)

The relations between the intrinsic and interdiffusion fluxes for the two components (Eq.
The sum of the interdiffusion fluxes is zero (Appendix A):

$$J_A^0 + J_B^0 = 0$$  \hspace{1cm} (4-13)

Substituting Eq. (4-12) in Eq. (4-13),

$$J_A^K + J_B^K + v^K(C_A + C_B) = 0$$  \hspace{1cm} (4-14)

Note that

$$(C_A + C_B) = C = \frac{1}{v}$$  \hspace{1cm} (4-15)

where $C$ is the total concentration of atoms and $V$, the molar volume. From the definition of the intrinsic fluxes, Eq. (4-11), and Eq. (4-15), Eq. (4-14) can be written as

$$-D_A \frac{\partial c_A}{\partial x} - D_B \frac{\partial c_B}{\partial x} + v^K C = 0$$  \hspace{1cm} (4-16)

Since $C$ is assumed to be composition independent,

$$\frac{\partial c_A}{\partial x} + \frac{\partial c_B}{\partial x} = \frac{\partial C}{\partial x} = 0$$  \hspace{1cm} (4-17)

$$\frac{\partial c_A}{\partial x} = -\frac{\partial c_B}{\partial x}$$

Using Eq. (4-17), Eq. (4-16) simplifies to

$$Cv^K = (D_A - D_B) \frac{\partial c_A}{\partial x}$$  \hspace{1cm} (4-18)
Since

\[ \frac{1}{C} \frac{\partial c_A}{\partial x} = \frac{\partial c_A}{\partial x} = \frac{\partial X_A}{\partial x} \quad (X_A = \frac{c_A}{C}) \] (4-19)

where \( X_A \) is the mole fraction of component A. Eq. (4-18) simplifies to

\[ v^K = (D_A - D_B) \frac{\partial X_A}{\partial x} \] (4-20)

Eq. (4-20) is an expression for the lattice velocity in a binary system. Substituting Eq. (4-20) in Eq. (4-12):

\[ J_A^o = J_A^K + c_A (D_A - D_B) \frac{\partial X_A}{\partial x} \] (4-21)

Using the definition of the intrinsic and interdiffusion fluxes given in Eqs. (4-10) and (4-11), Eq. (4-22) becomes

\[ -D^o \frac{\partial c_A}{\partial x} = -D_A \frac{\partial c_A}{\partial x} + c_A (D_A - D_B) \frac{\partial X_A}{\partial x} \] (4-22)

Simplifying

\[ D^o = X_B D_A + X_A D_B \] (4-23)

Eq. (4-23) is a relation between the interdiffusion and intrinsic diffusion coefficients.

Eqs. (4-20) and (4-23) can be solved simultaneously to obtain the relations

\[ D_A = D^o + X_A v^K \frac{1}{\frac{\partial X_A}{\partial x}} \] (4-24)
\[ D_B = D^o + X_B v^k \frac{1}{\frac{\partial X_B}{\partial x}} \]  

(4-25)

Eqs. (4-24) and (4-25) are useful relations for computing the intrinsic diffusion coefficients at any composition from a diffusion couple experiment containing inert markers throughout the diffusion zone. The interdiffusion coefficient, \( D^o \), is obtained from a Matano analysis, the concentration gradient \( \frac{\partial X_k}{\partial x} \) can be measured at \( X_k \), and the lattice velocity \( v^k \) can be determined at \( X_k \) from knowledge of the movement of the inert markers (an expression was provided in Chapter 3, a derivation of this expression is given in Appendix E).

4.2.2 Darken B: Relation Between Intrinsic and Tracer Diffusion—The Mobility Concept

In physics, the force acting on a particle in a potential field is equal to the negative gradient of its potential energy [Dar48]. Analogous to this law in physics, Darken proposed that a similar concept could be applied to the process of diffusion. In the case of normal diffusion, the only force acting on atoms in a concentration gradient is the chemical potential gradient, \( \nabla \mu \), or the gradient in the Gibbs partial molal free energy, \( \bar{G}_k \). Hence, the diffusion velocity is proportional to this driving force, i.e., the chemical potential gradient, and can be written as

\[ v_k = \frac{B_k}{N_o} (-\nabla \mu_k) \]  

(4-26)

where \( N_o \) is Avagadro’s number. Note that the chemical potential is usually defined in units of energy (J) per mole, hence \( N_o \) is needed for the conversion to energy per atom. Darken called \( B_k \), the constant of proportionality in Eq. (4-26), the mobility, which is the “velocity per unit driving force” for the atom. In general, one expects the mobility to be
a function of composition, but not on the driving force. The right hand side of Eq. (4-26) may also be viewed as a series expansion in which the higher order terms in the driving force are neglected. This is commonly referred to as a “phenomenological assumption,” and is used in developing the phenomenological relations in diffusion theory (Chapter 2).

Darken then proceeded to utilize Eq. (4-26) for developing relations between the mobilities and diffusion coefficients in flowing systems (intrinsic or interdiffusion coefficients). He also obtained relations between the mobilities and tracer diffusion coefficients in homogenous systems. The development of these relations is discussed in the next section.

4.2.2.1 Relation between intrinsic and interdiffusion coefficient, mobility and activity

If it is assumed, that the diffusion velocity in Eq. (4-26) is defined in the lattice or Kirkendall frame of reference \((\mathbf{R}^K)\), then the unidirectional diffusion flux for an A atom in a binary system is given by

\[
J_A^K = c_A v_A^K = c_A B_A \left( -\frac{\nabla \mu_A}{N_o} \right)
\]  

(4-27)

In Eq. (4-10), the diffusion flux in the lattice frame is also defined in terms of the intrinsic diffusion coefficient, \(D_A\). Equating the two expressions,

\[
-D_A \frac{\partial c_A}{\partial x} = \frac{1}{N_o} c_A B_A \left( -\frac{\partial \mu_A}{\partial x} \right)
\]  

(4-28)

Since,

\[
\frac{\partial \mu_A}{\partial x} = \frac{\partial \mu_A}{\partial c_A} \frac{\partial c_A}{\partial x}
\]  

(4-29)

it follows from Eq. (4-28) and (4-29) that
\[
D_A = \frac{1}{N_o} c_A B_A \left( \frac{\partial \mu_A}{\partial c_A} \right) = \frac{1}{N_o} X_A B_A \left( \frac{\partial \mu_A}{\partial X_A} \right) \quad \text{(where } X_A = c_A V) \tag{4-30}
\]

In obtaining Eq. (4-30), it is assumed that the molar volume is constant. Noting that the chemical potential of component A is given by

\[
\mu_A = \mu_A^0 + RT \ln \alpha_A = \mu_A^0 + RT (\ln \gamma_A + \ln X_A) \tag{4-31}
\]

the differential in Eq. (4-30) can be obtained:

\[
\frac{\partial \mu_A}{\partial X_A} = RT \left( \frac{\partial \ln \gamma_A}{\partial X_A} + \frac{1}{X_A} \right) = RT \frac{1}{X_A} \left( \frac{\partial \ln \gamma_A}{\partial \ln X_A} + 1 \right) \tag{4-32}
\]

where \( \alpha_A \) is the activity and \( \gamma_A \) the activity coefficient of component A. From Eqs. (4-30) and (4-32), it follows that

\[
D_A = \frac{1}{N_o} RT B_A (1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}) = k T B_A (1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}) \tag{4-33}
\]

where \( k \) is the Boltzmann constant (= \( R/N_o \)). Similarly, it can be shown that the intrinsic diffusion coefficient of B is related to the mobility of B by

\[
D_B = k T B_B (1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}) \tag{4-34}
\]

The terms in brackets in Eqs. (4-33) and (4-34) are known as “thermodynamic factors” and can be shown to be equal to each other by using the Gibbs-Duhem equation [Deh93]:

\[
X_A d \ln \gamma_A + X_B d \ln \gamma_B = 0 \tag{4-35}
\]

Dividing by \( dX_A \) and noting that \( dX_A = - dX_B \), it can be shown that

\[
X_A \frac{d \ln \gamma_A}{dX_A} = X_B \frac{d \ln \gamma_B}{dX_B} \tag{4-36}
\]
or
\[
\frac{d\ln \gamma_A}{d\ln X_A} = \frac{d\ln \gamma_B}{d\ln X_B}
\]  

(4-37)

Thus the equality of the thermodynamic factors for components A and B is established.

\[
1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A} = 1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B} = \Phi
\]  

(4-38)

where \( \Phi \) is the thermodynamic factor. It follows from Eqs. (4-33), (4-34) and (4-38) that

\[
\frac{D_A}{D_B} = \frac{B_A}{B_B}
\]  

(4-39)

4.2.2.2 Relation between tracer diffusivity and mobility

In the case of tracer diffusion, the diffusion flux is given by Fick’s first law:

\[
J_A^* = -D_A^* \frac{\partial c_A}{\partial x}
\]  

(4-40)

The diffusion flux in terms of the mobility is

\[
J_A^* = c_A^* v_A^* = c_A^* \frac{1}{N_o} B_A^* (-\nabla \mu_A^*)
\]  

(4-41)

In a manner similar to the previous section by comparing Eqs. (4-40) and (4-41), it can be shown that

\[
D_A^* = \frac{1}{N_o} X_A^* B_A^* \left( \frac{\partial \mu_A^*}{\partial X_A^*} \right)
\]  

(4-42)

Because the tracer forms a dilute solution with the rest of the homogenous system, the chemical potential of the tracer, \( \mu_A^* \), is given by
\[ \mu_A^* = \mu_A^{0*} + RT \ln a_A^* = \mu_A^{0*} + RT (\ln \gamma_A^{0*} + \ln X_A^*) \quad (4-43) \]

where \( \gamma_A^{0*} \) is the activity coefficient of \( A^* \) at infinite dilution or the Henry’s law constant, that is independent of composition. Hence the differential in Eq. (4-42) is given by

\[ \frac{\partial \mu_A}{\partial X_A^*} = \frac{RT}{X_A^*} \quad (4-44) \]

From Eqs. (4-42) and (4-44), the relation between the tracer diffusivity and mobility of \( A \) is obtained:

\[ D_A^* = \frac{1}{N_o} R T B_A^* = k T B_A^* \quad (4-45) \]

Similarly,

\[ D_B^* = k T B_B^* \quad (4-46) \]

Since the properties of an isotope tracer are almost identical to that of the major isotope, except for the slight difference in atomic mass, Darken suggested that the mobilities of the two were essentially the same. This important assumption in the Darken theory can be written for the two components in the binary systems as

\[ B_A = B_A^* \]

\[ B_B = B_B^* \quad (4-47) \]

The relations between the intrinsic and tracer diffusivities follows from Eqs. (4-33, 34, 45, 46 and 47):

\[ D_A = D_A^* (1 + \frac{\partial \ln \gamma_A}{\partial \ln X_A}) = D_A^* \Phi \quad (4-48) \]

\[ D_B = D_B^* (1 + \frac{\partial \ln \gamma_B}{\partial \ln X_B}) = D_B^* \Phi \quad (4-49) \]
and

$$\frac{D_A}{D_B} = \frac{D^*_A}{D^*_B} \tag{4-50}$$

From Eq. (4-23), the relation between the intrinsic and interdiffusivities, and Eqs. (4-48) and (4-49), it can be shown that

$$D^o = (X_B D^*_A + X_A D^*_B) \Phi \tag{4-51}$$

Eq. (4-51) is commonly known as the Darken-Hartley-Crank (D-H-C) equation. Hartley and Crank independently derived the same expression for liquid systems a year later [Har49].

An expression for the lattice velocity in terms of the tracer diffusivities can be obtained from Eqs. (4-20), (4-48) and (4-49):

$$v^K = (D^*_A - D^*_B) \Phi \frac{\partial X_A}{\partial x} \tag{4-52}$$

From Eqs. (4-48, 49 and 51), the intrinsic and interdiffusion coefficients can be obtained from knowledge of the tracer diffusion coefficients and the thermodynamic factor. The predicted values can then be compared with the experimental ones as a test of the Darken B theory.

Another way of testing the Darken B theory is by comparing the experimental lattice velocity with that predicted using Eq. (4-52). However, the concentration gradient cannot be directly predicted from the Darken theory, although it can be obtained with the aid of the simulation using the intrinsic diffusion coefficients predicted from the theory as the input. Hence, the experimental concentration gradient is utilized in testing
the theory. Usually, the velocity of the marker at the original interface, i.e., the Kirkendall interface, is the only velocity measurement carried out. Since the concentration gradient at the Kirkendall interface can be rather steep (e.g., see Fig. 3-3), measurement errors can be significant. Hence, if Eq. (4-52) is to be utilized for the test, it is preferable to utilize the oblique interface technique (see Appendix E) or the multi-foil technique (Heu57, Heu72, Phi91) for the measurement of lattice velocities at various locations within the diffusion zone where concentration gradients are not as steep.

4.3 Analysis of the Darken Theories with the Phenomenological Equations

The beauty of Darken’s theory of intrinsic diffusion (Darken A) is that there is no mention of a diffusion mechanism, it is purely phenomenological in character and can apply equally to liquids or gases. Indeed, Hartley and Crank [Har49] developed the same formalism for liquids. However, for diffusion in solid-state crystalline materials, it is necessary to invoke an atom-vacancy exchange mechanism in order to explain the Kirkendall effect. Hence, the vacancy flux can be related to the intrinsic fluxes as shown:

\[
J_v^K = -(J_A^K + J_B^K)
\]  

(4-53)

From Eqs. (4-14) and (4-15), the sum of the intrinsic fluxes is related to the product of the lattice velocity, \(v^K\), and the total concentration, \(C\). Hence, Eq. (4-53) simplifies to

\[
J_v^K = C v^K = \frac{1}{v} v^K
\]  

(4-54)

A further assumption necessary to explain the Kirkendall effect is the requirement that the concentration of vacancies is maintained at the equilibrium value during the diffusion process (even though the vacancy flux is not zero according to Eq. (4-54)), which means
that the chemical potential of vacancies is zero \((\mu_v = 0)\) [Deh93]. In the absence of this assumption, there would permanently exist vacancy supersaturations or depletions in regions of the diffusion couple and hence Kirkendall shifts would be difficult to explain. However, measurements of the vacancy concentrations on quenched samples have shown that they are near or almost equal to their equilibrium values [Bal52, Lec58]. Dislocation based mechanisms for the creation or annihilation of vacancies are assumed to operate during the diffusion process in order to maintain the equilibrium value [Bar51].

It turns out that this assumption \((\mu_v = 0)\) is also needed to connect the Darken B theory (Eqs. 4-48, 49 and 51) with the phenomenological equations of irreversible thermodynamics. In order to examine this and other assumptions inherent in the Darken B formalism, the phenomenological equations are first considered. For an isothermal system consisting of \(n-1\) atomic components and simple vacancies (taken to be the \(n^{th}\) thermodynamically independent component), in the absence of electrical fields, the phenomenological equations are [How64, All93]

\[
J^K_k = \sum_{i=1}^{n-1} L_{ki}(Y_i - Y_v) \quad (Y_i = -\frac{\partial \mu_i}{\partial x})
\]

(4-55)

where the flux of the \(n^{th}\) component, i.e., vacancies is given by the following expression assuming an atom-vacancy exchange mechanism:

\[
J^K_n = J^K_v = -\sum_{i=1}^{n-1} J_k
\]

(4-56)

The \(Y_i^{'}s\) are the driving forces in the phenomenological equations, that are equal to the chemical potential gradients in the present situation. If it is assumed that an equilibrium
concentration of vacancies is maintained, then since the chemical potential of vacancies is zero, \( Y_v = 0 \). Hence the phenomenological equation, Eq. (4-55), for a binary system can be written as

\[
J^K_A = L_{AA} Y_A + L_{AB} Y_B
\]  

(4-57)

and

\[
J^K_B = L_{BA} Y_A + L_{BB} Y_B
\]  

(4-58)

By virtue of the Gibbs-Duhem relation

\[
X_A Y_A + X_B Y_B = 0
\]  

(4-59)

Hence, Eq. (4-57) can be rearranged to give

\[
J^K_A = L_{AA} Y_A + L_{AB} \left(-\frac{X_A Y_A}{X_B}\right) = \left(L_{AA} - \frac{X_A}{X_B} L_{AB}\right) Y_A = L_A Y_A
\]  

(4-60)

where

\[
L_A = L_{AA} - \frac{X_A}{X_B} L_{AB}
\]  

(4-61)

From Eqs. (4-31) and (4-32), \( Y_A \) can be determined

\[
Y_A = -\frac{\partial \mu_A}{\partial X_A} = -\frac{\partial \mu_A}{\partial X_A} \frac{\partial X_A}{\partial X_A} = -RT \frac{1}{X_A} \left(1 + \frac{\partial \ln Y_A}{\partial \ln X_A}\right) \frac{\partial X_A}{\partial X_A}
\]  

(4-62)

Hence Eq. (4-60) becomes

\[
J^K_A = -L_A RT \frac{1}{X_A} \left(1 + \frac{\partial \ln Y_A}{\partial \ln X_A}\right) \frac{\partial X_A}{\partial X_A} = -L_A RT \frac{1}{X_A} \Phi \frac{\partial X_A}{\partial X_A}
\]  

(4-63)

From Eq. (4-11), the expression for the intrinsic flux in terms of the intrinsic diffusion coefficient is
\[ J_A^k = -D_A \frac{\partial c_A}{\partial x} = -\frac{1}{V} D_A \frac{\partial X_A}{\partial x} \quad (c_A = \frac{X_A}{V}) \] (4-64)

Comparing Eqs. (4-63) and (4-64), it can be seen that

\[ D_A = RT \frac{L_A}{c_A} \] (4-65)

A similar expression can be obtained for B:

\[ D_B = RT \frac{L_B}{c_B} \] (4-66)

where

\[ L_B = L_{BB} - \frac{X_B}{X_A} L_{BA} \] (4-67)

Comparing Eq. (4-33), the relation between the intrinsic diffusion coefficient and mobility of A, with Eq. (4-65), the relation between the mobility and \( L_A \) is obtained:

\[ B_A = \frac{N_o L_A}{c_A} \] (4-68)

Similarly,

\[ B_B = \frac{N_o L_B}{c_B} \] (4-69)

From the Darken relations, Eqs. (4-48) and (4-49), that relate the intrinsic and tracer diffusion coefficients, and Eqs (4-65) and (4-66), the relation between the tracer diffusion coefficients and the \( L_k \) 's are obtained:

\[ D_A^* = RT \frac{L_A}{c_A} \] (4-70)
The mobilities, $M_k$'s, used in the DICTRA [Agr82, And92, Bor00] formalism (see Eq. (3-4) in Chapter 3) are related to the $B_k$'s by

\[
M_A = \frac{B_A}{N_o} \quad (4-72)
\]

\[
M_B = \frac{B_B}{N_o} \quad (4-73)
\]

Comparing Eqs. (4-68) and (4-69) with Eqs. (4-72) and (4-73) it is seen that

\[
L_A = c_A M_A \quad (4-74)
\]

\[
L_B = c_B M_B \quad (4-75)
\]

and thus the resulting phenomenological flux expression in terms of $M_k$ is

\[
J_k^k = L_k Y_k = c_k M_k Y_k = -c_k M_k \frac{\partial u_k}{\partial x} \quad (k = A, B) \quad (4-76)
\]

4.4 Manning Theory

It has been generally understood for quite some time that the Darken relations between the tracer and intrinsic and interdiffusion coefficients are incomplete if one considers a rigorous analysis of the diffusion of the A and B tracers in the A-B alloy by invoking the phenomenological equations of irreversible thermodynamics. This point was first raised by Bardeen and Herring [Bar51] shortly after Darken proposed his theory and later discussed in great detail by LeClaire [Lec58], Howard and Lidiard [How64], Heuman [Heu83] and others since that time. To consider tracer diffusion in detail, it is necessary to consider the phenomenological flux equations of the type shown in Eqs. (4-
57) and (4-58), for each of the species in the system, i.e., A, A*, B and B*, and derive relations between the various diagonal and off-diagonal coefficients, and the tracer and intrinsic diffusion coefficients. These relations [How64] reveal that the Darken relations, Eqs. (4-48, 49, 51 and 52) only follow if the cross-coefficients (e.g., $L_{AB}$, $L_{A*B}$, $L_{BB*}$, etc.) are all zero. However, it was recognized that these coefficients would be non-zero for a vacancy mechanism of diffusion. Detailed studies of the content of the phenomenological coefficients were conducted by Manning [Man62, Man65, Man67, Man68, Man70] by analyzing the kinetics of atomic migration. The resultant equations of Manning were primarily derived for a “random alloy model”, a model system in which atoms and vacancies are randomly distributed on the lattice even though the atom-vacancy exchange rates may be different. From the relations between the phenomenological coefficients and the tracer diffusion coefficients, Manning obtained the relations between the intrinsic and tracer diffusion coefficients in a form similar to the Darken equations. These relations are

\[
D_A = D_A^* \Phi (1 + V_A) \quad (4-77)
\]

\[
D_B = D_B^* \Phi (1 - V_B) \quad (4-78)
\]

where

\[
V_A = \frac{2X_A}{M_o} \left( \frac{D_A^* - D_B^*}{X_A D_A^* + X_B D_B^*} \right) \quad (4-79)
\]

\[
V_B = \frac{2X_B}{M_o} \left( \frac{D_A^* - D_B^*}{X_A D_A^* + X_B D_B^*} \right)
\]

$M_o$ is a constant that depends on the crystal structure. In case of a fcc crystal, it is 7.15.
The important difference in Eqs. (4-77) and (4-78) is in the correction factor, \((I \pm V_k)\), to the Darken equations, Eq. (4-48) and (4-49). This is known as the “vacancy wind term” and derives from the notion that in the presence of a vacancy flux, vacancies will approach an atom more frequently from the up-stream side of the vacancy flux rather than the down-stream side. As a result, there is an inherent bias for atoms to migrate in a direction opposite to the vacancy flow. Since the net vacancy flux in a binary system is in a direction opposite to the flux of the faster diffusing component, this causes the intrinsic diffusion coefficient of the faster component to be enhanced due to the vacancy wind effect. However, the changes in the intrinsic coefficients given by the Darken relations (Eqs. (4-48) and (4-49)) due to the Manning corrections are usually not significant for most systems and within the realm of experimental error [Loo90a, Dal00a]. The change in the lattice velocity due to the Manning correction is more significant (a maximum of 25\%) since it depends on the difference between the intrinsic coefficients (see Eq. (4-52)).

The correction to the Darken relation (Eq. (4-51)) relating the tracer and the interdiffusion coefficient involves the factor \(S\), which only causes a very small change (5\%) to the Darken term:

\[
D^o = (X_B D_A^* + X_A D_B^*) \Phi S
\]  

(4-80)

where \(S\) is given by

\[
S = 1 + \frac{2X_A X_B (D_A^* - D_B^*)^2}{M_o (X_A D_B^* + X_B D_A^*) (X_A D_A^* + X_B D_B^*)}
\]  

(4-81)

Eqs. (4-77) to (4-81) are usually referred to as the Manning relations, that along with the Darken relations (Eqs. (4-48), (4-49) and (4-52)), are assessed with the aid of the intrinsic
diffusion simulation in this chapter. It should be mentioned that the Manning relations have also been derived by Heuman [Heu79] and more recently Lidiard [Lid86] using approaches that differ from the atomistic-kinetic approach of Manning. The important assumptions inherent in the original formalism of Manning have also been discussed by Lidiard [Lid86]. A detailed analysis is beyond the scope of the present study, however it should be apparent from the Manning relations, that the critical assumption $B_k = B_k^{*}$ (Eq. 47) in the Darken theory, is left intact. Monte Carlo simulations of diffusion [Mur84] on idealized lattices have demonstrated the validity of the Manning relations beyond the realm of his random alloy model, for e.g., in ordered systems [Bel96, Bel97]. While such tests have intrinsic merit from a fundamental viewpoint, the true test of the D-M relations should be based on the analysis of real-world systems, which is the goal of the present study.

4.5 Previous Tests of Darken-Manning Theories

Tests of the Darken-Manning theories are primarily restricted to binary systems, since complete tracer diffusion information for ternary systems is rarely available (the Cu-Ni-Zn system [Anu72] is an exception). Some of the important systems studied include: Au-Ni [Rey57, Dal00a], Ag-Cd [Ior73, But78], Ag-Zn [Che75], Cu-Zn [Sch66, Koz00], Fe-Ni [Koh70, Vig69a], Ag-Au [Heu57, Mey69, Dal72], Cu-Ni [Heu72, Dam82] and Cu-Au [Heu78]. Usually the theories are tested by comparing the experimental intrinsic and interdiffusion coefficients with those predicted from the D-M theories (Eqs. 4-48, 49 and 51). Definitive tests of these formalisms require reliable information on composition profiles, lattice shifts, thermodynamic activity data and tracer diffusion coefficients through an extended composition range. Where such
information is available (e.g., Ag-Cd, Ag-Zn, Cu-Zn, Cu-Ni, Au-Ni), a test of all the Darken-Manning relations (i.e., intrinsic and interdiffusion coefficients) reveals serious problems, that are beyond the realm of experimental error. It is often seen in such tests that a comparison between the predicted and measured interdiffusion coefficient is quite satisfactory and this has been regarded by several authors [She89, All93] as an adequate validation of particularly the Darken theory. However, a comparison between the predicted and measured intrinsic diffusion coefficients reveals significant differences, (e.g., Cu-Zn [Koz00]). The Manning correction to the Darken relations, in some instances, results in an improvement in the predicted value for one of the two binary intrinsic diffusion coefficients, but worsens it for the other (e.g., Ag-Cd [Ior73]). In case of the Au-Ni system [Dal00a], it was seen that the intrinsic diffusion coefficient for Ni predicted using the Darken theory compared quite favorably with the experimental one, however that for Au deviated noticeably especially for Au rich compositions.

Sometimes, for example, in case of the Ag-Cd system [Ior73], better agreement is obtained when the ratios of the tracer diffusivities are compared with the ratios of the intrinsic diffusivities predicted from the D-M theories (see Eq. 4-50). Ostensibly, this approach of testing the D-M theories is supposed to negate the error involved in the determination of the thermodynamic factor. However, it has been shown [Dal00a], that such an error cannot adequately explain the significant differences between the absolute values of the experimental and predicted intrinsic diffusivities. Tests of the D-M theories for some systems, that are discussed in a later section, validate this observation. Moreover, it should be noted that with the advent of modern CALPHAD [Kau70] techniques for the statistical assessment of thermodynamic data from various sources and
methods, uncertainties in the determination of the thermodynamic factor have been significantly reduced. In fact, most of the systems analyzed in this chapter, utilize CALPHAD assessed thermodynamic data for the computation of the thermodynamic factor.

There are no reported tests of the D-M theories for ternary systems at the time of this writing. This is because all the information needed for assessing these theories in ternary systems is rarely available. The measurement of intrinsic diffusivities over an extended composition range requires the utilization of multiple markers (e.g., using the oblique interface technique, see Appendix E), such measurements have not been reported in the literature for ternary systems. Tracer diffusivities in ternary systems are rarely measured, the Cu-Ni-Zn system [Anu72] is a notable exception. Thermodynamic assessments for ternary systems using CALPHAD techniques, that are required for reliable determination of thermodynamic factors, are increasingly available. Some important systems where tracer diffusion information is available, e.g., the Cu-Ni-Zn system, have just recently been assessed. Thus the experimental effort involved in obtaining the information necessary for testing the D-M theories for ternary or higher order systems is rather prohibitive. However, it is anticipated that the experimental challenges will be eventually overcome and permit a reliable test of these theories in the not-too-distant future for multicomponent systems as well.

A brief discussion of some of the previous tests of the D-M theories for binary systems is provided below. All the systems tested have face-centered cubic (fcc) crystal structures. In each case, this author’s analysis of the test is given.
Au-Ni (850-975°C) [Rey57, Dal00a]. The Darken relation (Eq. 4-51) between the interdiffusion coefficient and the tracer diffusion coefficients was proved to be satisfactory. This result has long been used as a validation of the Darken theory and is often mentioned in most diffusion texts. However, intrinsic coefficients were not measured, hence a comparison with the predicted intrinsic coefficients from either the Darken or Manning theories could not be verified by the authors. Recently, this system has been re-analyzed by van Dal et al. [Dal00a] using the multi-foil technique for the measurement of lattice velocities. Thus the authors were able to test the Darken B theory (Eqs. 4-48, 49 and 51) in great detail. Variations in molar volume that are appreciable in this system were also taken into account. The authors concluded that while the experimental intrinsic diffusion coefficient of the slower diffusing species, Ni, was in good agreement with that predicted from the Darken theory, that of the faster diffusing species, Au, was higher at compositions where Ni was less than 50 at pct. The Manning theory was not tested, since the authors felt that the Manning corrections are relatively minor and within the range of measurement errors in this system. This system is further analyzed in this chapter with the aid of the simulation.

Ag-Cd (600°C) [Ior73]. This system is a good choice for testing the D-M theories since the tracer diffusion coefficients vary over two orders in magnitude over the range of compositions considered (0 - 40 at pct Cd) within the single phase region. The experimental intrinsic diffusion coefficients were measured using incremental vapor-solid and solid-solid diffusion couples and were compared with the models of Darken and Manning. The experimental coefficients were found to be higher than the D-M models. However the ratios of the intrinsic coefficients were found to be in reasonable agreement
with the predicted coefficients from Manning’s theory. It appears that the primary source of the tracer diffusion data, the data of Schoen [Sch58], had been utilized by the authors for some compositions and ignored for others. Tracer diffusion coefficients for Ag at low Cd compositions appear to have been ignored and thus the calculation of the vacancy wind terms in the Manning theory were affected to some extent. The authors tended to support the Manning theory. This system is re-evaluated in this chapter with the aid of the simulation.

**Ag-Cd (1072-1179°C) [But78]**. The authors tested the D-M theories by measuring Kirkendall shifts using a traveling microscope as compared to the traditional Matano analysis. The experimental Kirkendall shifts were found in all cases to be greater than those predicted by Darken and equivalent to or slightly larger than those predicted by Manning. The tracer coefficients were obtained from the data of Schoen. The range of compositions over which the measurements were made were limited (from 0.034 to 0.164 atomic fraction Cd). The results support the Manning theory within the narrow range of compositions considered. It should be noted that in computing the Kirkendall shifts using the intrinsic coefficients predicted by the D-M relations, the authors used the experimental concentration gradients (see Eq. 4-52). In principle, the concentration gradients should rather have been computed either from the predicted interdiffusion or intrinsic diffusion coefficients with the aid of a simulation.

**Ag-Zn 600°C [Che75]** The experimental values for the intrinsic coefficient of Zn were close to those predicted by the model of Darken and Manning, while the experimental intrinsic coefficient of Ag was higher than those determined by both
models. Hence the test demonstrated a problem with the theories that seems to occur in other systems as well (e.g., Au-Ni [Dal00a]).

Fe-Ni (1200°C) [Koh70, Vig69a]. The authors measured tracer coefficients and intrinsic coefficients over the full composition range (0-100 at pct Ni) in this system. The results indicated that differences between the experimental and predicted intrinsic coefficients from the D-M theories were significant. The measured lattice shifts were corrected for porosity which occurred due to the large vacancy fluxes in this system. An assessment of their data using our simulation (in Chapter 3) indicated that the intrinsic coefficients reported by them give an almost identical fit with the experimental concentration and lattice velocity profiles as well as the intrinsic fluxes. Vignes and Badia [Vig69a] demonstrated that the presence of Kirkendall porosity in their diffusion couples affected the measurements causing an increase in the width of the diffusion zone as well as an increase in the intrinsic coefficient of Fe and a reduction for Ni. If the porosity was taken into account either through the application of uniaxial pressure or by the use of high purity, zone-refined Fe (containing low oxygen), the resultant intrinsic coefficients measured at 50 at pct Ni was consistent with Manning’s theory. However, the measurement was carried out at only a single composition, hence more evidence is needed over an extended composition range. The results from the simulation of this system in Chapter 3 suggest that the data of Kohn et al. [Koh70] is an excellent representation of the diffusion behavior in their Fe-Ni alloys, based on a comparison of concentration, lattice velocity and intrinsic flux profiles. In general, based on Vignes and Badia’s work it can be concluded that the prevention of porosity is a necessary requirement for the test of the D-M theories. It should be noted that the tracer
coefficients varied by a factor of 4-5 over the entire composition range, which is significantly smaller than for e.g., the Ag-Cd or Cu-Zn systems.

Cu-Zn (900°C) [Sch66, Koz00]. Schmatz et al. [Sch66] examined the Darken-Manning relations in an indirect fashion by comparing the ratio of tracer diffusivities \( \left( \frac{D_{Zn}^*}{D_{Cu}^*} \right) \) with that determined by manipulation of the Darken-Manning relations. They found that the Manning correction showed some improvement over the Darken analysis. However, a comparison with the absolute values of the tracer diffusivities revealed significant differences that could not be accounted for errors in the thermodynamic measurements. A recent analysis of the Darken relations performed by Kozeschnik [Koz00] found significant discrepancies between the predicted and experimental intrinsic diffusion coefficients measured by Horne and Mehl [Hor55], and Resnick and Baluffi [Res55]. Unlike the data of these authors that was applicable over an extended composition range (0-31 at pct Zn), the data of Hoshino [Hos82] valid over a narrower composition range near the pure Cu composition (0-5 at pct Zn), gave good agreement. This led Kozeschnik to suggest that the discrepancies between the predicted and experimental intrinsic diffusion coefficients of the earlier authors could be attributed to “microstructural effects.” A comparison between the predicted and experimental lattice shifts was however not performed.

A reassessment of this system based on a comparison between predicted and measured intrinsic diffusion coefficients, concentration profiles and lattice shifts is performed in this chapter. In addition, the thermodynamic parameters for this system that have been assessed by Kowalski and Spencer [Kow93] using CALPHAD techniques, are used to provide a more reliable test of the theory.
**Ag-Au (950°C)** [Mey69]. The author measured Kirkendall shifts under a hydrostatic pressure of 0 to 8 kbar and found that the shifts agreed within 2 pct with those predicted by Manning’s relations at zero pressure. Unfortunately, the measurements were carried out at only a single Kirkendall plane composition (50 at pct) and hence the test cannot be considered to be conclusive.

**Ag-Au (904°C)** [Dal72]. Kirkendall shifts were measured and compared with the predicted values from the D-M theories (see Eq. 4-52). The author observed, that if the Kirkendall interface were identified with the grain boundary between the halves of a diffusion couple, Manning’s model was consistent with the observed shifts; however, if inert markers were used, the measured shifts were considerably larger. Since inert markers are the true indicators of the motion of the lattice (Appendix E), it appears that the test was not satisfactory. This system is perhaps not the best system for assessing the D-M theories, since at the temperatures considered, the Ag and Au tracer coefficients vary by less than a factor of two over the entire composition range [Mal63, Mea57].

**Cu-Ni (1000°C)** [Dam82]. The intrinsic and tracer coefficients were measured up to 20 at pct Ni [Dam82]. Up to 12 at pct, the ratio of intrinsic coefficients agreed satisfactorily with Manning’s prediction. Beyond this, the measured ratio decreased while the predicted one increased with increasing Ni. Absolute values of the predicted intrinsic diffusion coefficients were not reported possibly due to the uncertainty in the thermodynamic parameters. A re-evaluation over the entire composition range is suggested using a recent and more reliable thermodynamic assessment of this system [Mey92], and the intrinsic measurements of Heumann and Grundhoff [Heu72]. It is seen that the tracer diffusion coefficients in this system vary by over two orders in magnitude.
Cu-Au (860°C or 1133 K) [Heu72]. Intrinsic coefficients were measured using Heuman’s thin plate technique [Phi91] from 1.25 to 17.43 at pct Au. Tracer coefficients were also measured in the composition range, 0 - 27.5 at pct Au. There was no agreement either with the absolute values or with the ratios of the intrinsic diffusion coefficients. The author has suggested that the possibility of ordering in this system and hence a non-random distribution of components, may not permit the use of Manning’s theory since it is meant to be used only for random alloys. It appears that the thermodynamic factor also needs re-evaluation. The author also points out that the use of Murch’s [Mur84] treatment of Manning’s theory applied to ordered systems does not appear to have a noticeable effect on the results.

4.6 Tests of Darken-Manning Theories with the Simulation

In the previous section, some of the shortcomings in the previous tests of the D-M theories were presented. In spite of these, there has been a reluctance by most authors in the diffusion community in recognizing that there are important problems with these theories that need to be addressed given the pervasive nature of diffusion processes in materials. A re-examination is particularly necessary at the present time, since multicomponent diffusion databases, that frequently utilize the D-M relations in the absence of interdiffusion or intrinsic diffusion data, are becoming increasingly important for the accurate modeling of evolutionary processes in materials, for e.g., in solidification simulation in superalloys [Kat96, Cam02]. Clearly, if these databases are based on relations that are not robust, the predictive capability of future modeling efforts may be compromised. Thus, the issue of the actual validity and limitations of the D-M relations needs to be explored in greater depth, which is the primary focus of this chapter.
This endeavor is undertaken here with the aid of the diffusion simulation developed in this work. It is expected that the utilization of the simulation will provide a more reliable and definitive test of the D-M relations than has been previously available.

4.6.1 A. Establishing Consistency of Experimental Measurements and Procedures

The first step in testing the Darken-Manning theories is to ensure that the experimental intrinsic diffusion information for the specified system is sufficiently accurate for the purpose of the analysis. In this work, the accuracy of the measurements is examined with the aid of the simulation (Fig. 4-2a). This is accomplished by using the experimental intrinsic diffusion coefficients as the input to the simulation and comparing the output with the experimental observables such as the concentration and the lattice shift profiles. If the diffusion measurements have taken into considerations variations in molar volume (e.g., Au-Ni [Dal00a]), the functional variation of the molar volume with composition should also be input to the simulation. If lattice shift information from multiple marker or oblique interface (Appendix E) marker experiments is not available, experimental Kirkendall shifts for a number of incremental couples may be compared with those obtained from the simulation with the experimental intrinsic diffusion coefficients as input.

A number of recommendations for the experimental determination and analysis of intrinsic diffusion data in single-phase diffusion couples are suggested in order to ensure the highest accuracy possible. Most of these have been summarized in a review article by van Loo [Loo90a] and in standard textbooks on diffusion analysis and experimental techniques [Phi91, Kir87, Gol02].
Figure 4-2. Procedure for testing the Darken-Manning theories using the intrinsic diffusion simulation: (a) Assessing the quality of the data and experimental procedures involved in the measurement of the intrinsic diffusion coefficients.

**Experimental requirements.** A primary requirement in diffusion studies is the need for using samples with the highest purity available, since impurities can have a noticeable effect on the diffusion measurements [Loo90a]. Concentration measurements using electron microprobe analyses using standard procedures and techniques in order to ensure the highest accuracy possible, is recommended [Zie64, Gol02]. Intrinsic diffusion
Figure 4-2. Continued. (b) Computing the intrinsic diffusion coefficients predicted from these theories and comparing the output with the experimental data.
measurements of lattice shifts using multiple markers (see Appendix E) for full-range and/or incremental couples should be used for the measurement of the intrinsic and interdiffusion coefficients as a function of composition rather than using Kirkendall shift measurements alone, since these are often subject to large errors, particularly for short diffusion annealing times. The use of fine Kirkendall markers (1-2 µm) that show up well in back-scatter SEM (e.g., ThO₂), is recommended for the measurement of lattice shifts. The phenomenological assumption that the diffusion coefficients are only a function of the local composition and not the gradients, should be preferably verified with the aid of incremental and overlapping long-range couples that have been subjected to sufficiently long and variable diffusion anneals (e.g., see [Vig69a, Loo90a, Dal00a]).

Errors in measurement due to steep concentration gradients in full-range diffusion couples may be overcome by using incremental couples where such gradients are smaller. Diffusion measurements should be performed on large-grained polycrystalline specimens in order to minimize contributions due to grain boundaries. The atmosphere should be carefully controlled to prevent oxidation problems and temperature control should be of high quality [Rot84]. Other sources of potential error involved in both experiment [Loo90a] and calculation [Kap90] should be understood and steps should be taken to minimize these errors. For example, in full-range diffusion couples, Kirkendall porosity that may develop as a result of high vacancy supersaturations and slow equilibration can be usually avoided by applying a small uniaxial pressure of a few MPa without affecting the measurements [Loo90a, Dal00a].

Data analysis. With the wide use and availability of high-performance computing facilities at the present time, the older graphical procedures that were utilized in the
measurement of the diffusion coefficients, are no longer needed. The measurement of concentration gradients or integrals (e.g., in the Boltzman-Matano (B-M) analysis (Eq. (4-4)) from noisy concentration data is facilitated with use of least-squares spline fitted functions rather than the use of a single polynomial function for all the data-points [Kap90]. The den Broeder [Bro69]/Sauer-Freise [Sau62] procedure for the evaluation of the concentration dependent interdiffusion and intrinsic diffusion coefficients is rather convenient as compared to the traditional B-M procedure, since the location of the Matano interface is not required; hence, it is recommended that this procedure be used. Moreover, this procedure is also suited for the measurements in cases where the molar volume of the system is not constant (e.g., in Au-Ni [Dal00a]).

4.6.2 B. Procedure for the Test of the Darken-Manning Theories

The procedure for the D-M theories that is employed in the present study is illustrated in Fig. 4-2b. The various steps involved in this procedure are discussed.

Tracer diffusion measurements. To begin with, reliable information regarding the tracer diffusion coefficients in the system of interest is essential. The most important requirement is that the purity of samples employed for the tracer measurements should be of high quality. It is for this reason, that some of the earlier references (usually before 1950) in which the purity levels are not known with high certainty, are to be avoided [Ask70]. Since diffusion measurements in moving systems are usually performed on large-grained polycrystalline specimens, a similar microstructure should be used. The book by Askill [Ask70], the papers by Rothman [Rot84] and Anusavice et al. [Anu72], provide useful guidelines for the proper procedures and techniques to be employed in tracer diffusion studies.
Thermodynamic measurements. Preferably, a CALPHAD\textsuperscript{2} based thermodynamic model for the system should be utilized for computing the thermodynamic factor in the phase of interest. The advantage of the CALPHAD method is that all types of thermodynamic data for all phases in the system of interest are considered in order to obtain suitable Gibbs excess free energy thermodynamic models for the various phases. The determination of the parameters in these models (e.g., Redlich-Kister model [Red48]) is based on a least squares optimization procedure that is available in standard thermochemical software such as ThermoCalc [And02] or Lukas [Luk77]. From the optimized free energy model, usually a polynomial function of composition and temperature, the thermodynamic factor needed for the computation of the diffusion coefficients with the Darken-Manning relations, can be readily obtained. In the absence of a CALPHAD assessment in the literature, the activity data for the concerned phase may be utilized to obtain an appropriate free energy model.

Test of the Darken-Manning theories.

(a) Comparison between experimental and predicted intrinsic and interdiffusion coefficients: The usual way of testing the D-M theories is to compare the diffusion coefficients predicted from these theories with the experimental values. In some of the earlier tests in the literature, only the interdiffusion coefficient was compared [Rey57] since intrinsic data was not readily available. However, a true test of these theories should be based on a comparison of the intrinsic diffusion coefficients as well. In some

\textsuperscript{2} CALculation of PHAse Diagrams. The classical reference is by Kaufman and Bernstein [Kau70]. A recent edition by Saunders and Miodownik [Sau98] provides an excellent summary of the progress to date. A journal by the same name has been in existence since 1973.
of the earlier studies, the ratios of the predicted intrinsic diffusion coefficients were compared with the experimental ones so as to cancel out the thermodynamic factor, which may not have been reliable enough [Ior73] at the time. In the present analysis, an absolute comparison is preferred since reliable thermodynamic information is available for all the systems considered.

(b) Comparison between experimental and predicted observables with the aid of the simulation: Using the intrinsic diffusion simulation, the intrinsic diffusion coefficients predicted from the D-M theories can be input to the simulation and the resulting output including concentration profiles, fluxes and lattice velocities and shifts, may be compared with the experimental measurements of these quantities. This improved procedure for testing the D-M theories in binary systems is applied to four systems for which the necessary thermodynamic, tracer and intrinsic diffusion information is available. These are the Ag-Cd, Au-Ni, Cu-Zn and Cu-Ni systems.

4.6.3 Silver-Cadmium (Ag-Cd) System

The Ag-Cd system is an excellent system for testing the D-M theories given the strong composition dependence of the tracer diffusion coefficients. At 600°C, the fcc solid solution phase in this system extends from pure Ag up to a composition of approximately 40 at pct Cd (Fig. 4-3a). This system was studied by Iorio et al. [Ior73] for the purpose of testing the D-M theories (by only comparing the intrinsic diffusion coefficients) as well as for determining the vacancy wind parameters in the Manning theory using a formalism developed by Dayananda [Day71]. The objective in the present case is to follow the procedure illustrated in Figs. 4-2a and b for testing the D-M theories.
4.6.3.1 Examining self-consistency of experimental intrinsic data

In Fig. 4-39b, the intrinsic diffusion coefficients in this system, that were determined using incremental couples, are plotted as a function of the cadmium composition. A regression analysis using a third order polynomial function was found to provide a good fit of the data. It can be seen from the figure, that the extrapolated Cd intrinsic diffusion coefficient on the pure Ag side is in good agreement with the tracer diffusion coefficient of Cd in pure Ag. However the extrapolated Ag intrinsic diffusion coefficient is higher than the Ag tracer diffusion coefficient in pure Ag (usually referred to as the self-diffusion coefficient). The interdiffusion coefficient is plotted in Fig. 4-3c. It is seen that the interdiffusion coefficient is nearly equal to the Cd tracer diffusion coefficient for pure Ag. The reason for this is provided in the Darken relations, Eqs. (4-23) and (4-51), which for the AgCd system can be written as

$$D^o = (X_{Cd} D^*_{Ag} + X_{Ag} D^*_{Cd}) \Phi$$  \hspace{1cm} (4-82)

$$D^o = X_{Cd} D_{Ag} + X_{Ag} D_{Cd}$$  \hspace{1cm} (4-83)

In the limiting case for pure Ag, the thermodynamic factor, $\Phi$, is unity and Eqs. (4-82) and (4-83) simplify to

$$D^o = D^*_{cd} = D_{cd} \hspace{1cm} \text{when} \hspace{0.5cm} X_{Ag} = 1, X_{Cd} = 0, \hspace{0.5cm} \Phi = 1$$  \hspace{1cm} (4-84)

Thus the interdiffusion coefficient is equal to the Cd tracer coefficient for pure Ag.

The fitted functions for the intrinsic diffusion coefficients were then used as the input to the simulation. The molar volume of the system was assumed to be constant (10.53 cc/mole) and was computed from the lattice parameter (4.12 Å) using the relation

$$V = \left( \frac{a_o \cdot 10^8}{n_e} \right)^3 N_o$$  \hspace{1cm} (4-85)
where $n_c$ is the number of atoms per unit cell that is equal to 4 for the fcc crystal structure, and $N_A$ is the Avagadro’s number ($6.023 \times 10^{23}$ atoms/mole).

It should be noted that the assumption of constant molar volume was also used by the original authors for measuring the intrinsic diffusion coefficients. The data of Owen and Roberts [Owe39] indicates that the lattice parameter varies from 4.079 (pure α fcc Ag) to 4.1536 Å at the fcc/ordered AgCd phase boundary (0.4 atomic fraction Cd) at 600°C, a variation of approximately 2 pct. The corresponding variation in the molar volume is about 6 pct. The value of the lattice parameter that was utilized for computing the molar volume in the simulation was the average value (4.12 Å).

The simulation was carried out for the same diffusion couples utilized by Iorio et al. [Ior73]. Their diffusion couples consisted of pure Ag bonded to alloys containing 0.096, 0.1588, 0.287 and 0.379 atomic fraction of Cd. These compositions served as the initial values in the simulation. Approximately 512 iterations were needed to obtain stable concentration and lattice shift profiles in the simulation. The normalized distance parameter (\( \frac{x}{\sqrt{t}} \)) was multiplied by the square root of the diffusion time (5 days) to obtain the concentration profiles for Cd that are shown in Figs. 4-4(a-d). Similarly the lattice shifts were obtained, Figs. 4-5(a-d). Since Cd is the faster diffusing element in the entire composition range (Fig. 4-3a), the lattice shifts are towards the Cd rich side of the diffusion couple, i.e., in the -x direction. Fig. 4-6a compares the concentration profile resulting from the simulation with that obtained by Iorio et al. (their Fig. 2) for the diffusion couple, 1Ag-0Cd / 0.904Ag-0.096 Cd. It is seen that the simulated concentration curve deviates from the experimental data near high Cd compositions.
A comparison between the simulated (predicted) and experimental Kirkendall shifts for all the diffusion couples studied by the authors, is illustrated in Fig. 4-6b. The simulated Kirkendall shifts obtained from the input experimental intrinsic diffusion coefficients are lower than the experimental measurements reported by the authors. The greatest deviation of about 33 pct is for the couple containing 0.279 atomic fraction Cd (5 days). These differences suggest that the experimental intrinsic diffusion coefficients measured by the authors have some inaccuracies. It should be noted that in their paper, the authors report a measurement error of ± 2 pct in the location of the Kirkendall plane and an error of ± 10 pct in the value of the concentration gradient at the Kirkendall plane (see Eqs. (4-24) and (4-25)). Since the Kirkendall shift depends upon the difference

![Figure 4-3. Phase diagram and diffusion coefficients in the Ag-Cd system. (a) Phase diagram of Ag-Cd [Mas90]. At 600°C, the fcc (Ag) phase has a solubility slightly less than 40 at pct Cd.](image)
Figure 4-3. Continued. (b) Experimental intrinsic diffusion coefficients of Ag (open circle) and Cd (filled circle) in the Ag-Cd system at 600°C from the data of Iorio et al. [Ior73]. The open and filled triangle represent the tracer diffusion coefficients of Cd and Ag in pure Ag. (c) the interdiffusion coefficient from the same data. The solid lines are the polynomial fits to the experimental data.
between the intrinsic diffusion coefficients (Eq. (4-20) at the Kirkendall interface ($v^K = x/2t$ at the Kirkendall interface), it appears that measurement errors in excess of 20 pct are not unlikely. From Fig. 4-6a and 4-6b, it appears that $D_{Cd}$ has been underestimated while $D_{Ag}$ has been overestimated by the authors. In spite of this, there appears to be good agreement between the predicted and measured Kirkendall plane compositions shown in (Fig. 4-6c) except for a small difference at the high Cd composition.

4.6.3.2 Darken-Manning relations for Ag-Cd

In order to compute the intrinsic diffusion coefficients predicted by the Darken theory, information regarding the tracer diffusion coefficients and the thermodynamic factor are needed.

**Tracer diffusion.** The tracer diffusion coefficients in this system have been measured by Schoen [Sch58] and are shown in Fig. 4-7a. The tracer diffusion coefficient of Cd is higher than Ag and shows the same composition dependence as the intrinsic diffusion coefficients. Both the tracer diffusion coefficients vary by over two orders in magnitude within the composition range considered.

**Thermodynamics.** In Fig. 4-7b and c, the activity coefficient and the activity computed from the data of Filby and Pratt [Fil63] are plotted as a function of the Cd composition. A strong negative departure from ideal mixing is evident (Fig. 4-7c). The thermodynamic factor computed using Eq. (4-38) is shown in Fig. 4-7d. It is positive over the composition range considered.

**Darken-Manning relations.** The $V_k$’s and the vacancy flow factors (Eqs. (4-82-84), that are needed to compute the intrinsic diffusion coefficients in the Manning theory are illustrated in Figs. 4-8a and b respectively. The vacancy flow factor for the slower
Figure 4-4. Simulated concentration profiles in the Ag-Cd system using the intrinsic diffusion coefficients obtained from the polynomial fits to the experimental intrinsic diffusion data (Fig. 4-3a) as the input to the simulation. $x_K$ denotes the location of the Kirkendall interface.
Figure 4-4. Continued. Simulated concentration profiles in the Ag-Cd system.
Figure 4-5. Lattice shift profiles for diffusion couples. Lattice profiles in (a) and (b) correspond to Figs. 4-4(a) and (b). Note that the sign of the lattice shift is negative, since the shift is in the -x direction, i.e., towards the Cd rich side. The maximum lattice shift is for the Kirkendall interface.
Figure 4-5. Continued. Lattice shift profiles in (c) and (d) correspond to the diffusion couples in Figs.4-4(c) and (d).
Figure 4-6. Simulated output in the Ag-Cd system using the experimental intrinsic diffusion coefficients. (a) Concentration profiles (solid line). The solid circles represent the data of Iorio et al. [Ior73]. (b) Simulated Kirkendall (solid circles) as a function of the measured shifts by the same authors.
diffuser, Ag, appears to have a stronger composition dependence as compared to Cd. The correction factor, $S$, for the interdiffusion coefficient in the Manning theory (Eqs. 4-85, 4-86), is very close to unity (Fig. 4-8c) for the range of compositions considered. Hence, one does not expect the interdiffusion coefficient predicted by the Darken theory to be significantly affected by this correction.

The intrinsic coefficients predicted from the Darken and Manning theories are shown in Figs. 4-9a and b. The tracer coefficients are also shown on the same graph. It is seen that for the slower diffuser, Ag, the intrinsic coefficient predicted by the Darken theory, is smaller than the experimental value in the entire composition range. The difference appears to be more significant for the low and high Cd compositions. The
Figure 4-7. Tracer diffusion coefficients and thermodynamic data in the Ag-Cd system at 600°C [Sch58]. (a) Tracer diffusion coefficients (circles). (b) Activity coefficient of Cd (circles) as a function of Cd composition [Fil63].
Figure 4-7. Continued. (c) Activity of Cd in Ag-Cd system at 600°C. A negative departure from ideal mixing is evident. (d) the thermodynamic factor, $\Phi$, obtained from the thermodynamic data is positive for negative departures from ideality.
Figure 4-8. Correction factors obtained from the Manning theory in the Ag-Cd system: (a) $V_k$ and (b) $1 \pm V_k$. The vacancy flow factor for the slower component, Ag, has a stronger composition dependence as compared to Cd, which is almost constant at unity.
<table>
<thead>
<tr>
<th>Atom fraction Cadmium ($X_{Cd}$)</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.02</td>
</tr>
<tr>
<td>0.2</td>
<td>1.04</td>
</tr>
<tr>
<td>0.3</td>
<td>1.06</td>
</tr>
<tr>
<td>0.4</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Figure 4-8. Continued. (c) The “S” correction factor for the interdiffusion coefficient predicted by the Manning theory. Since it is very close to unity in the composition range considered, the correction to the interdiffusion coefficient predicted by the Darken theory is not significant.

Manning correction for Ag increases this difference and is in fact in the wrong direction. Much better agreement is seen for the faster diffuser, Cd (Fig. 4-9b) except for the high Cd compositions. The Cd intrinsic coefficient from the Darken and Manning theories are quite close to each other. The Manning correction though small appears to be in the right direction. The interdiffusion coefficients predicted from the D-M theories are compared with the experimental ones in Fig. 4-9c. Again, the deviation for high Cd compositions is apparent.
In Fig. 4-10a, the ratios of the two intrinsic diffusion coefficients given by the D-M theories is compared with the experimental ratio. Since the uncertainty in the thermodynamic factor is removed by comparing the ratios, it has been suggested in previous studies as a better test of the D-M theories. However, even this test is not satisfactory. The ratio of the Darken intrinsic coefficients is almost constant while the experimental ratio has a clear composition dependence. The ratio of the Manning intrinsic coefficients appears to be significantly different from the experimental ratio for smaller Cd compositions. Perhaps a better test of the D-M theories is provided by comparing the difference between the intrinsic coefficients, see Fig. 4-10b. It is seen that only at intermediate compositions, the test is satisfied.

**Simulation results.** The simulation offers a more definitive test of the D-M theories as discussed earlier. Using the intrinsic coefficients predicted from these theories as the input to the simulation, concentration and lattice shift profiles were obtained for all the couples used in the study by Iorio et al. [Ior73]. In Figs. 4-11a and b, the concentration curves are compared with the experimental data of Iorio et al. [Ior73]. These should be compared with Fig. 4-6a, where the simulated concentration profiles were obtained using the experimental intrinsic diffusion coefficients as the input. It is seen that the differences, although small, are slightly more pronounced for Cd-rich compositions. A better test of the theories can be made by comparing the Kirkendall shifts as shown in Fig. 4-12a. The differences between the Kirkendall shifts predicted using the intrinsic diffusion coefficients given by the Darken and Manning relations in the simulation, and the experimental ones of Iorio et al. [Ior73], are clearly seen in the figure. The Kirkendall shifts computed using the experimental intrinsic diffusion
Figure 4-9. Comparison between the diffusion coefficients predicted by the Darken-Manning theories and the experimental coefficients. (a) Ag and (b) Cd intrinsic diffusion coefficient. Note that the Manning correction for Ag is in the wrong direction.
Figure 4-9. Continued. (c) Comparison between the interdiffusion coefficient predicted by the Darken-Manning theories and the experimental coefficient. Since the differences are higher for Cd-rich compositions, one may expect corresponding deviations in the simulated concentration profiles with the Darken-Manning intrinsic coefficients (see Fig. 4-11) as the input.

coefficients as the input to the simulation are also shown in the figure. The largest deviation is for the diffusion couple containing the highest Cd composition (0.379 $X_{Cd}$).

In Fig. 4-12b, the compositions at the Kirkendall interface are compared with the experimental compositions. The differences are not significant with the exception of one data-point obtained with the experimental intrinsic diffusion coefficients as the input. The Kirkendall interface compositions are not a sensitive indicator of differences between the intrinsic coefficients.
Figure 4-10. Test of the Darken-Manning theories in the Ag-Cd system. In (a) the ratio of intrinsic coefficients and (b) the difference between the two coefficients are compared. Test (a) is meant to correct for the error in the thermodynamic factor, while test (b) relates to differences between experimental and predicted lattice shifts.
Figure 4-11. Composition penetration curves obtained using the theoretical intrinsic diffusion coefficients as the input to the simulation: (a) Intrinsic coefficients predicted by the Darken theory and (b) the Manning theory. The data points of Iorio et al. [Ior73] are also shown (filled circles) in the figures.
Figure 4-12. Comparison between the experimental and predicted Kirkendall shifts and Kirkendall plane compositions. (a) Kirkendall shifts; (b) Kirkendall compositions.
Conclusions. It is suggested that Figs. 4-9a and b, 4-11a and b, and 4-12a be utilized for testing the D-M theories. It is concluded from these figures that the D-M theories are not satisfactory particularly for high Cd compositions, i.e., in the region where the tracer diffusion coefficients have a strong composition dependence and are much higher in magnitudes as compared to the low Cd compositions. It will be seen later that a similar conclusion holds for the Cu-Zn system.

4.6.4 Gold-Nickel (Au-Ni) System

The fcc phase in the Au-Ni system at 900°C was the subject of a well-publicized study by Reynolds et al. [Rey57] in the mid-50's. The authors undertook a comprehensive analysis for testing the Darken theory relating tracer diffusion with interdiffusion (Eq. (4-51)). The results published by the authors in 1957 are often quoted in textbooks as proof of the Darken B theories. Unfortunately, the authors did not examine the Darken relations between tracer and intrinsic diffusion (Eqs. (48), (49)). Van Dal et al. [Dal00a] have suggested this was on account of the poor accuracy in the measurement of Kirkendall shifts due to the use of thick tungsten wires (25 µm) as the inert markers for measurement. Since the time of the original study by Reynolds et al., techniques and procedures for the measurement of lattice shifts that are needed for the determination of the intrinsic diffusion coefficients, have significantly improved. The rather thick tungsten wires used as the inert markers have been replaced with fine ceramic powders (usually around 1 µm) of alumina (Al₂O₃) or thoria (ThO₂), thus improving the reliability of lattice shift measurements. Due to the fundamental importance of this system in relation to the Darken B theory, Van Dal et al. [Dal00a] undertook the task of re-examining the Darken theory from the viewpoint of assessing the
Darken relations between tracer and intrinsic diffusion. Intrinsic diffusion measurements were carried out using the technique of multi-foils [Koh70, Heu78, Phi91, Dal00a] for tracking the movement of inert ThO$_2$ markers (0.5 - 5 µm). The authors also took into account the large variation in the molar volume in the system (ignored by Reynolds et al.) by using the Sauer-Friese [Sau62]-den Broeder [Bro69] procedure for the measurement of the intrinsic and interdiffusion coefficients. After a re-evaluation of the thermodynamic factor, a test of the Darken B theory was possible in its entirety. Some important issues with the Darken relation between the intrinsic and tracer coefficients were raised based on these results. Due to the obvious importance of this system in relation to the Darken theory, and the recent findings by Van Dal et al., it was decided to undertake an analysis of this system, now with the aid of the simulation. In doing so, it was felt that a comparison between the predicted and experimental data, i.e., concentration profiles and lattice shifts, would serve as a much better test of the Darken theory. The Manning correction, that was ignored by Van Dal et al. on account of its relatively minor contribution that is within the realm of experimental error, is also examined.

4.6.4.1 Examining self-consistency of experimental intrinsic data

The phase diagram of the Au-Ni system is shown in Fig. 4-13 [Mas90]. The system exhibits an asymmetrical miscibility gap with a critical temperature of 810°C at a composition of 70.6 at. pct. Ni. At a temperature of 900°C, where most of the diffusion studies have taken place, the $\alpha$ fcc phase extends through the entire composition range. Diffusion measurements carried out in the original study of Reynolds et al. [Rey57] ignored the variation of molar volume in this system, but these have been included by
Van Dal et al. [Dal00a] in their recent study. As shown in Fig. 4-14a, the lattice parameter [Bie95] of the α phase shows a strong composition dependence. Since the molar volume depends on the cube of the lattice parameter, the variation in molar volume across the composition range is even more significant (approx. 35 %), see Fig. 4-14b). There is a slight positive departure from ideal mixing (2-3 %), hence for the purpose of the simulation, an ideal mixing model is used.

Van Dal et al. carried out diffusion experiments on both ‘normal’ and ‘multi-foil’, full-range diffusion couples in this system. The ‘normal’ couples contained pure Au and Ni as the end-members with the bonding plane between the two serving as the Kirkendall
interface. For the ‘multi-foil’ couples, a number of thin (20-25 µm) foils of pure Au and Ni were pressed together with ThO₂ particles (0.5-5 µm) between the foils serving as the inert markers. Both types of couples were diffusion annealed in vacuum at 900°C under a pressure of 5 MPa. The concentration penetration curves for both kinds of couples when plotted as function of the Boltzmann-Matano parameter, \( \lambda = \frac{x}{\sqrt{t}} \), were shown to match well (Fig. 4 in [Dal00a]). From knowledge of the movement of the inert markers using the multi-foil couple, the lattice velocity was computed using Philibert’s expression [Cor72, Phi91], see Appendix E. The Sauer-Friese procedure [Sau62] was utilized for the determination of the intrinsic and interdiffusion coefficients from the measured concentration profiles and lattice shifts. As compared to the traditional Boltzmann-Matano procedure that assumes a constant molar volume for the measurement of diffusion coefficients, the Sauer-Friese procedure takes into account molar volume variations.

**Intrinsic data.** The intrinsic and interdiffusion coefficients determined by Van Dal *et al.* are shown in Figs. 4-15a and b respectively. A fourth-order polynomial function obtained using regression analysis with the math software, MathCad [Mat01], was found to provide the best fit to the data. There is some uncertainty in the fit for the Ni intrinsic diffusion coefficient near the pure Ni side due to lack of data points, however it will be seen later from the results of the simulation, that the fitted function is found to provide an adequate representation of the experimental data. The intrinsic diffusion coefficients of both Au and Ni increase by about two to three orders of magnitude from the pure Ni side to the pure Au side, with that of Au being higher than Ni over the entire composition range. The interdiffusion coefficient shown in Fig. 4-15b is obtained from
the intrinsic diffusion coefficients using the relation (Eq. C-50).

\[
D^o = c_A \overline{V}_AD_B + c_B \overline{V}_BD_A \quad (\overline{V}_k = V_k^o, \text{ ideal mixing}) \tag{4-86}
\]

Note that only if the molar volume is constant, this equation simplifies to the well-known Darken relation given in Eq. (23). The solid line in Fig. 4-15b represents the data obtained from the fitted functions for the intrinsic diffusion coefficients shown in Fig. 4-15b, assuming an ideal mixing model for the molar volume. The interdiffusion data of Reynolds et al. is also shown in Fig. 4-15b (dashed line) and seems to be in reasonable agreement with the data of Van Dal et al. (with \(\overline{V}_k = V_k^o\)), even though the molar volume was assumed to be constant (by Reynolds) for the determination of the interdiffusion coefficient. The double extremum in the interdiffusion data of Reynolds et al. is however not seen in the data of Van Dal et al.. It is also evident from Fig. 4-15a, that the limiting value of the Ni intrinsic diffusion coefficient when \(X_{Au} \rightarrow 1\), is very close to the tracer diffusion coefficient of Ni in pure Au. In case of the Au intrinsic diffusion coefficient as \(X_{Ni} \rightarrow 1\), the minor deviation from the tracer coefficient of Au in pure Ni may be attributed to the lack of data near the pure Ni compositions. Van Dal et al. have reported that measurement problems due to steep concentration gradients in their full-range, multi-foil diffusion couples near the pure Ni compositions, made the determination of the Ni intrinsic diffusion coefficient rather imprecise and was hence not reported in Table 3 of their paper [Dal00a]. It should also be noted from Fig. 4-15a, that just as in the case for the Ag-Cd system discussed previously, the extrapolated values of the intrinsic diffusion coefficients of Au and Ni obtained from the fitted functions, appear to be significantly different from the self-diffusivities (i.e., tracer diffusion coefficient of component \(k\) in pure \(k\)) of these elements at the pure Au and Ni compositions.
respectively. The absence of intrinsic diffusion data near the pure element compositions makes this observation difficult to validate. Intrinsic diffusion experiments using incremental diffusion couples having end-member compositions near the pure components, are needed for verification.

**Output from experimental intrinsic data.** The fitted functions for the intrinsic diffusion coefficients and the molar volume were then input to the simulation to assess the quality of the data. The pure end-member compositions of a full-range diffusion couple served as the starting compositions in the simulation. In order to compare the concentration profile obtained using the simulation with that shown in Fig. 4 of Dal’s paper, it was necessary to determine the location of their initial interface (the origin in the present simulation), since this was not indicated in their figure (their origin is at the pure Au end of the diffusion couple). Initially, the concentration curve of Dal’s Fig. 4 was scanned and the data-points were extracted using the Un-Scan-It software [Uns00]. From knowledge of the Kirkendall plane composition (26.9 at pct Ni) for the full-range, multi-foil couple, the position (68 µm/hrs\(^{1/2}\)) of the Kirkendall plane in terms of the normalized distance (the Boltzmann variable, \(\lambda = x/\sqrt{t}\)) was obtained. The Kirkendall shift (90 µm) was obtained from their measured Kirkendall plane velocity (\(v^K = 12.5 \times 10^{-11} \text{ m/s}\)) by using the relation,

\[
v^K = \frac{x^K}{2t} \quad \text{for the Kirkendall plane} \tag{4-87}
\]

Then the normalized Kirkendall shift (9 µm/hrs\(^{1/2}\)) was obtained by dividing \(x^K\) with the square root of the annealing time (100 hrs) used by Dal *et al.* Since the Kirkendall shift represents the distance between the original (Kirkendall) interface and the position of this
interface after the diffusion anneal for the specified time, \( t \), and since the migration of the interface was in the direction of the faster diffusing component, (here Au) the location of the original interface was obtained by adding the normalized Kirkendall shift to the normalized Kirkendall plane position. This normalized position of their original interface (origin), 77 \( \mu \text{m/hrs}^{1/2} \), when corrected by one unit to 76 \( \mu \text{m/hrs}^{1/2} \) gave the best match with the output from the simulation. By using the same procedure for their “normal” full-range diffusion couple \((t = 50 \text{ hrs}, v^K = 14.2 \times 10^{-11} \text{ m/s})\) that is also shown in their Fig. 4, the position of their origin turned out to be approximately 76 \( \mu \text{m/hrs}^{1/2} \) thus confirming the earlier analysis. This offset of 76 \( \mu \text{m/hrs}^{1/2} \) was applied to determine the new normalized positions for their Fig. 4 and compared with the output from the simulation.

The resultant concentration profile in Fig. 4-16a showed some deviation from the experimental measurement of Van Dal et al. (their Fig. 4) particularly at the steeper portions of the curve near the pure Ni compositions. The simulated lattice shift curve shown in Fig. 4-16b also showed a deviation with a difference of about 10 pct at the Kirkendall interface\(^3\). It was initially felt, that the cause of this apparent deviation was due to the lack of intrinsic diffusion data near the pure Ni compositions. To examine if this was indeed the case, the self-diffusion coefficient of Ni (for pure Ni) was used an additional data point and a modified functional fit for the Ni intrinsic diffusion coefficient was obtained. This was then used as the input to the simulation. However, the resultant concentration and lattice shift profile did not improve the match with the

\(^3\) Note that the \( x \) co-ordinate for the lattice shift profile has been changed to \(-x\) in Fig. 4-16b to correspond to Fig. 5 of Van Dal et al. [Dal00a]. The lattice shift is in the direction of the faster diffuser, i.e., Au.
data, in fact the Kirkendall shift was off by about 15 pct. This prompted a re-
examination of the simulation setup parameters. An important issue turned out to be
concerning the number of iterations needed to obtain a stable, time-invariant output. In
order to examine this issue further, the number of iterations within the simulation was
increased to 2000. It was found in the resultant concentration profile indicated that the
deviation near the steeper portions of the curve reduced noticeably. In order to determine
the number of iterations needed to obtain a stable output with the simulation, the lattice
shift and the Kirkendall plane composition were plotted as a function of the number of
iterations (up to 2000) in Figs. 4-17a and b respectively (filled circles). An exponential
fit was obtained, that suggested that approximately 6000 iterations were needed. The
simulation was then carried out for this number of iterations. The open diamond symbols
shown in Figs. 4-17a and b are the output for 6000 iterations. The predicted values from
the exponential fit are in reasonable agreement with the actual output, thus demonstrating
the effectiveness of this procedure for determining the number of iterations required for
obtaining a stable output. In order to maintain semi-infinite conditions, the number of
slices was increased by 12 times the usual number (2 x 120) to 2880. The initial
interface was hence given by the position of the mid-plane slice, i.e., the 1441st slice.

The final results for the concentration and lattice shift profiles for 6000 iterations
are shown in Figs. 4-18a and b respectively (solid lines). The output for 512 iterations
(dashed lines) are also shown in these figures. The improved fits for both the
concentration and lattice profiles are apparent. It is see in Fig. 4-18b, that the simulated
Kirkendall shift is within 6 pct of the value published by Dal et al. [Dal00a].
Figure 4-14. Lattice parameter and molar volume as a function of composition in the Au-Ni system [Bie95]. (a) Lattice parameter; (b) molar volume. Molar volume variations in this system are significant, although the departure from ideal mixing is negligible.
Figure 4-15. Diffusion coefficients in the Au-Ni system at 900°C. (a) Intrinsic diffusion coefficients from the data of van Dal et al. [Dal00a]. (b) Interdiffusion coefficients from the same data and from Reynolds et al. [Rey57] (dashed line). The tracer diffusion coefficients of Au and Ni at the pure Au and Ni compositions are also shown (filled and open triangles respectively) [Kur55, Rey57].
Figure 4-16. Output using the intrinsic diffusion coefficients as input. (a) Concentration profile and (b) lattice shift variation. The data obtained by van Dal et al. [Dal00a] are also shown. The solid line corresponds to the output for 512 iterations. The difference between the experimental and simulated lattice shift at the Kirkendall interface ($x_K$) in (b) is approx. 10%.
Figure 4-17. Procedure for determining the number of iterations in the simulation, which are needed to obtain a stable output. The functions for the experimental intrinsic diffusion coefficients shown in Fig. 4-15(a) were used as the input to the simulation. (a) Kirkendall shift and (b) composition at the Kirkendall plane as a function of the number of iterations. The exponential fit for the data-points (filled circles) suggests that approx. 6000 iterations are needed. This is validated from the result at 6000 iterations (open diamond).
Figure 4-18. Output using the intrinsic diffusion coefficients as input to the simulation. (a) Concentration profile and (b) lattice shift variation. The dashed line corresponds to the output for 512 iterations and the solid line for 6000 iterations. The filled circles in (a) and (b) are the data points obtained from Figs. 4 and 5 of Van Dal et al. (Dal00a) respectively. In (b), the difference between the simulated (solid line) and experimental lattice shift at the Kirkendall interface is approximately 6 pct.
Figure 4-19. Diffusion fluxes as a function of the Boltzmann variable, $\lambda = x/\sqrt{t}$, obtained from the simulation (6000 iterations). (a) Intrinsic fluxes and vacancy flux and (b) volume weighted interdiffusion fluxes.
Figure 4-20. Mean volume \( (v') \), mean number \( (v^N) \), and lattice velocity \( (v^K) \) as a function of the Boltzmann parameter at 900°C. The mean volume velocity is zero since the partial molal volumes are taken to be equal to the molar volumes of the pure components. Note that the Kirkendall velocity, \( v^K \), is negative since the lattice movement is in the -x direction and towards the Au rich side of the diffusion couple.

In addition to the concentration profiles and the lattice shift, the simulation also provides the intrinsic fluxes and the vacancy flux (Fig. 4-19a), as well as the interdiffusion fluxes. Since the molar volume is not constant, it is seen from Fig. 4-19a, that volume weighted interdiffusion fluxes are equal in magnitude but opposite in sign as required by Eq. (A-27). Fig. 4-20 shows the lattice velocity, \( v^K \), the mean volume velocity, \( v' \), and the mean number velocity, \( v^N \). Since the partial molal volumes are equal to the molar volumes of the pure components, \( v' \) is zero (Appendix D). The lattice velocity, \( v^K \), is negative since the vacancy flux is negative and in the direction of the faster diffusing component, Au, which is located on the -x side of the diffusion couple.
4.6.4.2 Darken-Manning relations for Au-Ni

In order to compute the intrinsic diffusion coefficients using the Darken-Manning relations, the tracer diffusion coefficients and thermodynamics of the Au-Ni system need to be known at the desired temperature (900°C). These are discussed in some length.

Tracer diffusion. The tracer diffusion coefficient for Au, $D^*_{Au}$, in a number of Au-Ni alloys at various temperatures was measured by Kurtz et al. [Kur55], see Fig. 4-21. The results recorded on a semi-log plot of $D^*_{Au}$ against the reciprocal temperature (1/T) were straight lines consistent with the usual Arrhenius relation:

$$D^*_{Au} = D^*_{o,Au} \exp\left(-\frac{Q^*_{Au}}{RT}\right)$$  \hspace{1cm} (4-88)

where $D^*_{o,Au}$ is the frequency factor in cm$^2$/s, $Q^*_{Au}$, the activation energy in cal/mol and T, the absolute temperature. It was found that the frequency factors and activation energies reported in Table I of Kurtz et al. [Kur55] for some Ni rich compositions (65, 80 and 100% Ni) were incorrect and failed to reproduce the values shown in their Fig. 4 as well as in their Fig. 3, which is a plot of $D^*_{Au}$ as a function of composition at various temperatures. Hence the calculations were repeated here using the data-points given in their figure. From knowledge of the computed frequency factors and activation energies, $D^*_{Au}$ was computed and plotted as a function of composition at 900°C, see Fig. 4-22 (solid circles). The solid line represents a third order polynomial fit of these computed Au tracer diffusivities (log($D^*_{Au}$) vs $X_Ni$). This compares quite well with Fig. 3 of Kurtz et al. and Fig. 1 of Reynolds et al. [Rey57]. The dashed lines in this figure are the interpolated data for $D^*_{Au}$ and $D^*_{Ni}$ given in Table 10 of Reynolds et al. [Rey57].
The tracer diffusion coefficient of Ni, $D_{Ni}^*$, in Au-Ni alloys at 900°C was obtained by using the frequency factors and activation energies for Ni tracer diffusion given in Table 3 of Reynolds et al. The computed data points are shown in Fig. 4-22 (open circles). A fourth order polynomial fit (solid line) of $\log(D_{Ni}^*)$ with $X_{Ni}$ was found to adequately represent this data.

**Thermodynamics.** The activity measurements of Seigle et al. [Sei52] that were used by Reynolds et al. [Rey57] to determine the thermodynamic factor have been questioned by Sellars and Maak [Sel66]. These authors suggested that the electromotive force method used by Seigle et al., that utilized a fused mixture of alkali chlorides with NiCl₂, resulted in derived values of the enthalpy and entropy of mixing that were much higher in comparison with those obtained from calorimetric [Ori60, Day62] and specific heat measurements [Ori55] respectively. Sellars and Maak measured the activities for a number of Au-Ni alloys over a series of temperatures (775, 825, 900 and 935°C) using a galvanic cell with a solid oxide electrolyte (0.85 ZrO₂ 0.15 CaO). They confirmed that the enthalpies and entropies of mixing derived from their measurements were reasonably accurate when compared with the experimental data in the literature. Hence in this analysis, the activity data of these authors was primarily used to determine the thermodynamic factor and compared with the data of Reynolds et al. [Rey57]. The recent activity measurements by Bienzle et al. [Bie95] were also used to compute the thermodynamic factor. It will be seen that their values are somewhat different from those of Sellars and Maak.

For the purpose of the simulation, it is convenient to have an analytical expression for the thermodynamic factor as a function of composition for the entire system.
Figure 4-21. Tracer diffusion of gold as a function of reciprocal temperature for Au-Ni alloys (data points from Fig. 4 of Kurtz et al. [Kur55]). Note the correction in the labeling of the abscissa in Fig. 4 of Kurtz et al.
Figure 4-22. Tracer diffusion coefficients of Au and Ni in Au-Ni alloys at 900°C. Data for $D^*_\text{Au}$ was obtained from Kurtz et al. [Kur55], $D^*_\text{Ni}$ from Reynolds et al. [Rey57]. The solid lines are polynomial fits by this author, the dashed lines by Reynolds et al. [Rey57].
Figure 4-23. Thermodynamic data for the Au-Ni system at 900°C. (a) Activity of Ni as a function of composition. Redlich-Kister (R-K) polynomials were used to fit the activity data of Sellars and Maak [Sel66] and Bienzle et al. [Bie95]. (b) Thermodynamic factor computed from R-K polynomials. The thermodynamic factor of Reynolds et al. (Table 10 in [Rey57]) was obtained from the activity data of Seigle et al. [Sei52].
Figure 4-24. Intrinsic diffusion coefficients of Au and Ni computed using the Darken theory for the Au-Ni system at 900°C. In (a) $D_{Au}$ computed from the Darken theory is underestimated at low Ni compositions while in (b) $D_{Ni}$ is in reasonable agreement with the experimental data of Dal et al. [Dal00a]. The tracer coefficients, $D_{Au}^*$ and $D_{Ni}^*$, are also shown for comparison.
Typically, such expressions can be derived from Duhem-Margules [Gok95, Gok96, Tom96] or Redlich-Kister [Red48] type polynomial functions for the Gibbs excess free energy of mixing. The procedure for obtaining suitable Gibbs excess free energy parameters from a regression analysis of activity data is described in the next section.

The standard Gibbs free energy of a phase is given by the sum of an ideal and excess contribution [Deh93, Hil98]:

Figure 4-25. Interdiffusion coefficient for the Au-Ni system computed using the Darken theory compared with experimental data of van Dal et al. [Dal00a] (solid circles) and Reynolds et al. [Rey57] (open squares). The predicted values based on the thermodynamic data of Sellars and Maak [Sel66] and Bienzle et al. [Bie95], which were obtained in the present study, and those by Reynolds based on the thermodynamic data of Siegle et al. [Sei52] are shown in the figure. The tracer diffusion coefficients of Au and Ni (filled and open triangles) for pure Au and Ni compositions are also shown.
\[
\Delta G_{mix} = \Delta G_{mix}^{id} + \Delta G_{mix}^{xs}
\] (4-89)

The ideal term is given by the configurational entropic contribution to the free energy of this phase:

\[
\Delta G_{mix}^{id} = RT[X_1 \ln(X_1) + X_2 \ln(X_2)]
\] (4-90)

where \(X_1\) and \(X_2\) are the mole fractions of the components in a binary phase. The excess free energy contribution is usually represented using various types of polynomial expressions. A Redlich-Kister [Red48, Hil98] type polynomial expression for a binary is used in the present case:

\[
\Delta G_{mix}^{xs} = X_1X_2 \sum_{n=0}^{m} L_{ij}^n (X_i - X_j)^n = X_1X_2[ L_0^0 + L_1^1 (X_1 - X_2)^1 + L_2^2 (X_1 - X_2)^2 ]
\] (4-91)

The \(L_{ij}^n\) terms are the Redlich-Kister (RK) interaction parameters between components \(i\) (Au) and \(j\) (Ni) in the binary system and are usually determined from experimental thermodynamic and phase diagram information [Luk77, Bal83]. Usually higher order \(L_{ij}^n\) terms beyond those given in Eq. (4-91) are not needed (\(m = 0, 1, 2\)). The temperature dependence for each \(L\) parameter is usually expressed by

\[
L(T) = a + bT + cT \ln(T) + dT^2 + eT^3 + \frac{f}{T}
\] (4-92)

Again terms beyond the second term on the R.H.S. of Eq. (4-92) are not required in most cases. The Gibbs partial excess molal free energies can be obtained from Eq. (4-91) using standard procedures [Deh93] to give (omitting the subscripts for the \(L\)’s)

\[
\Delta \bar{G}_{1}^{xs} = X_2^2[ L_0^0 - L_1^1 (4X_2 - 3) + L_2^2 (12X_2^2 - 16X_2 + 5) ]
\] (4-93)

\[
\Delta \bar{G}_{2}^{xs} = X_1^2[ L_0^0 + L_1^1 (4X_1 - 3) + L_2^2 (12X_1^2 - 16X_1 + 5) ]
\] (4-94)
The Gibbs partial excess molal free energy for component 2, \( \Delta G_{2xs} \), can also be expressed in terms of \( X_2 \):

\[
\Delta G_{2xs}^x = 12L^2X_2^4 + (-32L^2 - 4L^1)X_2^3 + (29L^2 + 9L^1 + L^0)X_2^2 +
\]
\[
+ (-10L^2 - 6L^1 - 2L^0)X_2 + (L^2 + L^1 + L^0) \quad (4-95)
\]

The relation between the Gibbs partial molal free energy and the activity for component \( k \), \( a_k \), is [Deh93]:

\[
\Delta G_{k}^{mix} = RT \ln(a_k) = RT \ln(X_k \gamma_k) = RT \ln(X_k) + RT \ln(\gamma_k) \quad (4-96)
\]

where the activity is expressed in terms of the activity coefficient, \( \gamma_k \), and \( X_k \) as

\[
a_k = X_k \gamma_k \quad (4-97)
\]

The ideal term in Eq. (4-96) is given by

\[
\Delta G_{k}^{id} = RT \ln(X_k) \quad (4-98)
\]

and the excess term is

\[
\Delta G_{k}^{xs} = RT \ln(\gamma_k) \quad (4-99)
\]

Using Eqs. (4-97) and (4-99), the Ni activity data in Table II of Sellars and Maak’s paper [Sel66] for the Au-Ni system (Au = 1, Ni = 2) can be used to obtain the Gibbs partial molal excess free energy of Ni, \( \Delta G_{Ni}^{xs} \), at 900°C (1173 K). From Eq. (4-95), it can be seen that this data has to be fitted using a least squares regression analysis of a fifth order polynomial in order to have a three parameter R-K model:

\[
\Delta G_{2xs}^x = g_0 + g_1X_2 + g_2X_2^2 + g_3X_2^3 + g_4X_2^4 \quad (4-100)
\]

These regression parameters are related to the \( L^n \) parameters in Eq. (4-95) by

\[
g_0 = L^0 + L^1 + L^2 \quad (4-101)
\]
\[
g_1 = -2L^0 - 6L^1 - 10L^2 \quad (4-102)
\]
\[
g_2 = L^0 + 9L^1 + 29L^2 \quad (4-103)
\]
\[ g_3 = -4L^1 - 32L^2 \]  \hspace{1cm} (4-104)  
\[ g_4 = 12L^2 \]  \hspace{1cm} (4-105)  

Since there are only 3 independent \( L^n \) parameters in Eq. (4-95), this means that there are 2 equations among the 5 regression parameters\(^4\). These are

\[ g_1 + g_2 + g_3 + g_4 + g_5 = 0 \]  \hspace{1cm} (4-106)  
\[ g_1 + 2g_0 - g_3 - 2g_4 = 0 \]  \hspace{1cm} (4-107)  

Thus only 3 among the 5 regression parameters are independent. The constrained regression analysis was performed using SigmaPlot [Sig02] and the resulting R-K parameters based on the activity data of Sellars and Maak [Sel66] at 900°C were

\[ L^0 = 17289 \quad L^1 = -3470; \quad L^2 = 1889 \]  \hspace{1cm} (Sellars and Maak) (4-108)  

and those based on the activity data of Bienzle et al. [Bie95] were

\[ L^0 = 14700 \quad L^1 = -4080 \quad L^2 = 900 \]  \hspace{1cm} (Bienzle) (4-109)  

These R-K parameters were then used to determine the activities using Eqs. (4-94), (4-99) and (4-97). As seen in Fig. 4-23a, the R-K parameters determined in this study appear to provide a reasonable fit to the activity data. There is considerable scatter in the data of Seigle, which is also shown in the figure.

Using Eq. (4-38), (4-95) and (4-99), an analytical expression for the thermodynamic factor in terms of the R-K parameters can be shown to be

\[ \Phi = 1 + \frac{X_2}{RT} \left[ L^2 (48X_2^3 - 96X_2 + 58X_2 - 10) + L^1 (-12X_2^2 + 18X_2 - 6) + L^0 (2X_2 - 2) \right] \]  \hspace{1cm} (4-110)  

\(^4\) In the absence of these constraints on the regression parameters, the Gibbs-Duhem relation and the limiting laws at infinite dilution (Raoul’s and Henry’s law) [Deh93, Gok96] need not be obeyed for the regressed function.
It is seen in Fig. 4-23b, that the thermodynamic factors computed from Bienzle’s data are lower than Sellars and Maak’s or Seigle’s data. The thermodynamic factor obtained by Reynolds (see Table 10 of [Rey57]) from Siegle’s activity data shows a noticeable “kink” at $X_{Ni} = 0.55$, however this was not observed with the 3 parameter R-K models based on the Sellars and Maak, or Bienzle’s data. Conceivably, a 4 parameter R-K model might reproduce this behavior, however in view of the excellent fit of the activity data (Fig. 4-23a), this was not attempted here. It will be seen later that these differences in the thermodynamic factor are not significant enough to alter this author’s conclusions regarding the Darken theory for this system.

**Darken relations for Au-Ni.** From knowledge of the tracer diffusivities and the thermodynamic factor for the Au-Ni system at 900°C, the intrinsic diffusion coefficients were computed using the Darken relations, Eqs. (4-48) and (4-49), and compared with the experimental values obtained by van Dal et al. [Dal00a]. In Fig. 4-24a, the intrinsic diffusion coefficient of Au, $D_{Au}^{Dark}$, computed using the Darken theory is compared with the experimental data of van Dal. The computed values of Reynolds et al. (see Table 10 in [Rey57]), that were based on Seigle’s thermodynamic data [Sei52] are shown in the figure along with those computed in this study that were based on the thermodynamic data of Sellars and Maak [Sel66], and Bienzle et al. [Bie95]. The tracer diffusion coefficient of Au, $D_{Au}^t$ is also depicted in the figure so as to get a sense of the effect of the thermodynamic factor, $\Phi$, on $D_{Au}^t$. It is seen that for Ni mole fractions greater than approximately 0.5, the predicted values are reasonably close to the experimental ones. However for low Ni compositions, regardless of the source of the thermodynamic data, the predicted values are appreciably lower. In fact it is seen from the figure, that at these
low Ni compositions, the effect of the thermodynamic factor, $\Phi$, on $D^*_{Au}$ is in the opposite direction from that which would have been needed to conform to the experimental values. This occurs because $\Phi$ is less than unity for the entire composition range (Fig. 4-23b) in this system.

In comparison, the intrinsic diffusion coefficient for Ni, $D^*_{Ni}$, predicted by the Darken theory is in reasonable agreement with the experimental data. The computed value based on the Sellars thermodynamic data appears to show the best agreement in this case.

The interdiffusion coefficient was also computed from the Darken relation, Eq. (4-51), and compared with Dal’s and Reynold’s [Rey57] experimental interdiffusion data, see Fig. 4-25. There are minor differences depending on the source of the thermodynamic data, but overall it appears that the Darken theory for the interdiffusion coefficient in the Au-Ni system at 900°C is reasonably obeyed, thus confirming the previous assessments by Reynolds et al. [Rey57] and van Dal et al. [Dal00a].

**Manning relations for Au-Ni.** Using Eqs. (4-77) - (4-79), $V_{Au}$ and $V_{Ni}$ as well as the vacancy wind terms for Au and Ni were determined at 900°C (Fig. 4-26a, b). It was determined that the vacancy wind term for Ni, $(I - V_{Ni})$, became negative at Ni compositions greater than 0.9, while that for Au (the faster diffusing component), $(I + V_{Au})$, remained positive over the entire composition range (Fig. 4-26b). Under such circumstances, Manning has suggested that “non-random” effects are likely to be prevalent that prevent the application of his correction to the Darken theory under such conditions. Van Dal et al. [Dal00a] have stated that the Manning correction due to vacancy flow effect is too small to cause any major variations to the predicted values.
Figure 4-26. Vacancy Wind terms for the Au-Ni system at 900°C [Man70]. (a) $V_k$ (b) $1 \pm V_k$. 
Figure 4-27. Output using the intrinsic diffusion coefficients predicted from the Darken theory as input. (a) Composition profile and (b) lattice shift profile. The experimental data of van Dal et al. [Dal00a] (solid circles) as well as the output obtained using Dal’s intrinsic diffusion data (dashed line) are also shown in the figure. Since the intrinsic coefficient of Au from the Darken theory is underestimated (Fig. 4-24a), in (b) the lattice shifts are much lower than the experimental values. Note that in (b) the x co-ordinate has been changed to -x to conform with van Dal’s figure.
Figure 4-28. Concentration profiles using the intrinsic diffusion coefficients predicted from the Darken theory as input (solid lines) to the simulation. The dashed lines are those obtained using Dal’s experimental intrinsic coefficients as input. Since $c_k = X_k/V$ and $V$ reduces as the Ni composition increases (Fig. 4-14b), the far-field concentration at $X_{Ni} = 1$ is much higher than at $X_{Au} = 1$.

Simulation results. The Darken intrinsic diffusion coefficients computed using the thermodynamic data of Sellars were input to the simulation and the output compared with the experimental observables of van Dal et al. (Figs. 4-27 to 4-30). Since the predicted intrinsic coefficients based on the thermodynamic data of Bienzle or Seigle were not significantly different from the Sellars data, these were not utilized for the
comparison here. In Figs. 4-27 to 4-30, the solid lines represent the output obtained using the predicted Darken intrinsic coefficients. The dashed lines are the output from the experimental intrinsic data of van Dal et al. obtained earlier using the experimentally measured intrinsic coefficients of the same authors (Figs. 4-18 to 4-20), and are shown in these figures for comparison.

It is seen in Figs. 4-27a and b that there are significant differences between the predicted and measured concentration and lattice shift profiles. Since the predicted intrinsic diffusion coefficient of Au is underestimated (Fig. 4-24a), the lattice shifts are considerably smaller as compared to the experimental ones (approximately 80%).

In Fig. 4-28, the concentration profiles (in mol/cc) are compared with the computed output from Dal’s intrinsic data. It is seen that due to the underestimation of the Au intrinsic diffusion coefficient by the Darken theory, the depth of penetration of the components is also reduced resulting in steeper concentration gradients, particularly for Ni. Note that since the molar volume of Ni is lower than Au, the concentration of Ni near the Ni rich side is much higher than that of Au near the Au rich side of the diffusion zone. This appears to result in an unusual flux pattern as seen in Fig. 4-29a, where the intrinsic flux of the slower diffusing Ni, is actually higher than that of the faster diffusing Au over a significant distance, thereby causing a vacancy flux, $J_V^{\text{Dark}}$, that has the same sign (positive) as $J_{\text{Au}}^{\text{Dark}}$. This rather unusual behavior is not seen with the earlier output obtained using the experimental intrinsic data of van Dal as input (dashed lines). A similar behavior is also observed in the interdiffusion coefficients (Fig. 4-29b). In spite of this, it is seen both in Figs. 4-27b and 4-30, that the lattice shift and velocities ($v^{K\text{Dark}}$) are respectively positive across the diffusion zone, and in a direction opposite to the
Figure 4-29. Diffusion fluxes using the Darken intrinsic coefficients as input (solid lines). (a) intrinsic fluxes and vacancy flux; (b) interdiffusion fluxes. The fluxes obtained using Dal’s intrinsic data are also shown (dashed lines). In (a) it is seen that the Darken vacancy flux is positive while that obtained using Dal’s intrinsic data is negative. The Darken lattice shift, $x^\kappa$, is negative and hence in a direction opposite to the vacancy flux.
Figure 4-30. Mean volume ($v^V$), mean number ($v^N$), and lattice velocity ($v^K$) as a function of the Boltzmann parameter at 900°C obtained using the Darken intrinsic diffusion coefficients as input (solid lines) and the intrinsic data of Dal et al. [Dal00a] (dashed lines). Note that $v^N_{\text{Dark}}$ is greater than $v^K_{\text{Dark}}$ over a significant diffusion distance and the magnitudes of the velocities are substantially reduced as compared to those obtained with the experimental intrinsic coefficients.

vacancy flux. This can be explained by examining Eq. (A-52), which states that in the case of a system with varying molar volume, $J_v = C v^K v^N = C(v^K - v^N)$. In the present situation, it is seen that since $v^N$ is greater than $v^K$ and both are negative in sign, the resultant vacancy flux is positive. However for positions close to the Ni-rich end of the diffusion zone ($x/\sqrt{t} > 4$), the Au intrinsic flux (positive) is greater than Ni and hence, the vacancy flux is negative. The lattice velocity is also negative and hence in the same direction as the vacancy flux since in this case, $v^K$ is greater than $v^N$ and is negative in sign.
Conclusions regarding Darken-Manning relations for Au-Ni. Figs. 4-24 and 4-27 provide a definitive test of the Darken theory for the Au-Ni system at 900°C. In accordance with van Dal’s findings, it was seen in the present investigation, that while the predicted intrinsic diffusion coefficient of Ni was in reasonable agreement with the measured value, that for Au was underestimated at low Ni compositions. In fact, the effect of the thermodynamic factor on the tracer diffusion coefficient of Ni was in the wrong direction ($\Phi < 1$) at these compositions thus indicating a significant problem with the Darken theory. The thermodynamic measurements which were used to compute the thermodynamic factor have been performed several times as discussed earlier and are sufficiently close to one another (see Fig. 4-23). $\Phi$ is smaller than unity for all the compositions in this system at 900°C. A value greater than unity only near low Ni compositions is not conceivable, since this would require activities that exhibit a negative departure from ideality at low Ni compositions and a positive departure at the higher Ni compositions, a situation that is rarely observed. Thus errors in $\Phi$ cannot account for the deviation between the predicted and measured values of the intrinsic diffusion coefficients.

Since, it was demonstrated with the aid of the simulation, that the experimental intrinsic measurements of van Dal et al. [Dal00a] were sufficiently accurate in reproducing the experimental composition and lattice shift profiles (Fig. 4-18), inaccuracies in the experimental measurements are unlikely to be the source of this problem. However, intrinsic diffusion measurements using incremental diffusion couples in the range from pure Au to 0.4 at pct Ni would be useful for further examining the accuracy of the full-range diffusion couple measurements in this composition range.
While the tracer measurements for Au may be certainly called into question (Fig. 4-21), it seems unlikely that these errors could occur only near low Ni compositions (< 0.4 at pct) where the deviation between the Darken predictions and experimental measurements are the highest. Nevertheless, an independent tracer diffusion study of Au in Au-Ni alloys would be of value in confirming the measurements of Kurtz et al. [Kur55].

4.6.5 Copper-Zinc (Cu-Zn) System

The α fcc phase of the Cu-Zn system (Fig. 4-31) was the first system in which evidence of the Kirkendall effect was documented by Kirkendall and Smigelskas [Smi47]. Following this discovery, da Silva and Mehl [Sil51] and later Horne and Mehl [Hor55] carried out a number of intrinsic diffusion measurements in this and other binary single-phase systems that confirmed the findings of Kirkendall and Smigelskas. Two prior tests of the Darken-Manning relations in this system, by Schmatz et al. [Sch66] and Kozeschnik [Koz00] were briefly discussed in an earlier section. The study by Schmatz made a comparison between the observed ratio of the tracer diffusion coefficients with that obtained by a complicated manipulation of the Darken-Manning relations. Kozeschnik made the usual comparison between the predicted and experimental intrinsic diffusion coefficients and also compared the concentration profiles measured by Resnick and Balluffi [Res55], and da Silva and Mehl [Sil51] with those obtained from their own diffusion program for which the experimental “diffusivities” of da Silva and Mehl were used as input5 (see Fig. 8 of [Koz00]). Since da Silva and Mehl reported only interdiffusion coefficients in their paper, it is assumed here that the diffusion program

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5 It appears that the simulated concentration profile and the data-points of da Silva and Mehl shown in Fig. 8 of Kozeschnik’s paper [Koz00], are for a temperature of 885°C and not 915°C as reported.
used by Kozeschnik was an interdiffusion simulation. This is confirmed by the fact that his program did not report any lattice shift information. Thus there is no prior study that has compared both the concentration profiles and the lattice shifts using the experimental intrinsic diffusion measurements of Horne and Mehl as input. Hence, it was felt that such a study would be useful in assessing the Darken-Manning theories.

4.6.5.1 Examining self-consistency of experimental intrinsic data

Horne and Mehl [Hor55] have reported intrinsic diffusion coefficients in the Cu-Zn system as a function of composition within the \( \alpha \) fcc phase at three different temperatures: 780, 855 and 915°C. Among these three temperatures, the closest one at which a concentration profile has been published for the purpose of comparison in the present study is the first (the concentration profiles in Figs. 15 and 16 of da Silva and Mehl [Sil51] for sample B-35 are at 784°C). Hence, the Darken-Manning analysis for this system is conducted at this temperature. Fig. 4-32 shows the intrinsic diffusion coefficients as a function of the Zn composition at 780°C along with the tracer diffusion coefficients [Anu72] of Cu\(^{67}\) and Zn\(^{65}\) at the pure Cu composition. The solid lines were obtained by second order polynomial fits to the intrinsic diffusion data. The data-points (circles) are the smoothed values reported by Horne and Mehl, that were obtained at the Kirkendall interface for a number of incremental diffusion couples that were annealed at temperatures within ±4°C of 780°C (see Table V of [Hor55]). On account of the errors involved in the determination of the Kirkendall\(^6\) and Matano interfaces (where graphical

\(^6\)3 mil (1 mil = 25.4 \(\mu\)m) W wires were used as Kirkendall markers. The error in the measurement of the marker interface was reported to be within ±0.5 mil depending on the direction of the expected deviation from the wire interface [Hor55].
Proceedings were used, and the compositions\(^7\), a smoothing procedure was employed by the authors to obtain the intrinsic diffusion coefficients. From Fig. 4-32, it is seen that the extrapolated values of the intrinsic diffusion coefficients at the pure Cu composition are reasonably close to the tracer values. The preferable way of examining the accuracy of the measurement and smoothing procedures employed for the determination of the intrinsic diffusion coefficients is with the aid of the simulation.

Anusavice *et al.* [Anu72] determined the partial molal volumes of Cu, Ni and Zn in the \(\alpha\)-fcc phase of the Cu-Ni-Zn system and found them to be almost constant throughout the single-phase region. Hence, volume mixing changes in this system were assumed to be ideal and given by the weighted sum of the molar volumes of the pure components in the same phase form. The reported molar volumes of \(\alpha\)-fcc Cu, Ni and Zn\(^8\) were respectively 7.09, 6.59 and 8.47 cc/mol. However, since Horne and Mehl assumed a constant molar volume for the calculation of their intrinsic and interdiffusion coefficients in the concerned \(\alpha\)-fcc Cu-Zn system, an average (of Cu and Zn) molar volume of 7.78 cc/mol was used for the purpose of the simulation.

Horne and Mehl made a number of alloys in the \(\alpha\) Cu-Zn system with compositions: 0, 9.6, 19.4 and 29.4 at pct Zn (Table 1 in [Hor55]). Several diffusion couples were made by bonding various combinations of these alloys (6 in all) and subjected to annealing at various temperatures and times. These diffusion couple compositions were used as the input to the simulation. Composition profiles and lattice

\(^7\) Compositions were determined by chemical analysis of machined samples. The expected accuracy reported was \(\pm 0.5\) pct Cu.

\(^8\) Note that the molar volume of pure Zn in the stable hcp phase is 9.17 cc/mol, and is different from that in the fcc phase, which can be considered to be metastable.
shifts based on the intrinsic diffusion data at 780°C were obtained from the simulation and compared with the available data. However, since no composition profiles were published by Horne and Mehl for the mentioned diffusion couples, the composition profile published by da Silva and Mehl [Sil51] for diffusion couples B35-I and B35-II within the same system at 784°C for 691 hrs⁹ was utilized for the purpose of comparison. In Figs. 4-33a and b, the simulated composition profiles (solid lines) are compared with those given in Figs. 15 and 16 of their paper (solid circles). The initial compositions of the two sides of the diffusion couple that were also used in the simulation were: 0 and 29.49 at pct, and 0 and 29.5 at pct for samples B35-I and II respectively. From Figs. 4-33, it is seen that the intrinsic diffusion coefficients of Horne and Mehl result in composition profiles that are reasonably close to the experiment ones. A more thorough comparison would be possible if the composition profiles from the incremental couples prepared by Horne and Mehl were available.

Fortunately, a comparison with the Kirkendall shifts and the Kirkendall plane compositions for the couples of Horne and Mehl as well as the two couples of da Silva and Mehl (B35-I & II) was possible as seen in Figs. 4-34a and b respectively. The experimental shifts reported by these authors included an estimate of the “range”, i.e., the estimated shift based on the expected deviation (less than ±½ mil where 1 mil = 25.4 µm) from the observed Kirkendall wire interface (see Table III of ref. [Hor55]). It is observed in Fig. 4-33a, that the predicted Kirkendall shifts are slightly higher than the experimental shift or the experimental shift ranges, especially for smaller Kirkendall

⁹ The time of the diffusion anneal given in Figs. 15 and 16 of their paper [Sil51] should be 691 hrs and not 289 hrs as reported. This is evident from Table III of their paper.
Figure 4-31. Binary Cu-Zn phase diagram [Mas90]. The fcc (Cu) phase extends up to approximately 31 at pct Zn from room temperature to over 900°C.

Figure 4-32. Intrinsic diffusion coefficients in the fcc phase of the Cu-Zn system at 780°C [Hor55]. The tracer diffusion coefficients of Cu and Zn in pure Cu are also shown (triangles) [Anu72].
Figure 4-33. Simulated composition profile (solid lines) obtained using the intrinsic diffusion coefficients at 780°C reported by Horne and Mehl [Hor55] as input. The solid circles in (a) and (b) are the data-points of da Silva and Mehl shown in their Figs. 16 and 15 [Sil51] respectively. (a) Diffusion couple B 35-II and (b) couple B 35-I of da Silva and Mehl
Figure 4-34. Comparison between experimental and predicted Kirkendall shifts and Kirkendall plane compositions. (a) Kirkendall shifts; (b) Kirkendall plane compositions. The experimental shifts were obtained from Horne and Mehl [Hor55] (all couples in their Table III) and da Silva and Mehl [Sil51] (couples B 35-I and II).
shifts. The agreement is better for larger Kirkendall shifts which correspond to longer diffusion times and diffusion couples containing higher Zn compositions (Table III of [Hor55]). In Fig. 4-33a, it is seen that for Kirkendall shifts beyond 60 µm, the predicted shifts fall between the experimental and experimental range shifts (the data-point near 100 µm is from da Silva and Mehl [Sil51]). This suggests, that the experimental intrinsic diffusion coefficients reported by Horne and Mehl, are not very accurate near lower Zn compositions, most likely on account of the errors associated with the measurement of smaller Kirkendall shifts in diffusion couples containing lower Zn compositions. It should also be noted, that unlike the case of the Ag-Cd system considered earlier, the intrinsic diffusion coefficient of Zn in pure Cu was higher than the tracer value (compare Fig. 4-32 with Fig. 4-3a). In spite of this, the predicted and measured Kirkendall plane compositions show excellent agreement as seen in Fig. 4-34b. Thus, with some caveats near the low Zn compositions, the simulation provides a reasonable confirmation of the accuracy of the intrinsic diffusion data reported.

4.6.5.2 Darken-Manning relations for Cu-Zn system

Well-documented tracer diffusion and thermodynamic data in this system are readily available. This permits an analysis of the Darken-Manning theories for this system.

Tracer diffusion. An exhaustive tracer diffusion study of the radioisotopes Cu\(^{67}\), Ni\(^{66}\) and Zn\(^{65}\) in the \(\alpha\)-fcc Cu-Ni-Zn system was conducted at the University of Florida in the mid 60's to early 70's [Deh66, Anu68, Anu72]. The final report, in which all the results of the tracer diffusion studies are available, is provided in the paper by Anusavice et al. [Anu72]. The Arrhenius parameters (see Eq. 4-88), i.e., the frequency factor and
Figure 4-35. Tracer diffusion coefficients of Cu and Zn as a function of 1/T. (a) Cu; (b) Zn. The solid lines are the Arrhenius plots from Anusavice et al. [Anu72], the dashed lines are from other authors. The data-points (circles) are from [Anu72]. The 780°C isotherms are also shown in the figures.
Figure 4-36. Tracer diffusion coefficients of Cu and Zn as a function of composition at 780°C. The polynomial functions (solid lines) were obtained by fitting the data-points (triangles) which were in turn obtained from the Arrhenius functions of Anusavice et al. [Anu72].

the activation energy, that are given in Tables VIII, IX and X of reference [Anu72] for various compositions within the ternary system, were used to obtain a semi-log plot of $D^*_{Cu}$ and $D^*_{Zn}$ against the reciprocal temperature ($1/T$), see Figs. 4-35a and b. The experimental data-points obtained by these authors as well as some others [Kup54, Hin57] at various temperatures are also recorded on the same plots. It is clear from these figures, that the Arrhenius parameters reported in [Anu72] adequately represent the tracer diffusion data in this system. Hence, these could be reliably used to obtain the tracer diffusivities at the desired temperature of 780°C for various compositions within the binary α Cu-Zn system. Using a non-linear, least-square regression analysis, smooth polynomial fits to the interpolated values were obtained as shown in Fig. 4-36. It is
evident that the Cu and Zn tracer diffusion coefficients increase significantly with increasing Zn composition in the α Cu-Zn binary at 780°C.

**Thermodynamics of Cu-Zn.** Kowalski and Spencer [Kow93] have made a complete re-evaluation of this system using the extensive thermodynamic data in the literature, and obtained optimized Gibbs excess free energy parameters (see Eq. (4-91)) for the various phases in this system. Their assessed parameters for the α-fcc Cu phase in the Cu-Zn system are

\[
L^0(T) = -42803.75 + 10.02258 \, T \\
L^1(T) = -2936.39 - 3.05323 \, T \\
L^2(T) = -9034.2 - 5.39314 \, T
\] (4-111)

Using Eqs. (4-94) to (4-97), the variation in the activity of Zn as a function of the Zn composition at 780°C is shown in Fig. 4-37a. A negative departure from ideality is apparent. From Eq. (4-110), the thermodynamic factor, Φ, is obtained and plotted in Fig. 4-37b as a function of the Zn composition. It is seen that Φ is greater than unity and increases with increasing Zn concentration and at the phase boundary near 0.32 at pct Zn, it is about 2.65.

**Darken-Manning relations in the α-fcc Cu-Zn.** Using the tracer diffusivities and the thermodynamic factor, the intrinsic diffusion coefficients were obtained using the Darken relations, Eqs. 4-48 and 49, and the Manning relations, Eqs. 4-77 and 78. These are compared with the experimental intrinsic diffusion coefficients in Fig. 4-38a and b. The vacancy flow terms that are needed to compute the intrinsic coefficients using the Manning relations are shown in Figs. 4-39a and b.
Figure 4-37. Thermodynamic data in the α-fcc Cu-Zn system at 780°C. (a) activity of Zn and (b) thermodynamic factor (Φ) as a function of Zn composition. The Gibbs excess free energy model was obtained from Kowlaski and Spencer [Kow93]. A negative departure from ideality as evident in (a) results in Φ values shown in (b) that are greater than unity.
Figure 4-38. Intrinsic diffusion coefficients predicted by the Darken (solid lines) and Manning theories (dashed lines). (a) Cu; (b) Zn. The circles are the intrinsic data from Horne and Mehl [55], the dotted lines are the tracer data from Anusavice et al. [Anu72].
Figure 4-39. Correction factors obtained from the Manning theory at 780°C. (a) $V_k$ and (b) $1 \pm V_k$. The vacancy flow factor for the faster diffusing component, Zn, is almost constant at unity, however that for the slower one, Cu, is smaller than unity and has a strong composition dependence.
Figure 4-40. Ratio of the experimental and predicted intrinsic diffusion coefficients from the Darken and Manning theories for (a) Cu and (b) Zn. The solid and dashed lines are the ratios obtained using the fitted functions for the experimental intrinsic diffusion data [Hor55], while the symbols are the ratios obtained using the experimental data.
Figure 4-41. Interdiffusion predictions from the Darken and Manning theories for the α-fcc Cu-Zn system at 780°C. (a) Interdiffusion coefficient; (b) ratio of the experimental and predicted interdiffusion coefficients.
Figure 4-42. The “S” correction factor for the interdiffusion coefficient given by the Manning theory. Since this is very close to unity, the effect of this correction on the interdiffusion coefficient predicted by the Darken theory is not significant (Fig. 4-41).

It is observed from Fig. 4-38a that the Cu intrinsic diffusion coefficient predicted from the Darken theory (solid line) gives a good match to the experimental value (circle) for compositions less than approximately 0.2 at pct Zn. Beyond this, the deviation between the predicted and experimental values is noticeable. It appears that with increasing Zn composition beyond 0.15 pct Zn, the predicted Darken coefficient for Cu is increasingly underestimated. The Manning correction (dashed line) does not help the situation and is in fact in the wrong direction, further reducing the predicted Cu intrinsic coefficient since the vacancy wind term for Cu is less than unity (Fig. 4-38b). In comparison, the intrinsic diffusion coefficient for Zn predicted by the Darken theory (Fig.
4-38b) is seen to be smaller than the experimental one through the entire composition range.

Another way of assessing the differences between the predicted and experimental values is by comparing the ratios of the experimental and predicted intrinsic diffusion coefficients. In Fig. 4-40a, it is seen that the ratio of the experimental and predicted intrinsic coefficient of Cu increases with increasing Zn composition beyond approximately 0.15 at pct Zn for both the Darken and Manning predictions. In case of Zn, the ratio increases with increasing Zn for the entire composition range for both the Darken and Manning predictions.

A comparison between the interdiffusion coefficient predicted from the Darken-Manning theories (see Eqs. 4-80) and the experimental one is shown in Figs. 4-41a and b. The trend is similar to that seen for the Zn intrinsic coefficient; the deviation between the experimental and predicted interdiffusion coefficient increases with increasing Zn. The Manning prediction is not very different from the Darken one; this is because the Manning correction factor (Eq. (4-81)) does not deviate significantly from unity within the range of compositions considered (Fig. 4-42).

The preferred way of assessing the Darken-Manning predictions is with the aid of the simulation. In Figs. 4-43a and b, the simulated composition profiles (solid lines) using the Darken and Manning predicted intrinsic diffusion coefficients respectively as input to the simulation, are shown. It is observed, that in comparison with the experimental data, the match is not very good. The composition profile (dashed line) obtained using the experimental intrinsic diffusion coefficients of Horne and Mehl [Hor55], shows a much better match (also in Fig. 4-33a). Since the interdiffusion
coefficients predicted by the Darken-Manning theories are not very different (Fig. 4-41a), the composition profiles shown in Fig. 4-43a and b are quite similar.\textsuperscript{10}

A more sensitive test of these theories can be provided by a comparison of the experimental and predicted Kirkendall shifts and Kirkendall plane compositions, Figs. 4-44a and b. Significant differences between the predicted and experimental Kirkendall shifts are seen especially for the larger shifts (beyond 60 µm). However, for smaller experimental shifts, the predicted values are quite reasonable with the Manning predictions being better. Since the larger experimental shifts correspond to couples containing the higher Zn compositions (0-30 pct Zn couple in Table III of [Hor55] and Table III of [Sil51]), this suggests that the differences between the experimental and predicted intrinsic diffusion coefficients are more significant for higher Zn compositions. For lower Zn compositions, as seen in Figs. 4-34 a, 4-44(a, b), the predicted shifts appear to be more accurate than the experimental ones. However, a conclusive statement regarding the experimental and predicted intrinsic diffusion coefficients at lower Zn compositions cannot be made, due to the inherent uncertainties in the experimental measurements of small Kirkendall shifts by Horne and Mehl. Unfortunately, composition profiles obtained from incremental diffusion couples having lower Zn compositions are also not available at the temperature of interest (780°C) to permit a comparison. Thus, while it is clear from the present analysis, that the Darken-Manning predictions are not accurate at higher Zn compositions, at lower compositions, it is possible that the predictions can be reasonable.

\textsuperscript{10} This follows from Fick’s second law, Eq. (4-3), or more directly from the Boltzmann-Matano analysis used for the determination of the interdiffusion coefficient, see Eq. (4-4).
Figure 4-43. Comparison between the experimental and predicted composition profiles (solid line) using (a) the intrinsic coefficients predicted by the Darken theory and (b) the Manning theory. The dashed line is the output obtained using the experimental intrinsic coefficients measured by Horne and Mehl [Hor55]. The data-points are for couple B 35-II of da Silva and Mehl (Fig. 16 of [Sil51]).
Figure 4-44. Comparison between the experimental and predicted Kirkendall shifts using (a) intrinsic coefficients predicted by the Darken theory and, (b) Manning theory as input to the simulation. The Kirkendall shifts obtained using the experimental intrinsic coefficients as input are shown in Fig. 4-34(a).
The comparison between the predicted and experimental Kirkendall plane compositions shown in Fig. 4-44b is as good as that obtained with the experimental intrinsic diffusion coefficients (Fig. 4-34b), thus suggesting that this test is not a conclusive one.

Conclusions regarding Darken-Manning theories for Cu-Zn. Figs. 4-43 and 4-44 that compare the predicted concentration profiles and Kirkendall shifts with the experimental measurements provide useful evidence regarding the Darken-Manning relations for this system. The predicted intrinsic diffusion and interdiffusion coefficients from these theories do not produce satisfactory fits to the experimental measurements over the full range of compositions within the single phase region. It is seen from Figs. 4-33 and 4-34a, that the experimental intrinsic diffusion coefficients are able to provide
concentration profiles and Kirkendall shifts that are reasonably close to the experimental measurements. Hence, the usual comparison between the experimental and predicted intrinsic diffusion coefficients from these theories shown in Figs. 4-38a and b, and Fig. 4-41a, is also a good test in this case. The ambiguity regarding the Darken-Manning relations at low Zn compositions can only be resolved with the aid of future experiments involving incremental diffusion couples having very fine Kirkendall markers (1-2 µm) in this composition range and at the current temperature of interest (780°C). A multiple marker or oblique marker experiment that provides lattice shift information, as in the case of the Au-Ni system (Figs. 4-18b and 4-27b), would be desirable for a better test of these theories.

4.6.6 Copper-Nickel (Cu-Ni) System

The α-fcc phase of the Cu-Ni system (Fig. 4-46) has been the subject of a number of intrinsic diffusion studies, yet a comprehensive test of the Darken-Manning relations for the entire range of compositions (0 - 100 at pct Ni) has not been carried out. The most comprehensive study is the one by Heumann and Grundhoff [Heu72], who used the multi-foil technique [Heu57] for the measurement of the lattice shifts and hence, the intrinsic diffusion coefficients at 800°C in this system. An external hydrostatic pressure was found to be necessary to prevent the formation of Kirkendall voids in the full-range diffusion couple used by these authors. Other intrinsic diffusion measurements in this system by Levasseur and Philibert [Lev67] and Iijima et al. [Iij82] suffered from this problem of Kirkendall porosity due to which the intrinsic diffusivities were overestimated; hence, these are not given the same importance in the present analysis.
The study by Damköhler and Heumann [Dam82] was limited to Cu rich compositions (less than 18 at pct Ni), their reported values are somewhat lower than those of Heumann and Grundhoff. In addition to the intrinsic diffusion data in this system, the tracer diffusivities [Mon64] as well as a recently assessed thermodynamic model for this system [Mey92], are also readily available. Thus all the essential information required for the analysis of the Darken-Manning relations in this system with the aid of the simulation, is available.

4.6.6.1 Examining self-consistency of experimental intrinsic data

The intrinsic diffusion data of Heumann and Grundhoff [Heu72], Levasseur and Philibert [Lev67] and Damköhler and Heumann [Dam82] are shown in Fig. 4-47. The Cu intrinsic diffusion coefficient of Levasseur and Philibert is larger than that of.
Heumann and Grundhoff for $X_{Ni}$ less than 0.5, while the Ni intrinsic diffusion coefficient is larger for $X_{Ni}$ greater than 0.4. Evidently, this deviation is on account of the Kirkendall porosity in the full-range diffusion couples of Levasseur and Philibert. The data of Iijima et al. [Iij82] that was affected by the same problem is not considered in this study. As noted earlier, Heumann and Grundhoff utilized an external hydrostatic pressure to prevent the formation of Kirkendall porosity in their samples, hence their data is given the higher priority in the assessment of the Darken-Manning theories. The measurements of Damköhler and Heumann were limited to Cu-rich compositions; their Cu intrinsic coefficient data are smaller than those of Heumann and Grundhoff at the corresponding compositions.

A smooth cubic polynomial function (thin dash-dot line in Fig. 4-47) was initially obtained by a regression analysis of the interdiffusion data (crosses) of Heumann and Grundhoff. This could not be reliably done in case of the intrinsic diffusion data of Heumann and Grundhoff, since the data is insufficient near the Ni-rich compositions, i.e., beyond $X_{Ni}$ of 0.7. Since it is has been experimentally found that the limiting values of the extrapolated intrinsic (impurity) diffusion coefficients near the pure compositions are approximately equal to the impurity tracer diffusion coefficients as well as to the interdiffusion coefficient $D'$, an extra data-point for $D_{Cu}$ was obtained by extrapolating the regressed function for the interdiffusion data to the pure Ni composition. A cubic polynomial function for $D_{Cu}$ was then obtained by a regression analysis of the Cu intrinsic data using this extra data-point at the pure Ni composition as a constraint on the regression parameters. In case of $D_{Ni}$, the same procedure could not be used, since it is known that the matrix diffusion coefficients can be noticeably different from their
respective tracer (or self-diffusion) coefficients at the limiting compositions (e.g., see Fig. 4-15 or [Heu83]). Thus, there was no choice but to use the available data to obtain a quadratic fit for $D_{Ni}$, a cubic fit on the other hand resulted in extremely low values of $D_{Ni}$ near the pure Ni composition (less than $10^{-12}$ cm$^2$/s) and was hence not used at the present time. These regressed functions for the intrinsic diffusion coefficients appeared to be satisfactory, since the interdiffusion coefficient obtained from these functions at various compositions using the Darken relation, Eq. (4-23), was found to be reasonably close to the experimental values of Heumann and Grundhoff (short-dashed line in Fig. 4-47). The intrinsic diffusion data of Levasseur and Philibert were found to be adequately represented by cubic polynomial functions and are also shown in the figure (long dashed lines), although as mentioned earlier were likely compromised due to Kirkendall porosity.

The intrinsic diffusion functions obtained from Heumann and Grundhoff, and Levasseur and Philibert were input to the simulation to obtain the time-invariant concentration profiles and lattice shifts at 1000°C. A constant molar volume of 6.85 cc/mol, that was obtained by averaging the partial molal volumes of Cu and Ni as determined by Anusavice et al. [Anu72], was used in the simulation. Typically, 2000-3000 iterations for a slice-width of 1 µm was found to be adequate to obtain stable, time-invariant outputs. In Fig. 4-48a, the concentration profiles for 150 h are compared with the experimental data given in Fig. 7 of Heumann and Grundhoff’s paper. Except near the pure Ni compositions, the simulated concentration profiles are in agreement with the experimental data. The simulated profile based on the Heumann and Grundhoff intrinsic data appears to be slightly better than the Levasseur and Philibert data. The steepness of
Figure 4-47. Intrinsic diffusion coefficients in the α-fcc Cu-Ni system at 800°C. The intrinsic diffusion coefficients shown are: triangles - Heumann and Grundhoff [Heu72]; diamonds - Levasseur and Philibert [Lev67]; and circles - Damköhler and Heumann [Dam82] for Cu-rich compositions. The squares are the tracer coefficients at the limiting compositions given by Monma et al. [Mon64]. Polynomial functions (solid and long-dashed lines) were used to fit the intrinsic data-points of both [Heu72] and [Lev67] respectively. The thin dash-dot line is the fit for the interdiffusion coefficient, \(D^i\) (crosses), measured by Heumann and Grundhoff. The short dash line is the interdiffusion coefficient obtained from the intrinsic diffusion functions using Darken’s relation.
Figure 4-48. Simulated concentration (150 h) and lattice shift profiles (55 h) at 1000°C obtained with the intrinsic diffusion coefficients of Heumann & Grundhoff (solid lines) and Levasseur & Philibert (dashed lines) as input. The concentration data-points in (a) were obtained from Fig. 7 of [Heu72] (circles); however for the lattice shifts in (b) only a continuous curve (dash-dot line) is plotted, since no data-points are actually shown on the measured lattice shift profile (Fig. 6 in [Heu72]). \( x_K^H \) is the Kirkendall shift for Heumann’s data and \( x_K^L \) for Levasseur’s data.
the experimental concentration data near the pure Ni composition, suggests that the Ni intrinsic diffusion coefficient is not very accurate near this composition and is likely to be much smaller. However, in the absence of experimental intrinsic data near the pure Ni composition, a further refinement of the regressed function for $D_{Ni}$ based on the Heumann and Grundhoff data, was not attempted.

In Fig. 4-48b, the lattice shift profiles at 55 h are compared with the experimental one (dash-dot line) given by Heumann and Grundhoff (Fig. 6 in [Heu72]). The maximum lattice shift, that also corresponds to the Kirkendall shift in the present case, was found to be well-represented by the Heumann data (solid line), but is clearly over-estimated by the Levasseur data (dash line), thus confirming the earlier observations regarding the effect of porosity on the intrinsic measurements. The width of the lattice profiles are not well-represented, especially near the Ni-rich side where the simulated shifts are smaller than the experimental ones. Near the Cu-rich side of the diffusion couple, the simulated shift based on the Heumann data is somewhat overestimated. The reasons for this are not clear, but it is suggested that errors in the intrinsic diffusion data and the corresponding regressed functions used in the simulation, particularly near the Ni-rich composition where no intrinsic data is available, are the likely source of the deviations. Nevertheless, the fact that the Kirkendall shift obtained using the Heumann and Grundhoff data in the simulation (35 µm) is quite close to the experimental one (37 µm), is encouraging.

4.6.6.2 Darken-Manning relations for Cu-Ni

Heumann and Grundhoff [Heu72] and Damköhler and Heumann [Dam82] attempted to examine the Darken-Manning relations by comparing the measured and
predicted intrinsic diffusion coefficients (or their ratios) at a few select compositions in this system using the prevailing thermodynamic data at that time. In this study, the entire range of compositions is examined for the Darken-Manning relations with the aid of the simulation using a recently assessed thermodynamic model for this system.

**Tracer diffusion.** The Cu$^{64}$ and Ni$^{63}$ tracer diffusion coefficients at 1000°C for the Cu-Ni system were obtained from the corresponding Arrhenius parameters of Monma *et al.* [Mon64], which are given in the reference by Askill [Ask70]. The tracer diffusion coefficients for Cu$^{67}$ and Ni$^{66}$ in Cu-rich Cu-Ni alloys were also measured by Anusavice *et al.* [Anu72]. From the Arrhenius parameters determined by these authors, the tracer diffusion coefficients at 1000°C were obtained. These are shown in Fig. 4-49. Note that Anusavice *et al.* [Anu68, Anu72] have confirmed that the minor difference between the atomic weights of isotopes of Cu and Ni yielded results of comparable accuracy. It should also be mentioned that one of the authors, Oikawa, was associated with both of the above tracer diffusion studies. It was hence decided to use the tracer diffusion data of both Monma *et al.* [Mon64] and Anusavice *et al.* [Anu72] for the purpose of obtaining a smooth fit by regression analysis. In Fig. 4-49, it is seen that while the Cu tracer coefficient is well-behaved, there is a notable inflection in the curve for the Ni tracer coefficient that is caused by the Ni tracer data-point at 0.55 $X_{Ni}$. Unfortunately, besides the work by Monma *et al.* [Mon64], no other tracer measurements near this composition appear to be available to confirm the data near this composition.

**Thermodynamics of Cu-Ni.** The thermodynamic assessment of this system by an Mey [Mey92] provided the excess free energy Redlich-Kister parameters for the $\alpha$-fcc phase. The parameters are
The resulting activity of Ni and the thermodynamic factor are shown in Figs. 4-50a and b respectively. In Fig. 4-50a, the activity plot shows a positive departure from ideality. The resulting thermodynamic factor, $\Phi$, shown in b is smaller than unity and has a minimum at approximately 0.55 $X_{Ni}$.

**Darken-Manning relations for Cu-Ni.** Using the tracer diffusivities for Cu and Ni, and the thermodynamic factor, the intrinsic diffusion coefficients for Cu and Ni were computed using the Darken-Manning relations, Eqs. 4-48 and 4-49. These are shown in

$$L^0(T) = 8047.72 + 1.29093 T$$

$$L^1(T) = -2041.3 + 0.99714 T$$

(4-112)
Fig. 4-51a and b respectively for Cu and Ni. The vacancy flow terms for the Manning relations are shown in Figs. 4-52a and b.

In Fig. 4-51a, it is seen that the Cu intrinsic diffusion coefficient predicted by the Darken theory is smaller than the experimental data of Heumann and Grundhoff for compositions greater than about 0.4 $X_{\text{Ni}}$. For compositions lower than this, the agreement is quite good except near the pure Ni composition, where it is again smaller than the experimental value. The Manning prediction follows a similar trend with a very small improvement, since the vacancy wind term for Cu see in Fig. 4-52b, is not very far from unity. In case of the Ni intrinsic diffusion coefficient, the Darken prediction seen in Fig. 4-51b, deviates from the experimental value beyond a composition of about 0.4 $X_{\text{Ni}}$. However, the Manning prediction seems to work reasonably well at these compositions. This can be traced to the vacancy wind term for Ni shown in Fig. 4-52b, which reduces markedly for Ni compositions greater than about 0.5.

In Fig. 4-53, the interdiffusion coefficient predicted from the Darken and Manning theories is compared with the experimental data of Heumann and Grundhoff. Beyond 0.4 $X_{\text{Ni}}$, the predicted values are smaller than the measurements. Since the correction factor, “S”, for the Manning theory (Fig. 4-54) is very close to unity throughout the composition range, the interdiffusion coefficient predicted by the Manning theory is not very different from the Darken one.

A better test of the Darken-Manning theories for this system is to compare the experimental and predicted composition and lattice shift profiles with the help of the simulation. In Fig. 4-55a, it is observed that the concentration profiles predicted using the Darken intrinsic diffusion coefficients as input are as good or somewhat better than
Figure 4-50. Thermodynamic data in the α-fcc Cu-Ni system at 1000°C [Mey92]. (a) Ni activity and (b) thermodynamic factor (Φ).
Figure 4-51. Intrinsic diffusion coefficients predicted by the Darken (solid lines) and Manning (dashed lines) theories for (a) Cu and (b) Ni at 1000°C in the Cu-Ni system.
Figure 4-52. Correction factors from the Manning theory at 1000°C: (a) $V_k$ and (b) $1 \pm V_k$. In (b), it is seen that the vacancy flow factor for the slower diffuser, Ni, reduces quite noticeably beyond about 0.5 $X_{Ni}$. 
Figure 4-53. Interdiffusion coefficient predicted from the Darken (solid line) and Manning (dashed line) theories.

Figure 4-54. The “S” correction factor for the interdiffusion coefficient given by the Manning theory.
Figure 4-55. Composition profiles (solid lines) using the predicted intrinsic diffusion coefficients as input to the simulation. (a) Darken; (b) Manning theory. The dashed line is the output from the intrinsic data of Heumann and Grundhoff [Heu72].
Figure 4-56. Lattice shift profiles (solid lines) using the predicted intrinsic diffusion coefficients as input to the simulation. (a) Darken; (b) Manning theory. The dash-dot line represents the data of Heumann and Grundhoff [Heu72].
those with the experimental intrinsic diffusion coefficients. The concentration profiles from the Manning prediction are not very different. The penetration depth near the pure Ni composition is slightly smaller, this can be seen in context with Fig. 4-53, where the interdiffusion coefficient predicted by the Darken-Manning theories is smaller than the experimental one for Ni-rich compositions. In order to have a better basis for the test, it would have been preferable to have available composition profiles from incremental diffusion couples in the range where the deviation between the predicted and experimental intrinsic and interdiffusion coefficients is large (X_{Ni} > 0.4). Unfortunately, such data does not appear to be available at the present time.

A comparison between the experimental and predicted lattice shift profiles is shown in Figs. 4-56a and b. The Manning prediction is much better than the Darken one, especially the Kirkendall shift. In comparison with the lattice profile obtained using the experimental intrinsic diffusion coefficients of Heumann and Grundhoff (Fig. 4-48b), the Manning prediction is much better for Cu-rich compositions than for Ni-rich compositions. Again, additional Kirkendall or lattice shift measurements from incremental couples having Ni-rich compositions would be useful for a more critical examination of the theoretical predictions.

**Conclusions regarding Darken-Manning relations for Cu-Ni.** From Fig. 4-51a, it was seen that the intrinsic diffusion coefficient of Cu predicted by the Darken theory was underestimated, while from Fig. 4-51b, that for Ni was overestimated. Since the lattice shift depends upon the difference between the intrinsic diffusion coefficients (Eq. 4-20), the lattice shift predicted from the Darken theory was underestimated (by approximately 15 \%) with respect to the experimental one (Fig. 4-56a). In case of the Manning
prediction, the Cu intrinsic diffusion coefficient was underestimated to a lesser extent than the Darken prediction (Fig. 4-51a), however the Ni intrinsic diffusion coefficient was very close to the experimental measurement. Nevertheless, the Kirkendall shift predicted by the Manning theory was reasonably accurate; however there was some deviation in the lattice shift profile for Ni-rich compositions (Fig. 4-56b). This deviation in the lattice shift profile, particularly for Ni-rich compositions, was also evident with the polynomial function used to fit the experimental intrinsic diffusion data of Heumann and Grundhoff (Fig. 4-48b). The lack of intrinsic diffusion data for Ni-rich compositions beyond 0.7 \( X_{\text{Ni}} \) was suggested as the likely cause of this deviation.

The concentration profiles predicted by the Darken-Manning theories were as good or even better (for Ni-rich compositions) than that predicted from the experimental intrinsic diffusion data (Fig. 4-55), most likely for the same reason. The lack of sufficient experimental composition data-points for Ni-rich compositions makes a detailed comparison between the concentration profiles difficult, given the apparent difference between the predicted and experimental interdiffusion coefficient (Fig. 4-53) at these compositions. A more systematic assessment of the Darken-Manning theories in this system can only be performed, if additional intrinsic measurements using incremental couples containing Ni-rich compositions, were available. Nevertheless, with the aid of the simulation, it is still possible to make a comparison between the output obtained using the experimental intrinsic diffusion coefficients and those from the Darken-Manning predictions for a theoretical diffusion couple that is Ni-rich, see Fig. 4-57. In Fig. 4-57a, the differences in the concentration profiles can be attributed to the differences in the interdiffusion coefficient (Fig. 4-53). Since the interdiffusion
Fig. 4-57. Output for a proposed diffusion couple that is Ni-rich. (a) Concentration and (b) lattice shift profiles. Differences between the experimental intrinsic and interdiffusion coefficients and those predicted by the Darken-Manning theories, evident in Figs. 4-51 and 4-53, are highlighted in the above figures.
coefficient obtained from the experimental intrinsic diffusion coefficients was shown to be reasonably close to the experimental interdiffusion data that was independently measured (see Fig. 4-47), the differences in the concentration profile in Fig. 4-57a have significance. However, the differences in the lattice shifts seen in Fig. 4-57b, which are primarily due to the differences in the intrinsic diffusion coefficients, cannot be seen in the same light due to the insufficient intrinsic diffusion data near the high Ni compositions.
CHAPTER 5
KINETIC FORMALISM FOR INTRINSIC DIFFUSION BASED ON ATOM JUMP FREQUENCIES

The discussion in Chapter 2 demonstrates, that the phenomenological formalism for diffusion in multicomponent systems in its unabridged form, is too cumbersome to be practical, and too abstruse to be physically meaningful. A simplification of the multicomponent phenomenological formalism in which the driving forces for diffusion are the chemical potentials, ignores the cross-terms in the matrix of phenomenological coefficients. This abridged version of the phenomenological formalism, first proposed by Darken [Dark49], later by Kirkaldy [Kir87] and currently being used in the DICTRA software [Bor00, Agr82], has never been verified in ternary or higher order systems with the aid of independent intrinsic diffusion measurements;¹ nevertheless, the development of multicomponent databases based on this simplification has proceeded [And92, Cam02]. In the absence of intrinsic diffusion experiments for the measurement of the phenomenological coefficients (or the mobilities, see Eq. (4-76)), the multicomponent version of the Darken theory that connects the tracer and the phenomenological coefficients, is often used, for example, in the DICTRA software. In Chapter 4, it was

¹ If the off-diagonal phenomenological coefficients are ignored, i.e., $L_{i,j}^K = 0$ ($i \neq j$), the diagonal coefficients, i.e., the $L_{i,i}^K$'s, can be independently determined for every composition in a ternary diffusion couple using multiple markers (see Appendix E) for the measurement of lattice velocities. A test of the above assumption is whether the measured phenomenological coefficients are a unique function of composition. This can be verified with the aid of intrinsic diffusion measurements at locations where the diffusion composition paths for independent diffusion couples cross.
demonstrated with the aid of the simulation, that the Darken relations, especially those for intrinsic diffusion, are not satisfactory even for the binary systems analyzed in the chapter. While a conclusive analysis of these relations has not been performed for any ternary system at the present time, the analysis carried out for binary systems in Chapter 4 suggests that they are unlikely to work in multicomponent systems as well. An alternate formalism for the description of multicomponent diffusion is hence proposed.

5.1 Jump Frequency Formalism

In parallel with the evolution of the phenomenological formalism, there has been a continuing development of kinetic descriptions of diffusion processes. This approach seeks to devise flux equations for the components beginning with the jump frequency of the atoms. Early applications of this point of view established connections between tracer diffusion coefficients and the jump frequency of the tracer atoms. These studies identified correlation effects in self diffusion for different crystalline lattices [Bar51, Lec56, Com57, Man59] and demonstrated the complexities of tracer diffusion behavior even in dilute binary and ternary alloys. Applications of these descriptions to concentrated binary alloys was aided with the use of a “random alloy model,” first discussed by Manning [Man68, Man70, Man71] and later by other authors [Heu79, Ali93, Bel97]. However, the utilization of these approaches requires a level of detailed

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2 A recent study conducted by Cserháti et al. [Cse01] has explored the validity of the assumption, \( L_{ij}^K = 0 \ (i \neq j) \), in the ternary Cu-Fe-Ni system, by computing the tracer diffusion coefficients from experimental interdiffusion data at crossing diffusion paths (thereby invoking the Darken theory) [Rön96]. They reported that the computed tracer coefficients showed large scatter and sometimes were negative in sign. This caused the authors to question the validity of the above assumption as well as the accuracy of their own interdiffusion measurements.
information about the system (e.g., tracer diffusion coefficients) that is rarely experimentally accessible, especially in multicomponent systems.

A version of this kinetic approach has been developed at the University of Florida, along with a simulation of diffusion behavior that permits modeling and prediction of patterns of behavior of the experimental observables [Isw93, Deh02]. Unlike previous kinetic approaches, no connection with the phenomenological formalism is attempted. This theory begins with the assumption that the jump frequencies of the components in a multicomponent diffusion process are functions only of the local thermodynamic state, (i.e., functions of composition in an isothermal system). This hypothesis is analogous to the assumption in the phenomenological approach that the individual diffusivities or mobilities are functions only of the local composition.

Consider two adjacent lattice planes, labeled 1 and 2, a distance \( \lambda \) apart; \( \lambda \) is the jump distance in the diffusion formulation, Figure 5-1. Define \( \Gamma_k \) to be the effective intrinsic jump frequency\(^3\) of atoms of component \( k \); in general \( \Gamma_k \) is a function of composition, and therefore position in the isothermal system. \( \Gamma_k \ dt \) is the average number of jumps made by an atom of component \( k \) in a time interval \( dt \). Let \( c_k \) be the molar concentration of atoms of component \( k \) on plane 1, and \( \Gamma_k \) their jump frequency. Approximate the variation of these quantities with position as continuous functions. Then their values on the two planes are

\(^3\) \( \Gamma_k \) is an effective jump frequency which includes any correlation effects that may operate in the lattice. The effective jump frequency \( \Gamma_k \) is smaller than the actual jump frequency \( \Gamma_k' \) because a fraction of vacancy exchanges will return the atom to its original site [Bar51, Com57, Man59]. Such jump combinations do not contribute to the permanent displacement of the atom. Information about these correlation effects is not accessible in an intrinsic diffusion experiment.
Figure 5-1. Schematic representation of two adjacent planes in a solid, emphasizing the difference in the concentration and jump frequency of a particular species upon each of the planes.

\[ c_k \text{ (plane 1)} \]  \[ \text{and} \]  \[ c_k + \lambda \frac{dc_k}{dx} \text{ (plane 2)} \]  \[ (5-1) \]

\[ \Gamma_k \text{ (plane 1)} \]  \[ \text{and} \]  \[ \Gamma_k + \lambda \frac{d\Gamma_k}{dx} \text{ (plane 2)} \]  \[ (5-2) \]

If the cross sectional area normal to the flow direction is \( dA \), the volume associated with each plane is \( \lambda dA \). The number of atoms of component \( k \) in the slab associated with planes 1 and 2 is respectively
\[ c_k \cdot \lambda \, dA \quad \text{and} \quad \left[ c_k + \lambda \frac{dc_k}{dx} \right] \cdot \lambda \, dA \] (5-3)

Since each atom of \( k \) makes, on the average, \( \Gamma_k \, dt \) jumps in time \( dt \), the total number of jumps made by atoms of \( k \) on plane 1 in time \( dt \) is

\[ c_k \cdot \lambda \, dA \cdot \Gamma_k \, dt \] (5-4)

Let \( f_{k+} \) be the fraction of these atoms jumps that take the atom of \( k \) to plane 2. The number of \( k \) atoms transferred from plane 1 to plane 2 in time \( dt \) is

\[ dn_{k,1 \rightarrow 2} = f_{k+} \, (c_k \lambda \, dA) \, (\Gamma_k \, dt) \] (5-5)

In an isotropic crystal, in the absence of bias effects in the jumping process, \( f_{k+} \) would be 1/6.

This analysis can also be applied to atoms on plane 2 that jump to plane 1 using values for composition and jump frequency for \( k \) on plane 2. Let \( f_{k-} \) be the fraction of these atoms jumps that take an atom of \( k \) from plane 1 to plane 0. Then \( (f_{k-} + \lambda \frac{df_{k-}}{dx}) \) is the fraction of the jumps from plane 2 to plane 1 in a manner similar to Eqs. (5-1) and (5-2). The total number of atoms of \( k \) on plane 2 that make a jump to plane 1 in time \( dt \) is

\[ dn_{k,2 \rightarrow 1} = \left( f_{k-} + \lambda \frac{df_{k-}}{dx} \right) \left[ c_k + \lambda \frac{dc_k}{dx} \right] \lambda \, dA \cdot \left( \Gamma_k + \lambda \frac{d\Gamma_k}{dx} \right) \, dt \] (5-6)

To obtain the net number of atoms of \( k \) that transferred from plane 1 to plane 2 in time \( dt \) subtract the number that jump from 2 to 1 from the number that jump from 1 to 2.

\[ dn_{k,net} = dn_{k,1 \rightarrow 2} - dn_{k,2 \rightarrow 1} \]

\[ dn_{k,net} = f_{k+} \, c_k \lambda \, dA \Gamma_k \, dt - \left( f_{k-} + \lambda \frac{df_{k-}}{dx} \right) \left[ c_k + \lambda \frac{dc_k}{dx} \right] \lambda \, dA \left( \Gamma_k + \lambda \frac{d\Gamma_k}{dx} \right) \, dt \] (5-7)
Multiply the factors on the right side of the equation and neglect the term involving $\lambda^3$, since it is very small. Collect terms and simplify:

$$dn_{k\text{net}} = \left[ (f_{k+} - f_{k-}) \lambda c_k \Gamma_k - \lambda^2 \frac{df_{k-} c_k \Gamma_k}{dx} \right] dA dt$$

(5-8)

The flux of component $k$ from plane 1 to plane 2 is the number of atoms transferred per unit area per unit time:

$$J_k = \frac{dn_{k\text{net}}}{dA dt} = (f_{k+} - f_{k-}) \lambda c_k \Gamma_k - \lambda^2 \frac{df_{k-} c_k \Gamma_k}{dx}$$

(5-9)

This is a kinetic equation for the intrinsic flux of component $k$ (as contrasted to a phenomenological equation). All of the terms in the equation have a defined physical meaning. Note that this equation applies to component $k$ no matter how many components there are in the system.

The first term in this equation contains the factor $(f_{k+} - f_{k-})$. If the jumps between plane 1 and plane 2 are not biased by the flow process, then $f_{k+} = f_{k-} = 1/6$, and the first term in Eq. (5-9) is zero. If this term is not zero, then influences are operating to produce a bias in the directions of jumps for atoms of component $k$.

Define the biases ($\alpha_k$) in the jump direction as the deviation of the fraction of jumps from the isotropic values of 1/6:

$$\alpha_{k+} = f_{k+} - \frac{1}{6} \quad and \quad \alpha_{k-} = f_{k-} - \frac{1}{6}$$

(5-10)

Hence, the fractions of jumps in each direction may be expressed as

$$f_{k+} = \frac{1}{6} + \alpha_{k+} \quad and \quad f_{k-} = \frac{1}{6} + \alpha_{k-}$$

(5-11)
On a given plane the fractions of jumps in all six direction sum to 1. If it is assumed that the bias in jumps in the direction of diffusion does not affect the jumps occurring perpendicular to the flow direction

$$1 = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} + \frac{1}{6} + f_{k^+} + f_{k^-} = \frac{2}{3} + \left( \frac{1}{6} + \alpha_{k^+} \right) + \left( \frac{1}{6} + \alpha_{k^-} \right)$$

(5-12)

This yields the result that

$$\alpha_{k^+} = - \alpha_{k^-}$$

(5-13)

This means that the deviation from the isotropic values for the fractions for jumps in the direction of the flux and against it are equal in magnitude and opposite in sign. The difference

$$f_{k^+} - f_{k^-} = \alpha_{k^+} - \alpha_{k^-} = \alpha_{k^+} - (- \alpha_{k^-}) = 2 \alpha_{k^+}$$

(5-14)

The sign and magnitude of $\alpha_{k^+}$ varies with position in a couple and is a different function for each component.

Using Eqs. (5-11), (5-12) and (5-14), the net diffusion flux given in Eq. (5-9) can be shown to be

$$J_k = 2 \alpha_{k^+} \lambda \Gamma_k - \frac{1}{6} \frac{dc_k \Gamma_k}{dx} + \lambda^2 \frac{d\alpha_{k^+} c_k \Gamma_k}{dx}$$

(5-15)

Since the net number of atoms transferred is a very small fraction of the total number of atoms that jump it may be argued that $\alpha_{k^+}$ is very small in comparison to $1/6$. The third term in Eq. (5-15) represents an incremental change in the product $\alpha_{k^+} c_k \Gamma_k$. Hence, for ordinary gradients in ordinary diffusion couples this term is expected to be very small in comparison with the first term and can be neglected. Thus, the net diffusion flux simplifies to
Accordingly, the first term in Eq. (5-16) may be defined as a \textit{biased component} to the intrinsic diffusion flux. Presumably, this bias is associated with the fact that there is a direction to the net flow of atoms in the system. This term may be written

\[ J_k^B = 2a_k \alpha c_k \Gamma_k \]  

(5-17)

The second term in Eq. (5-16) is

\[ J_k^U = -\frac{1}{6} \lambda^2 \frac{\partial^2 c_k \Gamma_k}{\partial x^2} \]  

(5-18)

This is the value of the intrinsic flux if the biased term is zero and may thus be defined as the \textit{unbiased contribution} to the intrinsic atom flux.

With these evaluations the total flux of component \( k \) may be rewritten

\[ J_k = J_k^B + J_k^U = 2a_k \lambda c_k \Gamma_k - \frac{1}{6} \lambda^2 \frac{\partial c_k \Gamma_k}{\partial x} \]  

(5-19)

\textbf{Features of the Kinetic Flux Equation.} The intrinsic flux expression, Eq. (5-19), is based upon a physical description of the atomic processes involved. The product \( (c_k \Gamma_k) \) has the units (jumps of \( k \) atoms per m\(^3\) per second) and may be visualized as the \textit{local concentration of atom jumps of \( k \) per second}. This yields the physically visualizable and plausible result that the unbiased flux component is determined by the gradient of the local concentration of atom jumps of \( k \) per second.

There is no phenomenological assumption in Eq. (5-19), i.e., flux proportional to a driving force (although neglecting the higher order terms in a series expansion is also regarded by some as a phenomenological assumption). This does not mean that Eq. (5-
19) violates the tenet of irreversible thermodynamics that states that each flux is
influenced by all of the driving forces (concentration or chemical potential gradients).
Because the jump frequency of component \( k \) depends upon all of the \((c-1)\) concentration
variables, the gradient term in Eq. (5-19) implicitly contains all of the concentration
gradients. It is likely that \( \alpha_{k+} \) also depends on the magnitudes of the flows in the system,
and thus all of the independent gradients.

Eq. (5-19) describes the flux of component \( k \) no matter how many other
components there are in the system. It is a flux equation that applies to multicomponent
systems.

The number of descriptors in this equation, \( \Gamma_k (c_k) \) and \( \alpha_{k+} \), is much smaller than
the \( \frac{1}{2} c(c-1) \) descriptors for the phenomenological equations of multicomponent
diffusion. However, this simplification is mitigated by the fact that the content of \( \alpha_k \) is
as yet unknown. In a sense, all of the complexity of the kinetic approach is contained in
\( \alpha_k \) in the biased term. The challenge posed by this formalism is to develop an
understanding of what influences operate to bias the jump direction of atoms, and how
these influences operate. Based on previous discussions [Man68], one might expect \( \alpha_{k+} \)
to be dependent on factors such as the vacancy flux or the chemical potential gradient.
An analytical expression for \( \alpha_{k+} \) has not been formulated at the present time, however a
computational procedure for determining the bias factor, \( \alpha_{k+} \), directly from experimental
information is discussed in a later section of this chapter, and has provided some useful
insights.

The above equation is similar to Manning’s equation (51) in ref. [Man65] or
equation (3) in ref. [Man89]. An important difference is in the derivation of the present
flux equation, where the jump frequency is assumed to be a continuous function of composition or distance. This allows the evaluation of $\Gamma_k$ on plane 2 ($v_2$ in Manning’s formulation) in terms of $\Gamma_k$ on plane 1 (or $v_1$), see Eq. (5-2). The most important difference however is in the definition of the unbiased flux, Eq. (5-18), which is not the same as that in the traditional Fickian formalism. This is further discussed in the next section.

5.2 Unbiased Intrinsic Flux

As a first approximation, the effective jump frequencies used in the kinetic flux expression, Eq. (5-19), are the tracer jump frequencies, which are related to the tracer diffusion coefficients:

$$\Gamma_k^* = \Gamma_k; \quad D_k^* = \frac{1}{6} \lambda^2 \Gamma_k^*$$ (5-20)

This assumes that transferring an atom from a homogenous system to a gradient system, does not alter its average effective jump frequency, but merely alters the fractions of the total number of jumps in the diffusion directions. The unbiased component of the intrinsic flux expression, Eq. (5-18), can be expressed in terms of the tracer diffusion coefficients using Eq. (5-20):

$$J_k^U = -\frac{1}{6} \lambda^2 \frac{\partial c_k \Gamma_k^*}{\partial x} = -\frac{\partial c_k D_k^*}{\partial x}$$ (5-21)

which can be expanded as

$$J_k^U = -D_k \frac{\partial c_k}{\partial x} - c_k \frac{\partial D_k^*}{\partial x}$$ (5-22)
assuming the jump distance, $\lambda$, to be constant. It is seen that the conventional notion of the unbiased flux contained in Fick’s formalism contains only the first term

$$J_{k, \text{Fick}}^U = -D_k \frac{\partial c_k}{\partial x}$$  \hspace{1cm} (5-23)

In the present definition of the unbiased flux, Eq. (5-22), there is an additional term associated with the gradient of the tracer diffusivity. It is thus of some interest to explore the extent to which these definitions of the unbiased components of the intrinsic diffusion fluxes contribute to the overall diffusion process in the absence of the biased components of the fluxes. The binary fcc Cu-Zn and the ternary fcc Cu-Ni-Zn systems are chosen for the purpose of this comparison.

5.2.1 Cu-Zn

The tracer diffusion coefficients in fcc Cu-Zn system at 780°C were earlier examined in Chapter 4 (Fig. 4-36). The effective tracer jump frequencies were computed from them using Eq. (5-20). The unbiased intrinsic fluxes given by the jump frequency formalism, Eq. (5-21), and Fick’s formalism, Eq. (5-23), were used in the simulation to obtain the composition profiles for couple B35-II, that was used by da Silva and Mehl [Sil51]. In Fig. 5-1a, it is seen that neither of the formalisms are able to accurately predict the experimental composition profile. However, the unbiased jump frequency formalism appears to be better. In Fig. 5-1b, the experimental Kirkendall shifts for the diffusion couples of Horne and Mehl [Hor55] are compared with those obtained using the two formalisms. It is clear that the unbiased jump frequency formalism significantly overestimates, while Fick’s formalism underestimates the Kirkendall shifts. Thus,
Figure 5-2. Comparison between the unbiased jump frequency and Fick’s formalisms in the α fcc Cu-Zn system at 780°C. (a) Composition profile for couple B35-II of Silva and Mehl [Sil51] and (b) Kirkendall shifts for the diffusion couples of Horne and Mehl [Hor55]. $\Gamma_k^*$ and $D_k^*$ are the effective tracer jump frequency and the tracer diffusivity of component $k$ that are used in the two unbiased formalisms.
neither of the unbiased formalisms provides an adequate representation of the interdiffusion process in this system.

5.2.2 Cu-Ni-Zn

The fcc Cu-Ni-Zn system is perhaps the only system for which extensive tracer diffusion information is available. The tracer diffusion coefficients of Cu$^{67}$, Ni$^{66}$ and Zn$^{65}$ isotopes have been measured by Anusavice et al. [Anu72] at a number of temperatures ranging from approximately 800-1100°C. From the Arrhenius tracer diffusion parameters for various alloys within the fcc phase of this ternary, the tracer diffusion coefficients at 900°C were obtained. Using non-linear regression analysis for this data, the authors obtained polynomial functions for the tracer diffusion coefficients. These are as follows:

\[
\log_{10} D_{Zn}^{*} = -3.20 X_{Ni} + 5.21 X_{Zn}^{1.25} - 9.00 \\
\log_{10} D_{Cu}^{*} = -3.53 X_{Ni}^{1.16} + 3.60 X_{Zn}^{1.02} - 9.46 \\
\log_{10} D_{Ni}^{*} = -4.05 X_{Ni}^{1.30} + 3.28 X_{Zn}^{1.07} - 9.96
\] (5-24)

In their paper [Anu72], the authors demonstrated the validity of this fit by comparing with the experimental tracer data along the binary Cu-Zn and Cu-Ni sides and also plotted these functions in ternary composition space. It was found that the ratio of the tracer diffusivities was about the same at any specified composition, and is given by

\[D_{Zn}^{*}:D_{Cu}^{*}:D_{Ni}^{*} = 9:3:1.\]

All the tracer diffusivities were found to be highest in binary, high Zn alloys, and lowest in binary, high Ni alloys. The range of diffusivities between these two extremes varied by over two orders in magnitude for each tracer, thus demonstrating the strong composition dependence of the tracer diffusion coefficients.

This is evident in Fig. 5-3, where the tracer diffusion function for Cu is plotted in ternary
Figure 5-3. Tracer diffusion coefficient of Cu for the ternary Cu-Ni-Zn system at 900°C [Anu72].

space using an interpolating mesh. Similarly, plots for the other components may also be obtained.

In Fig. 5-4, the diffusion composition paths for the two unbiased versions in this system at 900°C were obtained with the aid of the simulation. In comparison with the experimental composition paths of Wan [Wan73] in Fig. 5-5a, it is seen that the
unbiased jump frequency approach is able to reproduce the undulations and patterns in the composition paths fairly well, see Fig. 5-5b. The composition paths obtained using the unbiased Fick’s approach, shown in Fig. 5-5c, do not appear to be show the extreme undulations evident in the experimental paths, especially for those that originate on the binary Cu-Ni side and end on the binary Cu-Zn side of the ternary system. The predicted Kirkendall shifts for the unbiased jump frequency model were again overestimated in comparison with Wan’s experimental measurements, usually be a factor of two but the
signs of the shifts were in right direction. In case of the unbiased Fick’s approach, the signs of Kirkendall shifts were often in the wrong direction and their magnitudes were considerably underestimated as in the binary Cu-Zn case. Obviously this formalism cannot be practically applied, hence a quantitative comparison is not attempted in the present discussion.

5.3 Biased Intrinsic Flux

The previous discussion concerning the unbiased tracer jump frequency formalism demonstrates that the bias terms need to be incorporated in the formalism in order to have an adequate representation of both the concentration and lattice shift profiles. The evaluation of the bias term is discussed in this section.

Evaluation of the Bias Factor from Experimental Intrinsic and Tracer Data. It has been shown that the total intrinsic flux, $J_k$, can be evaluated without simplifying assumptions from the intrinsic diffusivities, or, more directly from the experimental evaluation of the interdiffusion fluxes and lattice velocity distribution, see Eqs. (2-3, 2-5). The unbiased term in Eq. (5-19) may be evaluated in the simulation from tracer jump frequencies using Eq. (5-21). The biased term may then be evaluated from this experimental information by subtracting the unbiased term from the total flux as shown:

$$J_k^B = J_k - J_k^U$$  \hspace{1cm} (5-25)

The bias factor, $\alpha_k$, is hence given by

$$\alpha_k = \frac{J_k - J_k^U}{2 \lambda_c \Gamma_k^*}$$  \hspace{1cm} (5-26)

Thus with the input of the tracer and intrinsic diffusion coefficients, the behavior of the biased contribution to the flux, $J_k^B$, can be explored in the system. Since the other
factors in the expression for $J_k^B$ are known, this permits a direct focus on the experimental
determination of the content of the bias factor, $\alpha_{k^+}$. Eq. (5-26), can be directly
implemented in the simulation to compute the bias factor for component $k$, for any
system in which tracer and intrinsic diffusion information is available.

**Bias Factor in $\alpha$-fcc Cu-Zn.** Total, biased and unbiased components of the
intrinsic flux for a couple in the Cu-Zn system, computed by implementing this
procedure, are shown in Fig. 5-5. It is clear that the biased component of the flux cannot
be neglected in describing the behavior of the system: $J_k^B$ is a significant fraction of $J_k$
throughout the diffusion zone. Composition profiles for this couple are shown in Fig. 5-6a and the computed bias factors in Fig. 5-6b. It is quite interesting that the signs of the
biased factors for the two components, $\alpha_{1^+}$ and $\alpha_{2^+}$, are opposite in this case (Fig. 5-6b),
their magnitudes are different and extremely small (less than approx. $10^{-6}$) in comparison
with the fraction of isotropic jumps ($1/6$). These observations imply that the bias cannot
be explained simply as an effect due to the directed total flow of atoms or the

The decomposition of the intrinsic flux into a biased and unbiased component
provided by the kinetic formalism has the potential to provide a new level of insight into
the physical influences involved in diffusion in multicomponent systems. These effects
are just beginning to be explored. Other systems, such as the Au-Ni system, are to be
considered in future studies.
Figure 5-5. Total, biased and unbiased components of the intrinsic flux for a diffusion couple in the Cu-Zn system. (a) Cu, (b) Zn
Figure 5-6. Composition profiles and bias factors for the diffusion couple in the Cu-Zn system obtained from the biased fluxes shown in Fig. 5-5. (a) Composition profiles; (b) bias factors.
5.4 Unbiased Intrinsic Flux Using Effective Jump Frequencies

In contrast with this rigorous analysis of the bias terms in the complete jump frequency formalism, some success has been attained in describing patterns of diffusion behavior in ternary systems by using a simplified version of the kinetic flux equation in which the biased term is neglected [Isw93]. Fig. 5-2 demonstrates that this is a bad assumption in the rigorous treatment of even binary systems if the jump frequencies are computed from tracer data. It is apparent from Fig. 5-2b that the predicted Kirkendall shifts are significantly higher than the experimental ones. If the requirement that the input jump frequencies are the tracer jump frequencies is relaxed so that the input jump frequency surfaces over the Gibbs triangle are allowed to be modeled unconstrained by tracer information, then models have been devised that provide a reasonable explanation of most of the experimental observables in some ternary systems.

It is unlikely that full information about the pattern of tracer diffusion coefficients will be explored in ternary systems other than Cu-Ni-Zn. This model approach sacrifices the rigor of the full kinetic equation for a practical version that can be made to work. If the biased term is neglected, Eq. (5-19) becomes

\[ J_k = -\frac{1}{6} \lambda \frac{\partial c_k \Gamma_k}{\partial x} \]  (5-27)

Given a set of functions describing the composition dependence of the jump frequencies, \( \Gamma_k(X_k) \), the simulation may be used to compute intrinsic fluxes as a function of position for any assumed initial couple. The experimental observables, i.e., composition distributions, composition paths and Kirkendall shifts, may be evaluated from this information and compared with observed patterns.
These jump frequency functions may be developed on the basis of an informed trial-and-error iteration by comparing patterns of composition paths with those obtained for a collection of such models. Two examples of this approach are given: the Fe-Ni-Co and the Fe-C-Si systems.

5.4.1 Effective Jump Frequency Model for Fe-Ni-Co

The diffusion paths in the Fe-Ni-Co system at 1315°C have been determined by Vignes and Sabatier [Vig69b]. By observing patterns in the composition paths, DeHoff and Iswaran [Isw93] were able to devise a simple composition dependent, jump frequency model for this system. Fig. 5-7 compares the pattern of composition paths derived from applying the simulation (a) with that observed experimentally (b) using the simple jump frequency model given in (c). All of the simulated composition paths have the same shape as the experimentally observed ones. In most cases the computed compositions are within a few atomic per cent of the experimental ones.

5.4.2 Darken’s “Uphill Diffusion” Experiment

The effective jump frequency approach can also be applied to devise a model to explain the behavior observed in the Fe - C - Si. This textbook example for “uphill diffusion”, due to Darken [Dark49], examines the composition profile produced in a couple that places an Fe - 0.441% C alloy against a ternary Fe - 0.478 C - 3.8% Si alloy. Although the carbon content is essentially the same on both sides of the couple it is found that carbon atoms significantly redistribute during diffusion, producing the profile shown in Fig. 5-8 (solid circles). Carbon flows out of the silicon rich side, where its concentration is reduced, and into the silicon free side where its concentration increases. Thus there is a range of composition for which the carbon atoms flow from low carbon
content to high, up its concentration gradient. This observation was explained on the basis of the effect of silicon additions on the chemical potential of carbon in this system. The activity of carbon increases with silicon content. Thus the flow of carbon from the high silicon side of this ternary couple to the low silicon side is a flow down the chemical potential gradient of carbon, consistent with the mobility form of the phenomenological equations.

This behavior can also be reproduced by constructing a jump frequency model in which the jump frequency of carbon atoms increases with silicon content, and applying Eq. (5-27). Fig. 5-8 shows the composition profile produced by this approach. This more physical explanation of the observation immediately invites additional questions regarding the effect of silicon on the jump frequency of carbon atoms.

This modeling approach results in a workable description of the experimentally observed pattern of intrinsic diffusion in a ternary system on the basis of a formalism that has physical meaning. The data base is a set of jump frequency values and their composition and temperature dependence. The operation of the governing Eq. (5-27) is easy to visualize. The approach can be extended easily to quaternary and higher order systems.

The trouble is, in order to invoke this approach it is necessary to ignore the results of the more rigorous analysis that recognizes that the jump frequencies are those obtained from tracer experiments, and that a significant component of the intrinsic flux derives from a physical bias in the jump directions of the components with respect to the flow direction. Implementation of the formalism without assumptions provides a new opportunity to explore the patterns of behavior of the biased contribution to the intrinsic
Figure 5-7. Composition paths and jump frequency model for the Fe-Co-Ni system. (a) Comparison of simulated and (b) experimental composition paths in the Fe-Co-Ni system [Vig69b]. (b) The jump frequency model employed for this simulation [Isw93].
Figure 5-8. Simulation (solid line) of Darken’s experiment [Dark49] demonstrating uphill diffusion of carbon in \( \gamma \) iron at 1050°C using a jump frequency model for carbon that is a function of the silicon concentration, \( \Gamma_C = (16X_{\text{Si}} + 1) \times 10^9 \), \( \Gamma_{\text{Fe}} = \Gamma_{\text{Si}} = 10^6 \text{ sec}^{-1} \). The open circles represent concentrations from Darken’s experiment. The simulated concentration profile was obtained by multiplying the normalized concentration profile (512 iterations) with the square root of the annealing time (13 days).

flux and perhaps gain a new level of insight into the influences that are important in the diffusion process. Implementation of the formalism with empirically derived jump frequency models provides a practical avenue for predicting diffusion behavior in multicomponent systems.

5.4.3 Evaluation of Effective Jump Frequencies from Intrinsic Data

The jump frequency functions in the previous approach may be developed on the basis of an informed trial-and-error iteration by comparing patterns of composition paths with those obtained for a collection of such models. Alternatively, jump frequency
functions may be obtained by inverting Eq. (5-27) and integrating the result:

$$d (c_k \Gamma_k) = -\frac{6}{\lambda^2} J_k(x) \, dx$$

$$[c_k \Gamma_k(x)] - [c_k \Gamma_k] = -\frac{6}{\lambda^2} \int_{x_1}^{x_2} J_k(x) \, dx$$  \hspace{1cm} (5-28)

The integrand is the intrinsic flux of component $k$ determined experimentally from a distributed marker experiment. The second term on the left side of this equation is the value of the $c_k\Gamma_k$ product at the left end of the couple. If $c_k$ is chosen to be zero, or if $\Gamma_k$ has been determined previously, $\Gamma_k$ can be determine as a function of composition for the set of compositions that exist in the couple.

Eq. (5-28) can be easily applied to determine the jump frequencies of all components in a multicomponent system, if the intrinsic fluxes are known. The test of this version of the simulation can be performed with the aid of two or more independent diffusion couples in a ternary system, that have a common crossing point in the composition paths. Eq. (5-28) can be applied to each diffusion couple and the jump frequencies at the common crossing composition can be compared. If the jump frequencies are truly a unique function of the local composition, the values at the common intersecting compositions should be equal. If this test is validated, this formalism can be utilized for constructing diffusion databases in multicomponent systems from knowledge of the intrinsic fluxes, which can be measured using the oblique marker technique discussed in Appendix E.
CHAPTER 6
CONCLUSIONS AND FUTURE WORK

Conclusions

The development of an intrinsic diffusion simulation, and its application for the assessment of the Darken-Manning and Jump Frequency formalisms were the major focus of this work. Initially, considerable effort was spent in testing the robustness of the simulation with the aid of model systems having constant and variable molar volumes. A systematic procedure for testing these relations was utilized to test the Darken-Manning relations in four binary systems. Based on this work, it was found that these relations when taken in their entirety are not satisfactory for the four systems tested in this work. Of specific mention are the tests for the Au-Ni and Cu-Zn systems, which demonstrated that the intrinsic diffusion coefficients predicted from the Darken theory resulted in lattice shifts that are significantly different from the experimental values.

As an alternative to the phenomenological formalisms and their problems, which were also highlighted, a jump frequency formalism was proposed. The unbiased and biased components of the intrinsic flux in this formalism were examined. A novel procedure for evaluating the bias terms was demonstrated with the aid of the simulation. An unbiased version of this formalism based on effective jump frequencies was shown to be quite successful in modeling diffusion in ternary systems, including Darken’s “uphill diffusion” experiment in Fe-C-Si. An oblique marker technique for measuring lattice velocities and hence intrinsic fluxes was discussed (Appendix E). A method for
computing the effective jump frequencies from these fluxes was proposed, and if validated, offers the potential of developing multicomponent diffusion databases which are physical meaningful and easy to comprehend.

**Specific accomplishments.** The results and accomplishments from the three major chapters (3, 4 and 5) of this dissertation are summarized below.

A. **Intrinsic simulation (Chapter 3, Appendix A-D).**

1. A computer code for modeling intrinsic diffusion was developed using the MathCad software. This was based on the algorithm originally developed by Iswaran [Isw93] in TurboPascal. A significant improvement in this algorithm was achieved with the inclusion of molar volume effects. This was instrumental in tackling the complexities of diffusion in various reference frames, which were discussed in some detail in the appendices. The various steps in the simulation were described in Chapter 3 with clarity and rigor. Because of the generic treatment of the diffusion process in this simulation, it can be utilized for diffusion studies in liquid and gaseous systems as well.

2. Significant effort was spent in the understanding the complexities of diffusion in different reference frames, since this was of direct relevance to the diffusion modeling effort. The treatments of this topic in the literature were synthesized and presented in a concise fashion in Appendix A-D. Some of the derivations (e.g., in Appendix D) do not appear to be readily available in the literature; hence it is hoped that the clarity shown in these derivations will be useful.

3. The self-consistency and robustness of the simulation was successfully demonstrated with the aid of intrinsic model systems which had constant and variable molar volumes. It should be noted that the present approach for modeling intrinsic
diffusion is based on invoking the intrinsic flux equation. Because of this, the modeling was significantly simplified, the problem of handling different reference frames was easily handled within the body of the simulation, for e.g., in the variable molar volume model, and there are no mass balance errors. In contrast, previous modeling efforts in the literature are based on the solution of the conservation equation (Fick’s second law), which are handled in the laboratory frame of reference. Hence, the conversion to the other frames, including the lattice frame, requires additional computation efforts, which have not been explored with the aid of model systems as in the present study.

B. Darken-Manning relations (Chapter 4). The procedure for analyzing the Darken-Manning relations (Fig. 4-2) was successfully utilized for the tests in four binary systems discussed below.

1. In the Ag-Cd system, the predicted intrinsic diffusion coefficient of Ag was smaller than the experimental one for most of the composition range, while that for Cd was smaller for high Cd compositions (Fig. 4-9). As a result, the predicted concentration profiles (Fig. 4-11) and Kirkendall shifts (Fig. 4-12) were notably different from the experimental ones, specially near high Cd compositions.

2. In the Au-Ni system, the problem was with the predicted Au intrinsic diffusion coefficient for Au-rich compositions (Fig. 4-24). In fact, the Darken prediction was in the wrong direction in this composition range. The Ni intrinsic diffusion coefficient was well predicted for the entire composition range. Because of the problem with the Au intrinsic diffusion coefficient, the resultant lattice shift profile was noticeably different from the experimental one for the full-range diffusion couple considered in the comparison (Fig. 4-27b).
3. In the Cu-Zn system, the predicted Zn intrinsic diffusion coefficient was significantly smaller than the experimental one, while that for Cu deviated from the experimental one for high Zn compositions (Fig. 4-38). As a result, both the concentration profiles (Fig. 4-43) and Kirkendall shifts (Fig. 4-44) showed large differences in comparison with the experimental data.

4. In the Cu-Ni system, the Ni intrinsic diffusion coefficient predicted by the Manning theory appeared to be much better than the Darken prediction, especially for Ni-rich compositions (Fig. 4-51). That for Cu was smaller than the experimental data for compositions greater than 0.4 $X_{Ni}$ for both the Darken and Manning predictions. The predicted interdiffusion coefficients were underestimated in comparison with the experimental one for Ni-rich compositions (Fig. 4-53). In spite of these differences, the predicted concentration (Fig. 4-55) and lattice shift profiles (Fig. 4-56) for the full-range diffusion were quite good, especially the Manning prediction. However, the above differences became apparent when a theoretical Ni-rich incremental diffusion couple was examined for the concentration and lattice shift profiles (Fig. 4-57).

C. Jump frequency formalism (Chapter 5).

1. A kinetic expression for the intrinsic flux in terms of the effective jump frequencies was derived, taking into consideration the bias in atomic jumps. An explicit separation of the intrinsic flux into the biased and unbiased components was obtained. Special features of the formalism were discussed.

2. The unbiased term of the jump frequency formalism using the tracer jump frequency was compared with the traditional Fick’s version of the unbiased term using the tracer diffusion coefficient for the Cu-Zn system. It was found that the former
overestimated and the later underestimated the Kirkendall shifts in this system. For the ternary Cu-Ni-Zn system, it was found that the unbiased tracer jump frequency formalism gave a very good representation of the experimental composition paths, even though the Kirkendall shifts were not accurate; however the unbiased Fick formalism was not able to reproduce the pattern in the composition paths and the Kirkendall shifts were not accurate either.

3. A novel procedure to directly compute the bias terms from the experimental intrinsic fluxes and the unbiased tracer jump frequencies with the aid of the simulation was applied to the Cu-Zn system. It was found that the bias factors for Cu and Zn were very small (smaller than $10^{-6}$) and had opposite signs and different magnitudes.

4. An unbiased version of the jump frequency formalism, in which effective jump frequency models were constructed using “informed trial-and-error methods” was found to provide a good representation of the composition paths in the Fe-Ni-Co and the Fe-C-Si (Darken’s “uphill diffusion experiment”) systems.

5. A procedure to compute these effective jump frequencies in the unbiased jump frequency formalism from experimental interdiffusion and intrinsic data, obtained using the oblique interface marker technique (discussed in Appendix E) was proposed as a practical way of building jump frequency models in multicomponent systems with minimal effort.

Recommendations for Future Work. The common theme that arises throughout the course of this work is the need for intrinsic diffusion measurements both in binary and ternary systems. The oblique marker technique is recommended for this purpose and its development using the procedure laid out in Appendix E is suggested. Such
measurements, especially those in ternary systems, are needed to assess the various phenomenological formalisms as well as the effective jump frequency formalism discussed in this work. While problems with the Darken-Manning formalisms in binary systems were found in this investigation, definitive tests in ternary systems are sorely lacking. The Cu-Ni-Zn system is one system in which very good tracer diffusion and interdiffusion data is available; a recent thermodynamic model from the ADAMIS database developed by Prof. Ishida’s group has also become recently available. Thus, if intrinsic diffusion data were to become available using the procedure outlined in Appendix E or any other procedure, all the available diffusion formalisms in the literature can be assessed once and for all. This is sorely needed at the present time, since considerable efforts are currently underway for developing diffusion databases using simplified versions of the phenomenological formalism, which may be compromised if the underlying assumptions are found to be incorrect.

While the unbiased version of the effective jump frequency formalism has shown some success in ternary systems, future experiments in ternary systems are needed for validation. In case this approach does not work, the bias terms in the complete formalism become central to the future development, and hence should be the subject of future analysis. The work by Manning and others should be useful in this context. The use of Monte-Carlo and other approaches based on first principles is strongly recommended as an aid towards understanding the fundamental diffusion processes and the physical content of the bias terms. Such approaches are particularly useful in analyzing diffusion mechanisms in intermetallic or ceramic systems.
The logical step in advancing the simulation is in multiphase systems, where the complexities are many. Even in binary multi-phase systems, there can be significant complications, most notably in thin films, due to issues related to nucleation, stress, finite boundary conditions and grain boundary effects. Significant innovation and expertise will be needed to include all these effects within a multi-purpose simulation. Almost certainly, the ability to interface thermodynamic and diffusion databases seamlessly will be required; such capability is already becoming available, although the purists might well prefer to develop their own codes. For ternary or multicomponent, multiphase systems, the general diffusion problem is three dimensional and hence a three dimensional version of the simulation appears necessary. The phase-field method is becoming increasingly popular for modeling microstrucutral evolution on a very fine scale. Some of the concepts involved in this method may find useful application in classical diffusion modeling, and are indeed currently being explored.
APPENDIX A
FRAMES OF REFERENCE

Diffusion fluxes and forces and hence diffusion coefficients or other kinetic descriptors of diffusion are measured with respect to a frame of reference. Normally in case of semi-infinite diffusion couples, it is customary to choose one end of the sample as the reference point from which all subsequent measurements are measured. This frame of reference is commonly referred to as the “laboratory frame of reference” and can be arbitrarily selected by the observer as any fixed point with reference to which the diffusion measurements can be made. However it can be shown that if there are molar volume changes during the course of the diffusion process, the laboratory frames selected by different observers of the same diffusion experiment may result in different values of the diffusion coefficients. Hence it is necessary to select appropriate reference frames with respect to which the values of the diffusion coefficients and fluxes are invariant. In general, different applications may require different reference frames for the measurements and therefore it is desirable to know the relationships between the various reference frames and establish standard procedures for the conversions.

The following treatment is based on earlier discussions in the diffusion literature [Phi91, Haa69, Bra75, Gro62, Kir60, Mil86]. Let $R^o$ be defined as the laboratory frame of reference, i.e., a frame of reference selected by the observer. If $c_k$ is the concentration of component $k$ in moles/cc and $v_k^{R^o}$, the velocity of the local centroid of atoms in cm/s, then the local flux of atoms of $k$, $J_k^{R^o}$, in the laboratory frame is given by
The superscript “o” is often used to denote the laboratory frame of reference in place of the full notation $R^o$.

Since $v_k^{R^o}$ is a vector, the flux of atoms of $k$ is also a vector and has the same direction as that of $v_k^{R^o}$. However since the present work focuses on diffusion in one direction only, the vector notation is omitted. The local flux of component $k$ is defined to be the number of moles of $k$ that flow across an area in the system per cm$^2$ per second. In order to define a frame of reference $R$ that is independent of the laboratory frame of reference chosen by the observer, an average reference velocity $v^{RR^o}$ of the components participating in the diffusion process is first defined:

$$v^{RR^o} = \sum_{k=1}^{c} \omega_k^R v_k^{R^o}$$  \hspace{1cm} (A-2)

The above equation came be written in a simpler notation as

$$v^R = \sum_{k=1}^{c} \omega_k^R v_k^{R^o}$$  \hspace{1cm} (A-3)

where $v^R \equiv v^{RR^o}$

$\omega_k^R$ is a weighting factor in the R frame given by

$$\sum_{k=1}^{c} \omega_k^R = 1$$  \hspace{1cm} (A-4)

The total number of components in the system is given by $c$, for example, in a binary system $c = 2$ and for a ternary $c = 3$. The average reference velocities are always defined
with respect to the laboratory frame of reference, hence the subscript $R_0$ is omitted. The diffusion velocity $v_k^R$ of component $k$ is defined with respect to the reference velocity:

$$v_k^R = v_k^{R_0} - v^R$$  \hspace{1cm} (A-5)

and the diffusion flux of $k$ is given by

$$J_k^R = c_k v_k^R = c_k (v_k^{R_0} - v^R)$$  \hspace{1cm} (A-6)

Using Eq. (A-1) the above relation can also be written as

$$J_k^R = c_k (v_k^{R_0} - v^R) = J_k^{R_0} - c_k v^R$$  \hspace{1cm} (A-7)

It can be shown using Eqs.(A-3 to A-7), that the diffusion fluxes defined using an average velocity are not independent and the relation between the fluxes is of the form

$$\sum_{k=1}^{c} \frac{\omega_k^R J_k^R}{c_k} = 0$$  \hspace{1cm} (A-8)

 Following Kirkwood [Kir60], it can be shown using Eq. (A-7) that the fluxes are converted from one frame to another using the relation

$$J_k^R = J_k^Q + c_k v^{QR}$$  \hspace{1cm} (A-9)

where

$$v^{QR} = v^Q - v^R = v^{QR} - v^{RR}$$  \hspace{1cm} (A-10)

Multiplying both sides of Eq. (A-9) by $\frac{\omega_k^R}{c_k}$ and summing over the components:
Using Eqs. (A-8) and (A-4) this simplifies to

\[ 0 = \sum_{k=1}^{c} \omega^R_k \frac{J^Q_k}{c_k} + v^{QR} \]  

(A-12)

Hence an expression for \( v^{QR} \) can be obtained.

\[ v^{QR} = -\sum_{k=1}^{c} \omega^R_k \frac{J^Q_k}{c_k} \]  

(A-13)

Substituting Eq. (A-13) in Eq. (A-9):

\[ J^R_k = J^Q_k - c_k \sum_{j=1}^{c} \frac{\omega^R_j J^Q_j}{c_j} \]  

(A-14)

Eq. (A-14) is a convenient expression for converting between fluxes in different reference frames.

**Mean molar frame of reference or Number-fixed frame \( \mathbf{R}^N \)**

The weighting factor in this frame is given by

\[ \omega^N_k = X_k = c_k V \]  

(A-15)

where \( X_k \) is the mole fraction of component \( k \) and \( V \) is the molar volume in cc/mole.

From Eq. (A-8) it is seen that

\[ \sum_{k=1}^{c} \frac{X_k J^N_k}{c_k} = 0 \]  

(A-16)

This simplifies to

\[ \sum_{k=1}^{c} \frac{X_k J^N_k}{X_k} \frac{X_k}{V} = 0 \]  

\( (c_k = \frac{X_k}{V}) \)  

(A-17)
\[ \sum_{k=1}^{c} J_k^N = 0 \]  \hspace{1cm} (A-18)

Hence the molar weighted fluxes sum to zero. This means that in a binary system the molar weighted fluxes are equal and opposite in sign.

Similarly the mean molar velocity \( v^N \) is given by

\[ v^N = \sum_{k=1}^{c} X_k v_k^o \]  \hspace{1cm} (A-19)

A relation between \( v^N \) and the interdiffusion fluxes in the lab frame can be obtained as follows:

\[ J_k^N = c_k (v_k^o - v^N) = J_k^o - c_k v^N \]  \hspace{1cm} (A-20)

Summing both sides over the number of components in the system and using Eq. (A-18)

\[ \sum_{k=1}^{c} J_k^N = \sum_{k=1}^{c} J_k^o - v^N \sum_{k=1}^{c} c_k \]

\[ 0 = \sum_{k=1}^{c} J_k^o - \frac{1}{V} v^N \left( \sum_{k=1}^{c} c_k = C = \frac{1}{V} \right) \]  \hspace{1cm} (A-21)

Hence the molar weighted average velocity is given by

\[ v^N = V \sum_{k=1}^{c} J_k^o \]  \hspace{1cm} (A-22)

Thus the fluxes in the lab frame do not sum to zero unless \( v^N \) is zero. It will be later shown that this is true only if the partial molal volumes are constant and equal to each other, hence the volume of the system is constant throughout the diffusion zone.
\( v^N = 0 \)  
\[ \text{if } \bar{V}_1 = \bar{V}_2 = \bar{V}_k = V_k^o = V \]  

(A-23)

where \( V_k^o \) is the molar volume of pure component \( k \) which is equal to its partial molal volume if it is constant.

Substituting for \( v^N \) from Eq. (A-22) in Eq. (A-20) an expression for the number weighted flux in terms of the lab fluxes is obtained with no assumptions.

\[
J_k^N = J_k^o - c_k V \sum_{j=1}^c J_j^o = J_k^o - X_k \sum_{j=1}^c J_j^o
\]  

(A-24)

The above relation between the fluxes in the number and lab frames of reference can also be directly obtained using Eq. (14).

**Mean volume or Fickian frame of reference \( R^V \)**

The weighting factor in this frame is the volume fraction of component \( k \):

\[
\omega_k^V = c_k \bar{V}_k = \frac{X_k}{V} \bar{V}_k
\]  

(A-25)

From Eqs. (A-8) and (A-25)

\[
\sum_{k=1}^c \frac{c_k \bar{V}_k J_k^V}{c_k} = 0
\]  

(A-26)

The relation between the volume weighted fluxes is

\[
\sum_{k=1}^c \bar{V}_k J_k^V = 0
\]  

(A-27)

Thus in a binary system, unlike the molar weighted fluxes, the volume weighted fluxes are *not* equal and opposite in sign. By defining \( J_k^{vV} = \bar{V}_k J_k^V \) an alternate definition of
the volume weighted flux is obtained with units of cc/cm²-s and for which \( \sum_{k=1}^{c} J_k^V = 0 \).

While this definition may be convenient for liquid systems, for the sake of consistency of units and terminology, the original definition (Eq. (A-7)) in which the weighted flux is defined in units of mol/cm²-s is to be followed throughout this manuscript.

The diffusion flux in the volume frame is given by

\[
J_k^V = c_k (v_k^o - \nu^V) = J_k^o - c_k \nu^V
\]  

(A-28)

and the volume weighted average velocity can be shown to be

\[
\nu^V = \sum_{k=1}^{c} \bar{V}_k J_k^o
\]  

(A-29)

Substituting for \( \nu^V \) in Eq. (A-28) an expression for the volume weighted flux in terms of the lab fluxes is obtained with no assumptions.

\[
J_k^V = J_k^o - c_k \sum_{j=1}^{c} \bar{V}_j J_j^o
\]  

(A-30)

From Eqs. (A-28) and (A-29) it is seen that the volume and lab frame fluxes become equal only if the volume weighted average velocity is zero. It will be later shown that this is true only if the partial molal volumes are constant (but not necessarily equal) and hence equal to the molar volumes of the pure components. This necessarily means that the volume of the system is a linear function of composition (Vegard’s law for ideal mixing) and that the overall volume of the system is conserved. This follows from the fact that since atoms are conserved and the volume of each atom (or mole of atoms) is constant, the total volume of the system is also necessarily conserved.
\[ \mathbf{v} \cdot \mathbf{V} = 0 \]
\[ \text{if } \overline{V}_k = V_k^o \]  \hspace{1cm} (A-31)

The condition that \( \mathbf{v} \cdot \mathbf{V} = 0 \) does not necessarily imply that \( \mathbf{v} \cdot \mathbf{N} = 0 \). However the reverse situation is always true, i.e., if \( \mathbf{v} \cdot \mathbf{N} = 0 \) then \( \mathbf{v} \cdot \mathbf{V} = 0 \). In many solid-state systems, the assumption of constant partial molal volumes implying that \( \mathbf{v} \cdot \mathbf{V} = 0 \) is found to be a reasonable one. In case of diffusion in liquid systems that are constrained in a container, the overall volume is fixed and again \( \mathbf{v} \cdot \mathbf{V} = 0 \). Hence the volume frame of reference is the one most commonly used in diffusion studies since if \( \mathbf{v} \cdot \mathbf{V} = 0 \), the volume diffusion fluxes are equal to the lab frame fluxes which can be directly measured from experiment. Indeed the original laws of diffusion proposed by Adolf Fick [Fic55] refer to this frame of reference. The mean volume velocity is considered to be practically identical to the “convective velocity” of the system and hence the condition \( \mathbf{v} \cdot \mathbf{V} = 0 \) corresponds to the absence of convection according to the experimenter [Haa69].

In contrast the average velocity in the number frame \( \mathbf{v} \cdot \mathbf{N} \), cannot be assumed to be negligible in some solid state systems (indeed in many liquid systems) where partial molal volumes can vary by significant amounts. For example, in the fcc Cu-Ni-Zn system at 900°C [Anu72], it has been shown that the approximation that the partial molal volumes are equal to the molar volumes of the pure components is reasonable, however the individual molar volumes vary by significant amounts (approx. 30% between Cu and Zn).

\[ \overline{V}_{Cu} = 7.09, \quad \overline{V}_{Ni} = 6.6, \quad \overline{V}_{Zn} = 8.47 \]  \hspace{1cm} (A-32)

\[ V_{Cu}^o = 7.09, \quad V_{Ni}^o = 6.59, \quad V_{Zn}^o = 9.17 \quad (\text{in } \text{cc/mole}) \]
Excepting for Zn, the partial molal volumes are virtually identical to the molar volumes of the pure components. Since the maximum amount of zinc in the fcc phase at 900°C is about 30%, the difference between the partial molal and molar volume of zinc is reflected as a deviation from ideal mixing primarily in the metastable region of the fcc phase near the zinc corner. Hence $v' = 0$, is still a valid approximation in the stable region.

In practice, errors in diffusion measurements for single phase solid systems are usually comparable or higher than the errors involved in assuming that $v'$ and $v^n$ are negligible [Loo90a]. Hence molar volume effects on solid-state diffusion are generally ignored in the literature although the additional effort involves only the measurement of molar volume (through density or lattice parameter measurements) or the partial molal volumes as a function of composition. $v^n$ can be determined from knowledge of the lab flux and $V$ (Eq. (A-22)), however $v'$ requires the additional determination of the partial molal volumes from the derivatives of the volume change on mixing as a function of composition, which can be rather inaccurate. This can be difficult to perform especially for “line compounds”, since data regarding the lattice parameter or density as a function of composition is often not available and experiments are difficult to perform. In such cases, measurements in the number frame are to be preferred.

Mean mass or barycentric frame of reference $R^M$

The weighting factor in this frame is the mass fraction of component $k$ which is given by:

---

1 In practice, a so-called line compound has a range of compositions over which it can exist, however the range is often too small to be measured using conventional techniques, such as the electron microprobe, for measuring composition.
\[ \omega_k^M = \frac{\rho_k}{\rho} = \frac{M_k c_k}{\rho} = \frac{M_k X_k}{M} \]  \hspace{1cm} (A-33)

where \( \rho_k = M_k c_k = \frac{M_k X_k}{V} \) and \( \rho = \frac{M}{V} \)

\( M_k \) is the molar weight of component \( k \) and \( M \) the molar mass of the solution in g/mol; \( \rho_k \) is the local mass density and \( \rho \) the mass density of the solution in g/mol.

From Eqs. (A-8) and (A-33)

\[ \sum_{k=1}^{c} \frac{M_k c_k}{\rho} \frac{J_k^M}{c_k} = 0 \]  \hspace{1cm} (A-34)

Hence the relation between the mass weighted fluxes is

\[ \sum_{k=1}^{c} M_k J_k^M = 0 \]  \hspace{1cm} (A-35)

The diffusion flux in the mass frame is given by

\[ J_k^M = c_k (v_k^o - v^M) = J_k^o - c_k v^M \]  \hspace{1cm} (A-36)

The mass weighted average velocity is given by

\[ v^M = \frac{1}{\rho} \sum_{k=1}^{c} M_k J_k^o \]  \hspace{1cm} (A-37)

Substituting for \( v^M \) in Eq. (A-36) an expression for the mass weighted flux in terms of the lab fluxes is obtained with no assumptions.

\[ J_k^M = J_k^o - \frac{c_k}{\rho} \sum_{j=1}^{c} M_j J_j^o \]  \hspace{1cm} (A-38)
The solvent frame of reference is often used in liquid systems where diffusion of various components in a common solvent, that does not actively participate, is of interest.

The weighting factor in this frame is the Kronecker delta:

\[ \omega_k^S = \delta_{ks} \]

\[ \text{where } \delta_{ks} = 0 \text{ if } k \neq s, \quad \delta_{ks} = 1 \text{ if } k = s \]

From Eqs. (A-8) and (A-39)

\[ \sum_{k=1}^{c} \frac{\delta_{ks} J_k^S}{c_k} = 0 \]  

(A-40)

Hence in this frame, the flux of the component chosen as the solvent or the major constituent is zero.

\[ J_s^S = 0 \]  

(A-41)

The diffusion flux in the solvent frame is given by

\[ J_k^S = c_k (v_k^o - v^S) = J_k^o - c_k v^S \]  

(A-42)

By substituting for \( k = s \) in Eq. (A-42) and noting Eq. (A-41), it is seen that the solvent weighted average velocity is simply the velocity of component \( s \) in the lab frame.

\[ v^S = \frac{J_s^o}{c_s} = \frac{c_s v_s^o}{c_s} = v_s^o \]  

(A-43)

Substituting for \( v^S \) in Eq. (42) an expression for the solvent weighted flux in terms of the lab fluxes is obtained with no assumptions.

\[ J_k^S = J_k^o - \frac{c_k}{c_s} J_s^o \]  

(A-44)
Lattice, inert marker or Kirkendall frame of reference $R^K$

This frame is fixed to inert markers or lattice planes that moves due to an imbalance in the net flux of all the components. It is not connected to an average velocity of components as in the earlier cases but rather to the velocity of inert markers or lattice planes (in case of crystalline solid). The flux of $k$ in this frame is referred to as the “intrinsic flux” by Hartley and Crank [Har49] and Darken [Dar48] and is given by

$$J_k^K = c_k (v_k^o - v^K) = J_k^o - c_k v^K$$  \hspace{1cm} (A-45)

Summing both sides over $k$ and noting the relation between the lab fluxes and $v^N$ (Eq. (A-22)):

$$\sum_{j=1}^{c} J_k^K = \sum_{j=1}^{c} J_k^o - v^K \sum_{j=1}^{c} c_k$$  \hspace{1cm} (A-46)

$$\sum_{j=1}^{c} J_k^K = \frac{v^N}{V} - \frac{v^K}{V} = \frac{v^N - v^K}{V} = \frac{v^{NK}}{V}$$  \hspace{1cm} (A-47)

where $v^N \equiv V \sum_{k=1}^{c} J_k^o$

Hence the velocity in the K frame is given by

$$v^{KN} = -V \sum_{j=1}^{c} J_k^K$$  \hspace{1cm} (A-48)

The same relation can also be obtained by first writing an expression for the flux in this frame with respect to the flux in the number frame.

$$J_k^K = J_k^N + c_k v^{NK}$$  \hspace{1cm} (A-49)
Summing both sides and noting that the sum of the number weighted fluxes is zero, Eq. (A-47) is again obtained.

$$\sum_{j=1}^{c} J_k^K = \sum_{j=1}^{c} J_k^N + v^{nk} \sum_{k=1}^{c} c_k = 0 + v^{nk} C = \frac{v^{nk}}{V} \quad (A-50)$$

Thus unlike the fluxes in the previous frames, there is no relation between the fluxes in the Kirkendall or lattice frame. However in crystalline systems, it is still possible to formulate an approach based on an average velocity by considering the flux of vacancies in addition to the primary component fluxes such that:

$$\sum_{j=1}^{c} J_k^K + J_v^K = 0 \quad (A-51)$$

Hence the binary system can now be considered as a ternary with vacancies being the third constituent. $v^K$ can now be regarded as an average velocity taken over lattice sites and can be related to the vacancy flux using Eqs. (A-48) and (A-51):

$$J_v^K = -\sum_{j=1}^{c} J_k^K = \frac{v^{kn}}{V} = C v^{kn} \quad (A-52)$$

Hence the intrinsic flux Eq. (A-49) can be expressed in terms of the vacancy flux:

$$J_k^K = J_k^N + c_k \left( \frac{J_v^K}{V} \right) = J_k^N - X_k J_v^K \quad (A-53)$$
APPENDIX B
THERMODYNAMIC RELATIONS FOR DIFFUSION ANALYSIS

A number of thermodynamic relations are utilized throughout the course of this work. While some of these are well-known and recognized, a few are not so common and hence their derivations are discussed in some detail. Since an important focus of the present work is the analysis of the Darken-Manning relations for binary systems, the relations are presented for binary systems containing components A and B.

\[ X_A \bar{V}_A + X_B \bar{V}_B = V \]  \hspace{1cm} (B-1)

where \( X_A \) and \( X_B \) are the mole fractions and \( \bar{V}_A \) and \( \bar{V}_B \) are the partial molal volumes (in cc/mole) of components A and B respectively. \( V \) is the molar volume of the solution in cc/mole.

The relations between the mole fractions are

\[ X_A + X_B = 1 \]  \hspace{1cm} (B-2)
\[ dX_A + dX_B = 0 \]  \hspace{1cm} (B-3)

By virtue of the Gibbs-Duhem relation at constant temperature and pressure:

\[ X_A d\bar{V}_A + X_B d\bar{V}_B = 0 \]  \hspace{1cm} (B-4)

The concentration is defined in units of mol/cc:

\[ c_A = \frac{X_A}{V}, \quad c_B = \frac{X_B}{V}, \quad c_A + c_B = \frac{1}{V} = C \]  \hspace{1cm} (B-5)

Dividing Eq. (B-4) by \( V \):
\[ c_A \bar{d}V_A + c_B \bar{d}V_B = 0 \]  
(B-6)

Taking the differentials of Eq. (B-1) and using Eq. (B-4):

\[ \bar{V}_A \bar{d}X_A + \bar{V}_B \bar{d}X_B = dV \]  
(B-7)

Dividing Eq. (B-1) by \( V \):

\[ \frac{X_A}{V} \bar{V}_A + \frac{X_B}{V} \bar{V}_B = 1 \]  
(B-8)

\[ c_A \bar{V}_A + c_B \bar{V}_B = 1 \]

Differentiating Eq. (B-8) and noting Eq. (B-6):

\[ \bar{V}_A \bar{d}C_A + \bar{V}_B \bar{d}C_B = 0 \]  
(B-9)

A relation between the differentials of concentration and mole fraction can be obtained as shown:

\[ dc_k = d \left( \frac{X_k}{V} \right) \]  
(B-10)

\[ dc_k = \frac{1}{V} dX_k - \frac{X_k}{V^2} dV = \frac{1}{V} dX_k - \frac{X_k}{V^2} \left( \sum_{k=1}^{c} \bar{V}_k dX_k \right) \]  
(B-11)

Simplifying

\[ dc_k = \frac{\left( \sum_{k=1}^{c} \bar{V}_k X_k \right) dX_k - X_k \left( \sum_{k=1}^{c} \bar{V}_k dX_k \right)}{V^2} \]  
(B-12)

For a binary, the above relation can be simplified to give

\[ dc_A = \frac{\bar{V}_B dX_A}{V^2}, \quad dc_B = \frac{\bar{V}_A dX_B}{V^2} \]  
(B-13)

Earlier from Appendix A, Eq. (A-33) the mass fraction of component \( k \) was defined as
\( \omega_k^M = \frac{\rho_k}{\rho} = \frac{M_k c_k}{\rho} = \frac{M_k X_k}{M} \)  

(B-14)

where \( \rho_k = M_k c_k = \frac{M_k X_k}{V} \) and \( \rho = \frac{M}{V} \)

\( M_k \) is the molar weight of component \( k \) and \( M \) the molar mass of the solution in g/mol; \( \rho_k \) is the local mass density and \( \rho \) the mass density of the solution in g/mol.

A relation between \( d \omega_k^M \) and \( dc_k \) can be obtained by differentiating Eq. (B-14):

\[ d \omega_k^M = d \left( \frac{M_k c_k}{\rho} \right) \]

(B-15)

The final result for a binary is

\[ d \omega_A^M = \frac{M_A M_B}{V_B \rho^2} dc_A \]

\[ d \omega_B^M = \frac{M_A M_B}{V_A \rho^2} dc_B \]

(B-16)
APPENDIX C
DIFFUSION COEFFICIENTS IN DIFFERENT FRAMES OF REFERENCE

The multicomponent version of Fick’s first law [Kir87, Mil86] can be stated as

\[ J_i^R = -\sum_{j=1}^{n-1} \hat{D}_{i,j}^{R,n} \left( \frac{\partial c_j}{\partial x} \right)_{P,T,t,c_m} \quad (i = 1,2,...,n) \]  

(C-1)

where \( n \) is the total number of components in the system, \( P \) is the pressure, \( T \) is the temperature, \( t \) is the time in seconds, \( c_j \) is the concentration of component \( j \) in cc/mole, \( x \) is the distance in cm and \( J_i^R \) is the flux of component \( i \) in mol/cm²-s. The flux \( J_i^R \) is defined with respect to the frame of reference \( R \) that has been earlier discussed in Appendix A. One among the total \( n \) fluxes is a dependent flux by virtue of the relation between the fluxes in the frame of reference (Eq. (A-8)). The multicomponent version of Fick’s law states that at any time, the flux of component \( i \) is proportional to each of the independent concentration gradients in the system. One among the total \( n \) concentrations is not independent by virtue of the Gibbs-Duhem relation (Eq. (A9)). The concentration of component \( n \) is taken to be the dependent one in Eq. (C-1). The diffusion coefficient above, depends on the frame of reference \( R \) as well as the choice of the dependent concentration variable, here the concentration of component \( n \).

The original Fick’s law was formulated for binary systems and can be expressed as

\[ J_k^V = -\hat{D}^V \left( \frac{\partial c_k}{\partial x} \right) \quad (k = 1,2) \]  

(C-2)
It turns out that this equation, that suggests a unique diffusion coefficient \( D^V \), is only applicable if the flux is defined in the volume reference frame. For other component velocity averaged reference frames (but not the lattice frame \( R^K \)), it can be shown that the fluxes can still be described in terms of this same unique diffusion coefficient only if appropriate units of concentration (rather than \( c_k \) in Eq. (C-2)) are used. This form of Fick’s first law for binary systems first suggested by De Groot [Gro62] is

\[
J^R_k = -D^V \left( 1 - \frac{\omega_k^R}{1 - X_k} \right) \left( \frac{\partial X_k}{\partial x} \right) \quad (k = 1, 2)
\]  

(C-3)

where \( \omega_k^R \) is a weighting factor for the R frame (see Appendix A) and \( X_k \), the mole fraction of component k. Clearly if the concentration variables are left unaltered, for example \( c_k \) as in Eq. (C-2), the diffusion coefficients in different reference frames will have different values even in the binary case. Hence Eq. (C-3), in which the fluxes are expressed in terms of a single diffusion coefficient, is preferred.

**Fick’s first law for the volume frame of reference \( R^V \)**

Fick’s law in this frame is

\[
J^V_k = -\tilde{D}_k^V \left( \frac{\partial c_k}{\partial x} \right) \quad (k = 1, 2)
\]  

(C-4)

Let A and B are the two components in this system. Then Eq. (C-4) can be written as

\[
J^V_A = -\tilde{D}_A^V \left( \frac{\partial c_A}{\partial x} \right), \quad J^V_B = -\tilde{D}_B^V \left( \frac{\partial c_B}{\partial x} \right)
\]  

(C-5)

By virtue of the relation between the volume weighted fluxes Eq. (A-27):

\[
\bar{V}_A J^V_A + \bar{V}_B J^V_B = 0
\]  

(C-6)

Substituting for the fluxes defined in Eq. (C-5) into Eq. (C-6):
Using Eq. (B-9), the above equation becomes

\[
\bar{V}_A(-\hat{D}_A^V \frac{\partial c_A}{\partial x}) + \bar{V}_B(-\hat{D}_B^V \frac{\partial c_B}{\partial x}) = 0
\]  
\hspace{1cm} (C-7)

Rearranging terms

\[
\bar{V}_A \frac{\partial c_A}{\partial x} (\hat{D}_B^V - \hat{D}_A^V) = 0
\]  
\hspace{1cm} (C-8)

Hence for binary systems, there exists a single diffusion coefficient in the volume frame:

\[
\hat{D}_A^V = \hat{D}_B^V = \hat{D}^V
\]  
\hspace{1cm} (C-9)

No assumptions are involved in deriving Eq. (C-10).

**Fick’s first law for the laboratory frame of reference \( R^o \)**

The fluxes in the lab frame are given by

\[
J_A^o = -\hat{D}_A^o \left( \frac{\partial c_A}{\partial x} \right), \quad J_B^o = -\hat{D}_B^o \left( \frac{\partial c_B}{\partial x} \right)
\]  
\hspace{1cm} (C-10)

From Eq. (A-22) the sum of fluxes in the lab frame is related to the volume weighted velocity:

\[
v^V = \bar{V}_A J_A^o + \bar{V}_B J_B^o = \bar{V}_A (-\hat{D}_A^o \frac{\partial c_A}{\partial x}) + \bar{V}_B (-\hat{D}_B^o \frac{\partial c_B}{\partial x})
\]  
\hspace{1cm} (C-11)

Using Eq. (B-9) the above equation can be expressed in terms of the concentration gradient of A:

\[
v^V = -\bar{V}_A \hat{D}_A^o \frac{\partial c_A}{\partial x} - \bar{V}_B \hat{D}_B^o \left( \frac{\bar{V}_A}{V_B} \frac{\partial c_A}{\partial x} \right)
\]  
\hspace{1cm} (C-12)
or

\[ \nu^V = -\frac{\partial c_A}{\partial x} \bar{V}_A (\tilde{D}_A^o - \tilde{D}_B^o) \]  

(C-14)

It will be shown later that \( \nu^V = 0 \) if the partial molal volumes of A and B are constant and equal to the molar volumes of the pure components. Hence from Eqs. (C-14) and (A-28)

\[ \tilde{D}_A^o = \tilde{D}_B^o = \tilde{D}^o = \tilde{D}^V \quad \text{if} \quad \nu^V = 0 \quad (\bar{V}_A = V_A^o \text{ and } \bar{V}_B = V_B^o) \]  

(C-15)

Thus if \( \nu^V = 0 \), the diffusion coefficient measured in the lab frame (also known as the interdiffusion coefficient) is equal to the standard Fickian diffusion coefficient measured in the volume frame.

Fick’s first law for the number frame of reference \( \mathbb{R}^N \)

The fluxes in the number frame are given by

\[ J_A^N = -\tilde{D}_A^N \left( \frac{\partial c_A}{\partial x} \right), \quad J_B^N = -\tilde{D}_B^N \left( \frac{\partial c_B}{\partial x} \right) \]  

(C-16)

Since the sum of the fluxes in the number frame are zero from Eq. (A-18):

\[ \tilde{D}_A^N \frac{\partial c_A}{\partial x} + \tilde{D}_B^N \frac{\partial c_B}{\partial x} = 0 \]  

(C-17)

Expressing \( dc_B \) in terms of \( dc_A \) (Eq. (B-9))

\[ \tilde{D}_A^N \frac{\partial c_A}{\partial x} + \tilde{D}_B^N \left( -\frac{\bar{V}_A}{\bar{V}_B} \frac{\partial c_A}{\partial x} \right) = 0 \]  

(C-18)

Grouping terms

\[ \frac{\partial c_A}{\partial x} \left( \bar{V}_B \tilde{D}_A^N - \bar{V}_A \tilde{D}_B^N \right) = 0 \]  

(C-19)
It can be shown that if the partial molal volumes of A and B are equal to each other and constant, the number weighted average velocity \( \nu^N = 0 \). From Eqs. (C-19) and (A-20) it follows that:

\[
\tilde{D}^N_A = \tilde{D}^N_B = \tilde{D}^N = \tilde{D}^V \quad \text{if} \quad \nu^N = 0 \quad (\overline{V}_A = \overline{V}_B = V)
\]  

(C-20)

However in general the number weighted diffusion coefficients defined by Eq. (C-16) are not equal to each other. In order to retain the same value of the diffusion coefficient \( D^V \) in the number frame without any assumptions, it seems necessary to alter the definition of Fick’s law for this frame. To arrive at a suitable form (rather than use Eq. (C-3) directly), first consider the relation between the number and volume weighted fluxes:

\[
J^N_k = J^V_k + c_k \nu^{VN}
\]  

(C-21)

Noting that the sum of the number weighted fluxes is zero,

\[
\nu^{VN} = -V \sum_{k=1}^{n} J^V_k
\]  

(C-22)

Hence Eq. (C-21) can be expressed as

\[
J^N_k = J^V_k + c_k(-V \sum_{k=1}^{n} J^V_k) = J^V_k - X_k \sum_{j=1}^{n} J^V_j
\]  

(C-23)

For component A in a binary the above equation becomes

\[
J^N_A = J^V_A - X_A(J^V_A + J^V_B)
\]  

(C-24)

Using Fick’s law for the definition of the fluxes in the volume frame (Eq. (C-5)) in Eq. (C-24):
\[
J_A^N = -\tilde{D}^V \frac{\partial c_A}{\partial x} - X_A ( -\tilde{D}^V \frac{\partial c_A}{\partial x} - \tilde{D}^V \frac{\partial c_B}{\partial x}) \quad (C-25)
\]

or

\[
J_A^N = -\tilde{D}^V (X_B \frac{\partial c_A}{\partial x} - X_A \frac{\partial c_B}{\partial x}) \quad (C-26)
\]

Using Eq. (B-13):

\[
J_A^N = -\tilde{D}^V [X_B (\frac{\bar{V}_B}{V^2} \frac{\partial X_A}{\partial x}) - X_A (\frac{\bar{V}_A}{V^2} \frac{\partial X_B}{\partial x})] = -\tilde{D}^V \frac{\partial X_A}{\partial x}(X_B \bar{V}_B + X_A \bar{V}_A) \quad (C-27)
\]

The term in brackets is the molar volume of the system, see Eq. (B-1). Hence

\[
J_A^N = -\frac{\tilde{D}^V}{V} \frac{\partial X_A}{\partial x} = -\tilde{D}^N \frac{\partial X_A}{\partial x} \quad (C-28)
\]

where

\[
\tilde{D}^N = \frac{\tilde{D}^V}{V} \quad (C-29)
\]

Similarly

\[
J_B^N = -\frac{\tilde{D}^V}{V} \frac{\partial X_B}{\partial x} = -\tilde{D}^N \frac{\partial X_B}{\partial x} \quad (C-30)
\]

Thus if the number weighted flux is expressed in terms of the gradient of the mole fraction, there is a single binary diffusion coefficient \(\tilde{D}^N\) which is related to Fickian diffusion coefficient \(\tilde{D}^V\) by Eq. (C-29). Eq. (C-30) can also be directly obtained from Eq. (C-3), however the procedure discussed above is more transparent.
An expression for $v^{VN}$ can also be obtained. From Eqs. (C-22) and (C-5):

$$v^{VN} = -V \sum_{k=1}^{n} J_k^V = -V (-\tilde{D}^V \frac{\partial c_A}{\partial x} - \tilde{D}^V \frac{\partial c_B}{\partial x})$$  \hspace{1cm} (C-31)

which by virtue of Eq. (B-5) simplifies to

$$v^{VN} = V \tilde{D}^V \frac{\partial (1/V)}{\partial x} = -\frac{\tilde{D}^V}{V} \frac{\partial V}{\partial x}$$  \hspace{1cm} (C-32)

The expressions for the number weighted flux (Eq. (C-28) and (C-30)) and $v^{VN}$ can also be obtained as follows:

The concentration $c_k$ is given by

$$c_k = \frac{X_k}{V}$$  \hspace{1cm} (C-33)

Differentiating with respect to $x$ and multiplying both sides by $-\tilde{D}^V$:

$$-\tilde{D}^V \frac{\partial c_k}{\partial x} = -\frac{\tilde{D}^V}{V} \frac{\partial X_k}{\partial x} + c_k \frac{\tilde{D}^V}{V} \frac{\partial V}{\partial x}$$  \hspace{1cm} (C-34)

Since

$$J_k^V = J_k^N + c_k v^{NV}$$  \hspace{1cm} (C-35)

Comparing Eqs. (C-34) and (C-35), it can be seen that the expressions for the number weighted flux, Eqs. (C-28) and (C-30), and for $v^{VN}$, Eq. (C-32), can be directly obtained.

Fick’s first law for the mass frame of reference $R^M$

The relation between the volume and mass fluxes is

$$J_k^V = J_k^M + c_k v^{MV}$$  \hspace{1cm} (C-36)
From Eq. (A-33)

\[ c_k = \frac{\omega_k^M \rho}{M_k} \quad (\omega_k^M = \frac{M_k c_k}{\rho}) \]  

(C-37)

Taking the differentials of both sides and multiplying by \(-\bar{D}^V\)

\[ -\bar{D}^V \frac{\partial c_k}{\partial x} = -\frac{\rho}{M_k} \bar{D}^V \frac{\partial \omega_k^M}{\partial x} + c_k \left( -\frac{\bar{D}^V}{\rho} \frac{\partial \rho}{\partial x} \right) \]  

(C-38)

Comparing Eqs. (C-36) and (C-38)

\[ J_k^M = -\frac{\rho}{M_k} \bar{D}^V \frac{\partial \omega_k^M}{\partial x} = -\bar{D}^M \frac{\partial \omega_k^M}{\partial x} \]  

(C-39)

and

\[ \nu^{MV} = -\frac{\bar{D}^V}{\rho} \frac{\partial \rho}{\partial x} \]  

(C-40)

where

\[ \bar{D}^M = \frac{\rho}{M_k} \bar{D}^V \]  

(C-41)

The expression for the flux in the mass frame, Eq. (C-39), can also be obtained directly from Eq. (C-3), noting that \( J_k^* = M_k J_k^M \), where \( J_k^* \) is the flux obtained from Eq. (C-3).

Fick’s first law for the lattice or Kirkendall frame of reference \( R^K \): Intrinsic fluxes

This frame is connected with the movement of the lattice planes due to an imbalance in the net flux of the components (see Appendix A). If vacancies are introduced as a third component then the net flux over all the lattice sites is zero.

\[ J_A^K + J_B^K + J_V^K = 0 \]  

(C-42)
In order to obtain Darken’s equation relating the diffusion coefficients in the volume and lattice frames, note the relation between fluxes:

\[ J^V_k = J^K_k + c_k v^{KV} \] (C-43)

Multiplying both sides by \( \bar{V}_k \), summing over \( k \) and noting the relation between the volume weighted fluxes Eq. (A-27), an expression for \( v^{KV} \) is obtained.

\[ v^{KV} = \sum_{k=1}^{n} -\bar{V}_k J^K_k \] (C-44)

For a binary

\[ v^{KV} = -(\bar{V}_A J^K_A + \bar{V}_B J^K_B) \] (C-45)

Define the intrinsic fluxes as follows:

\[ J^K_A = -D_A \left( \frac{\partial c_A}{\partial x} \right), \quad J^K_B = -D_B \left( \frac{\partial c_B}{\partial x} \right) \] (C-46)

The intrinsic diffusion coefficients are distinguished from the diffusion coefficients in the other frames by omitting the “tilde”. Substituting for the fluxes in Eq. (C-45)

\[ v^{KV} = \bar{V}_A D_A \frac{\partial c_A}{\partial x} + \bar{V}_B D_B \frac{\partial c_B}{\partial x} \] (C-47)

Using Eq. (B-9)

\[ v^{KV} = (D_A - D_B) \bar{V}_A \frac{\partial c_A}{\partial x} \] (C-48)

From Eqs. (C-43) and (C-47)
\[-\tilde{D}^V \frac{\partial c_A}{\partial x} = -D_A \frac{\partial c_A}{\partial x} + c_A (D_A - D_B) \bar{V}_A \frac{\partial c_A}{\partial x}\]  

(C-49)

Noting Eq. (B-8), the relation between the intrinsic diffusion coefficients defined in the volume frame and \(\tilde{D}^V\) is obtained from the above equation.

\[\tilde{D}^V = c_B \bar{V}_B D_A + c_A \bar{V}_A D_B\]  

(C-50)

If the intrinsic diffusion coefficients are defined with respect to the number frame \(R^N\) where

\[J^N_k = J^K_k + c_v^{KN}\]  

(C-51)

and the fluxes defined as

\[J^N_A = -\tilde{D}^V \left( \frac{\partial X_A}{\partial x} \right), \quad J^K_A = -\frac{D_A^{\prime}}{V} \left( \frac{\partial X_A}{\partial x} \right), \quad J^K_B = -\frac{D_B^{\prime}}{V} \left( \frac{\partial X_B}{\partial x} \right)\]  

(C-52)

the relation between \(\tilde{D}^V\) and the intrinsic diffusion coefficients defined in the number frame can be shown to be

\[\tilde{D}^V = X_B D_A^{\prime} + X_A D_B^{\prime}\]  

(C-53)

Thus the original form of the Darken relation is retained when the intrinsic diffusion coefficients are measured in the number frame, however the Darken relation is modified if the intrinsic diffusion coefficients are measured in the volume frame.
Similarly it can be shown that for the mass frame

$$\tilde{D}^V = \omega_B^M D_A^{''} + \omega_A^M D_B^{''}$$  \hspace{1cm} (C-54)

To summarize, the intrinsic fluxes defined in the various reference frames are

$$J_A^K = -D_A \frac{\partial c_A}{\partial x} \hspace{1cm} (D_A \text{ in volume frame } R^V)$$

$$J_A^K = -\frac{D_A'}{V} \frac{\partial X_A}{\partial x} \hspace{1cm} (D_A' \text{ in number frame } R^N) \hspace{1cm} (C-55)$$

$$J_A^K = -D_A'' \rho \frac{\partial \omega_A^M}{\partial x} \hspace{1cm} (D_A'' \text{ in mass frame } R^M)$$

The relations between the intrinsic diffusion coefficients defined in these frames are

$$D_A' = D_A \frac{\overline{V}_B}{V}, \quad D_B' = D_B \frac{\overline{V}_A}{V}$$  \hspace{1cm} (C-56)

$$D_A'' = D_A \rho \frac{\overline{V}_B}{M_B}, \quad D_B'' = D_B \rho \frac{\overline{V}_A}{M_A}$$

It should be recognized that no simple relations can be obtained either for $v^K$ or $\tilde{D}^V$ in the lab frame $R^*$. 
APPENDIX D
MOLAR VOLUME EFFECTS ON REFERENCE VELOCITIES

The conservation of atoms during diffusion, that is embodied in Fick’s second law, can be stated as

\[
\left( \frac{\partial c_k}{\partial t} \right)_{P,T,x} = -\left( \frac{\partial J^\alpha_k}{\partial x} \right)_{P,T,t} \quad (k = 1, 2, \ldots n)
\]  \hspace{1cm} (D-1)

For an \( n \) component system, there are \( n \) conservation equations of the type shown in Eq. (D-1). By invoking Fick’s first law for the interdiffusion flux, \( J^\alpha_k \), in terms of the interdiffusion coefficient, \( D^\alpha_k \), and the concentration gradient of component \( k \) (see Eq. (C-11)), the Boltzman-Matano analysis for the above conservation equation can be used to obtain an expression for \( D^\alpha_k \) (Eq. 4-4). However, the typical Boltzman-Matano analysis can only be used, if the conservation equation is of the form given in Eq. (D-1), which is only applicable in the laboratory (\( \mathbb{R}^n \)) frame of reference and not in the other frames, unless the corresponding reference velocities (defined in Appendix A) are zero.\(^1\)

The conditions under which the reference velocities can be neglected are therefore examined in this chapter.

\(^1\) Even if the reference velocities are not zero, which is the case when the volume of the system is not constant during diffusion, it is still possible to obtain an equation of the type given in Eq. (D-1) by suitable transformations of the distance coordinate, \( x \) [Coh53]. This analysis discussed by Sauer-Freise [Sau62] and den Broeder [Bro69], hence permits the determination of concentration dependent diffusion coefficients in other non-laboratory frames, besides providing other useful benefits [Kai99].
In the absence of molar volume assumptions discussed in this chapter, the laboratory fluxes \( J_k^o \) in a binary system are independent, each with its own diffusion coefficient. The associated diffusion coefficients, \( D_A^o \) and \( D_B^o \), are related in a complex way through \( v^r \), Eq. (C-14). If a binary system is modeled as having a composition independent diffusion coefficient, say \( D_A^o \), then by Eq. (C-14), \( D_B^o \) is composition dependent. For a semi-infinite diffusion couple this classic assumption yields the textbook error function solution for component A, but not for component B.

**Reference velocity in the number frame \( v^N \).** Expressing the lab flux in terms of the flux in the number frame, the continuity equation can be expressed as

\[
\frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x} (J_k^N + c_k v^N) \quad (D-2)
\]

Summing over the components

\[
\sum_{k=1}^{n} \frac{\partial c_k}{\partial t} = -\sum_{k=1}^{n} \frac{\partial}{\partial x} (J_k^N + c_k v^N) \quad (D-3)
\]

Since the sum of the differential is the differential of the sum:

\[
\frac{\partial \sum_{k=1}^{n} c_k}{\partial t} = -\frac{\partial}{\partial x} \sum_{k=1}^{n} J_k^N - \frac{\partial}{\partial x} \sum_{k=1}^{n} c_k v^N \quad (D-4)
\]

The fluxes in the number frame sum to zero, hence

\[
\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} \sum_{k=1}^{n} c_k v^N \quad (\sum_{k=1}^{n} c_k = C = \frac{1}{V}) \quad (D-5)
\]

If the molar volume of the system is constant, the left hand side of Eq. (D-5) is zero.

Hence
or

\[ v^N \frac{\partial C}{\partial x} + C \frac{\partial v^N}{\partial x} = 0 \]  

The first term is again zero since the molar volume is constant.

\[ \frac{\partial v^N}{\partial x} = 0 \]  

Now since \( v^N \) is zero at the ends of the diffusion zone (assuming semi-infinite conditions), Eq. (D-8) implies that \( v^N \) is zero throughout the diffusion zone. Thus,

\[ v^N = 0 \quad \text{if} \quad V = \text{constant} \quad (\bar{V}_A = \bar{V}_B = V) \]  

Hence \( v^N \) is zero if the molar volume is constant at every location in the diffusion couple, this necessarily means that the partial molal volumes of all the components in the system are equal to the molar volume. However, in reality, even if the assumption that the partial molal volumes are constant is a reasonable one, the assumption that they are equal is never true for binary or higher order systems; hence \( v^N \) is not zero for practical systems.

**Reference velocity in the volume frame \( v^\bar{V} \).** Expressing the lab flux in terms of the flux in the volume frame, the continuity equation can be expressed as

\[ \frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x} (J_k^\bar{V} + c_k v^\bar{V}) \]  

Multiplying both sides by \( \bar{V}_k \):
\[ \bar{V}_k \frac{\partial c_k}{\partial t} = -\bar{V}_k \frac{\partial}{\partial x} \left( J_k V + c_k v V \right) \] (D-11)

If \( \bar{V}_k \) is constant and hence equal to the molar volume of pure \( k \), \( V_k^o \), Eq. (D-11) can be written as

\[ \frac{\partial c_k V_k^o}{\partial t} = -\frac{\partial}{\partial x} \left( V_k^o J_k V + c_k V_k^o v V \right) \] (D-12)

Summing over the components and again noting that the sum of the differentials is the differential of the sum

\[ \frac{\partial}{\partial t} \sum_{k=1}^{n} c_k V_k^o = -\frac{\partial}{\partial x} \sum_{k=1}^{n} V_k^o J_k V - \frac{\partial}{\partial x} \sum_{k=1}^{n} c_k V_k^o v V \] (D-13)

The left hand side of Eq. (D-13) is zero by virtue of Eq. (B-8). Similarly the first term on the right hand side is also zero by virtue of Eq. (A-27). Hence

\[ \frac{\partial}{\partial x} \sum_{k=1}^{n} c_k V_k^o v V = 0 \] (D-14)

Differentiating

\[ v V \frac{\partial}{\partial x} \sum_{k=1}^{n} c_k V_k^o + \sum_{k=1}^{n} c_k V_k^o \frac{\partial}{\partial x} v V = 0 \] (D-15)

Using Eq. (B-8)

\[ v V \frac{\partial}{\partial x} (1) + (1) \frac{\partial}{\partial x} v V = 0 \] (D-16)

Hence

\[ \frac{\partial}{\partial x} v V = 0 \] (D-17)
Since \( v^V \) is zero at the ends, this necessarily means that \( v^V \) is zero throughout due to Eq. (D-17). Thus if the partial molal volumes are constant (but not necessarily equal) and hence equal to the molar volumes of the pure components, the volume weighted reference velocity \( v^V \) is zero.

\[
v^V = 0 \quad \text{if} \quad \overline{V}_k = V_k^o \quad \text{(D-18)}
\]

Only under this assumption does Eq. (D-10) simplify to the classical form of the conservation equation (D-1). It was shown earlier in Appendix C (see Eqs. C-5 and C-10), that there exists a single, unique diffusion coefficient in the volume frame \((\tilde{D}^V_A = \tilde{D}^V_B = \tilde{D}^V)\). If \( v^V \) is zero, by substituting the flux expression in the volume frame, Eq. (C-5), in Eq. (D-1), the Boltzman-Matano analysis can be used to obtain \( \tilde{D}^V \) from an experimental concentration profile in a diffusion couple.

Alternatively, if \( \tilde{D}^V \) is modeled to be constant, and \( v^V \) is zero by the above assumption, the classic error function solution can be used to obtain the concentration profile. These arguments can be extended to apply to models for ternary and higher order systems.

In case of the mass or barycentric velocity \( v^M \), it can be shown that it is zero only if the density of the system is constant. Note that the condition that the molar volume is constant does not imply that \( v^M \) is zero.

\[
v^M = 0 \quad \text{if} \quad \rho = \text{constant} \quad \text{(D-19)}
\]
APPENDIX E
MEASUREMENT OF LATTICE VELOCITY USING AN OBLIQUE INERT MARKER INTERFACE

In order to measure the intrinsic flux of a component as a function of position in a diffusion couple, it is necessary to have knowledge of the interdiffusion flux of that component and the lattice velocity profile over the entire diffusion zone. The determination of interdiffusion fluxes is relatively straightforward from the concentration profiles by using the equation given by Dayananda and Kim [Day79]. Unfortunately, the measurement of the lattice velocity distribution has not been easy to perform due to the experimental difficulties involved in placing markers across the diffusion zone. Usually the Kirkendall velocity, i.e., the velocity of the marker at the original weld interface, is the only measurement carried out, hence the intrinsic flux can be only determined at a single (unique) composition associated with the Kirkendall interface. Techniques for measuring the lattice velocity distribution from the movement of inert markers have been discussed by Philibert [Phi91]. The method of “Many Foils ” first used by Heuman’s group [Heu57, Heu72] and later by Philibert’s group for studying diffusion in Fe-Ni and Fe-Co systems [Koh70], has been successful, but the procedure for preparing and bonding thin (microns) slices is rather laborious and inconvenient to utilize in many cases. In some instances, plastic deformation may result as a result of the diffusion bonding process and corrections have to be employed during the measurement of marker shifts to account for this contribution [Dal00a, Heu72]. However, this
technique has been utilized by many, e.g., Heumann: Ag-Au, 900°C [Heu57] and Cu-Ni, 1000°C [Heu72]; Kohn: Fe-Ni, Fe-Co 1200°C [Koh70]; Krishtal: Fe-Cr and Ni-Cr, 1100, 1200 and 1300°C [Kri91]; Neverov: Fe-Ni, 1583 K [Nev92]; van Dal [Dal00a].

The “Oblique Interface Technique” has been suggested by Philibert, Cornet and Calais [Phi91, Cor72, Cor74], but has not been used widely, since the experimental procedure for placing oblique markers is not trivial. Hirano’s group in Japan appears to have used this technique the most, although their procedure for placing the oblique markers is different [Iij82] from the one to be discussed in the next section (they prefer to use the term “multiple markers.”) The results of the first multiple marker experiment ever performed was published as early as 1982. A few binary systems have been analyzed with this technique (e.g., Hirano and Iijima: γ Au-Fe at 1000°C [Iij96], Cu-Ni (25-80 % Cu) at 1000°C [Iij82], Onishi: Cu-Zn at 966-1183 K [Oni84]. The results from both techniques, i.e., multiple foils or multiple markers, show good agreement for the systems where such measurements have been made.

In this discussion, an experimental procedure for utilizing the Oblique Interface Technique for measuring marker shifts (lattice shifts) is first presented. An equation for computing the lattice velocity from the lattice shift is then derived. Finally, it is proved that the velocity of an inert marker is identical to that of the lattice on which it resides.

**Oblique Interface Technique**

**Experimental Setup.** The measurement of lattice shifts across a diffusion zone can be achieved by designing a diffusion couple with a marker plane at an angle to the original weld plane. The procedure of slicing a standard semi-infinite diffusion couple at an angle and rebonding after placing markers on the oblique interface, is basically flawed
since it is impossible to realign the original weld interface. A misalignment of the original weld interface introduces a concentration gradient in a direction that is not normal to the original weld interface in the region of the weld (Fig. E-1a). Hence the diffusion problem is no longer one dimensional. The procedure that is suggested reverses the sequence of steps in preparing the diffusion couple with the oblique interface (Fig. E-1b). If A and B correspond to the two halves of the desired couple, the initial step involves preparing two couples A-A and B-B separately with markers at the weld plane by diffusion bonding. These same composition couples are then cut at a desired angle to give A and B specimens each containing an oblique interface at the same angle. Markers are again placed on these new interfaces and the required A-B diffusion couple is prepared by diffusion bonding at an appropriate temperature. In this procedure, it is not possible to align the oblique interface in each half of the couple. However, this has no effect on the analysis, a simple translation in a direction parallel to the A-B weld interface is all that is required. The inert markers should preferably have a high atomic number contrast and a narrow size distribution (mean of 1-2 microns) since their detection in an SEM (backscatter mode) or electron microprobe analyzer is easier. Techniques such as electrophoresis can be used to place the markers uniformly on the polished surfaces.

The determination of the shifts after the diffusion anneal is illustrated with the aid of Fig. (E-2). The coordinates of the markers at the Kirkendall interface and the oblique interface are initially noted using an electron microprobe analyzer or an SEM. The original oblique interface can be determined by constructing a tangent to the oblique markers that are well outside the diffusion zone. Normals (to the Kirkendall interface)
can then be constructed from the coordinates of the displaced oblique markers to intersect the tangent. The distance between an oblique marker and the intersection point of its normal on the tangent (the original oblique interface) is the marker or lattice shift. The lattice shifts can then be used to determine the lattice velocities by a procedure discussed in the next section. The shifted oblique marker interface intersects the Kirkendall (original weld) interface at a point (Kirkendall Point). The normal drawn from this Kirkendall point intersects the tangent line in a point (Matano Point). A line parallel to the Kirkendall interface through this Matano point is in fact the Matano interface and the distance between the Kirkendall and Matano points is the Kirkendall shift. Thus the oblique interface technique also provides an alternate but direct way of determining the Matano interface. The geometrical procedure described above can be avoided by developing a computer code that directly calculates all the desired parameters from the input coordinates of the Kirkendall and oblique markers.

**Determination of Lattice Velocities from Measured Marker Shifts**

The velocity of an inert marker during diffusion is the velocity of the lattice plane on which it resides (a proof is presented later). An inert marker place at the original weld (or the Kirkendall interface) of a diffusion couple moves with a fixed composition. However markers placed at other locations do not move with a fixed composition. This is because markers that are somewhat removed from the original interface remain essentially stationary for some time or have a certain incubation period before they begin to move. Thus the local lattice velocity is a function of: \( x \), the position of the marker at time \( t \); \( x_0 \), the initial position of the marker at \( t=0 \); and \( t \), the time of the diffusion experiment. Hence,
\[ \mathbf{v}^K = \left( \frac{\partial x}{\partial t} \right)_{x_o} \]  

(E-1)

and

\[ dx = \left( \frac{\partial x}{\partial x_o} \right)_t dx_o + \left( \frac{\partial x}{\partial t} \right)_{x_o} dt \]  

(E-2)

The second term on the R.H.S. of Eq. (E-2) is the local lattice velocity, \( \mathbf{v}^K \). In order to obtain an expression for \( \mathbf{v}^K \), an independent relation between \( dx, dx_o \) and \( dt \) is needed.

Experimentally and in our simulation, it is found that a plot of \( \lambda = x/\sqrt{t} \) versus \( \lambda_o = x_o/\sqrt{t} \) is time invariant. This implies a functional relation between \( \lambda \) and \( \lambda_o \):

\[ \frac{x}{\sqrt{t}} = g \left( \frac{x_o}{\sqrt{t}} \right) = g(\lambda_o) \]  

(E-3)

Taking the differential on both sides of Eq. (E-3),

\[ d \left( \frac{x}{\sqrt{t}} \right) = \frac{dg(\lambda_o)}{d\lambda_o} d\lambda_o = \frac{1}{\sqrt{t}} dx - \frac{x}{2t^{3/2}} dt \]  

(E-4)

Rearranging and solving for \( dx \),

\[ dx = \sqrt{t} \frac{dg(\lambda_o)}{d\lambda_o} d\lambda_o + \frac{x}{2t} dt \]  

(E-5)

Since

\[ \lambda_o = \frac{x_o}{\sqrt{t}} \]  

(E-6)

\( d\lambda_o \) can be obtained:

\[ d\lambda_o = \frac{1}{\sqrt{t}} dx_o - \frac{x_o}{2t^{3/2}} dt \]  

(E-7)
Substitute for $d\lambda_o$ in Eq. (E-5)

$$dx = \sqrt{t} \frac{dg(\lambda_o)}{d\lambda_o} \left( \frac{1}{\sqrt{t}} dx_o - \frac{x_o}{2t^{3/2}} dt \right) + \frac{x}{2t} dt$$  \hspace{1cm} (E-8)

Factoring terms

$$dx = \frac{dg(\lambda_o)}{d\lambda_o} dx_o + \left( \frac{x}{2t} - \frac{dg(\lambda_o) x_o}{d\lambda_o} \right) dt$$  \hspace{1cm} (E-9)

Comparing coefficients of Eq. (E-9) with Eq. (E-2)

$$\left( \frac{\partial x}{\partial x_o} \right)_t = \frac{dg(\lambda_o)}{d\lambda_o} dx_o$$  \hspace{1cm} (E-10)

and

$$\left( \frac{\partial x}{\partial t} \right)_{x_o} = \frac{1}{2t} \left( x - \frac{dg(\lambda_o) x_o}{d\lambda_o} \right) = \frac{1}{2t} \left( x - \left( \frac{\partial x}{\partial x_o} \right)_{x_o} \right)$$  \hspace{1cm} (E-11)

Alternatively in terms of $\lambda$ and $\lambda_o$, Eq. (E-11) can be written as

$$\left( \frac{\partial x}{\partial t} \right)_{x_o} = \frac{1}{2\sqrt{t}} \left( g(\lambda_o) - \left( \frac{dg(\lambda_o)}{d\lambda_o} \right) \lambda_o \right) = \frac{1}{2\sqrt{t}} \left( \lambda - \frac{d\lambda}{d\lambda_o} \lambda_o \right)$$  \hspace{1cm} (E-12)

Eqs. (E-11) and (E-12) are expressions for the lattice velocity, $v^K$. Using the oblique marker technique, the initial and final positions of markers can be determined. A plot of $\lambda$ versus $\lambda_o$ can then be used to obtain the lattice velocity distribution using Eq. (E-12).

**Equivalence of Lattice and Marker Velocities**

The utilization of inert markers for the measurement of lattice velocities is based on the intuitive assumption that the marker velocity is in fact the velocity of the lattice on which the marker resides. A proof of this is presented below.
Consider an inert marker in the diffusion zone. As the diffusion process is occurring, this marker moves with the lattice plane on which it resides. Let \( x_o \) be the position of the marker at time \( t = 0 \) and \( x_K \) be the position at time \( t \) in the laboratory frame of reference. The accumulated displacement of the marker in time \( t \) is \( \Delta x_K \), the lattice shift. The shift is due to the flow of vacancies across this lattice plane. The total number of vacancies that flow across this plane in time \( t \) is

\[
n_v(x_L,t) = \int_0^t J_v(x_L,t) A_o \, dt \tag{E-13}
\]

where \( A_o \) is the cross-sectional area and \( x_L \) is the position of the lattice plane. If it is assumed that there is no accumulation of vacancies, these vacancies are annihilated in the volume on one side of the marker plane. This produces the lattice (or Kirkendall) shift. The volume of vacant sites annihilated is related to the volume change due to the shift which is \( \Delta x_K A_o \). The corresponding number of moles of sites is

\[
n_v(x_L,t) = \frac{1}{V} \Delta x_K (x_L,t) A_o \tag{E-14}
\]

where \( V \) is the molar volume assumed to be constant in this development. Comparing Eqs. (E-13) and (E-14):

\[
\frac{1}{V} \Delta x_K A_o = \int_0^t J_v A_o \, dt = \int_0^t C v_L A_o \, dt = \frac{1}{V} \int_0^t v_L A_o \, dt \tag{E-15}
\]

where \( v_L \) is the lattice velocity. The total concentration \( C \) is simply the reciprocal of the molar volume \( V \), that is constant, hence it can be taken outside the integral. Simplifying Eq. (E-15), it is seen that
Figure E-1. Procedure for preparing an “Oblique Interface” in a diffusion couple. (a) Incorrect procedure: (i) original AB diffusion couple; (ii) oblique section through the couple; (iii) rebonded AB diffusion couple with oblique interface. It is apparent that the misalignment of the original weld interface results in a two-dimensional diffusion problem. (b) Corrected procedure: (i) same composition AA and BB diffusion couples; (ii) pieces of AA and BB couples obtained by electrodischarge machining (EDM) original AA and BB couples; (iii) individual pieces of AA and BB each containing an oblique interface rebonded to give desired AB diffusion couple with oblique interfaces. It is obvious that the diffusion problem is now one-dimensional.
Figure E-2. Experimental determination of lattice shift as a function of marker position. The shifted marker positions are schematically illustrated.
\[ \Delta x_K = \int_0^t v_L \, dt \]  \hspace{1cm} (E-16)

or

\[ v^K = \frac{d\Delta x_K}{dt} = v_L \]  \hspace{1cm} (E-17)

Hence, the marker velocity, \( v^K \), is in fact the velocity of the lattice as might be expected.
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BIOGRAPHICAL SKETCH

Nagraj Kulkarni was born in Pune, India, on August 20, 1966. His primary and secondary education was at Loyola High School, Pune, which is located near the National Chemical Laboratory, where his father was employed. He pursued his higher education at the College of Engineering, Pune, where he obtained a B.E. in metallurgical engineering (sandwich) in 1988. As part of his degree requirements, he also completed one year of industrial metallurgical training at Tata Engineering and Locomotive Company Ltd. (TELCO), Pune. His interest in the then emerging field of materials science and engineering brought him to the United States of America.

He obtained his master’s degree at the Department of Materials Science and Engineering, University of Florida, Gainesville, in 1992. His thesis topic was “Ultrasonic Characterization of Green and Sintered Ceramics.” He continued on with his Ph.D. in the area of solid state diffusion and also worked in diverse fields within materials sciences including intermetallics, capillarity theory and plasma etching. His experience during this period included a consulting project with General Electric in the area of thermodynamic modeling of solid-gas interactions, and sintering in oxide ceramics. He has publications in reputed journals and is a member of several professional societies in materials science. He is currently a research associate in the Metals and Ceramics Division at Oak Ridge National Laboratories in Knoxville, Tennessee.