TERNARY DIFFUSION IN COPPER-SILVER-GOLD ALLOYS

by

THOMAS OWENS ZIEBOLD

B.E., Yale University (1956)
S.M., Massachusetts Institute of Technology (1963)

Submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY
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Signature of Author

Signature of Professor in Charge of Research

Signature of Chairman, Departmental Committee
ABSTRACT

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****

Submitted to the Department of Metallurgy on January 11, 1965, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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This thesis reports a general investigation into the nature of diffusion in a three-component metal system. The theory section reviews the phenomenological descriptions of multicomponent diffusion wherein the experimentally measurable diffusivities are related to more fundamental coefficients and thermodynamic properties. A model for diffusion in multicomponent solids based on the concepts of Darken is presented.

Experimental analysis of diffusion samples covering the entire copper-silver-gold system at 725°C has been carried out. Experimental coefficients are computed at twenty-eight points in the ternary system. It is found that the direct coefficient for copper is nearly independent of the silver content for low silver alloys and that the cross coefficient for silver correlates with the thermodynamic properties. This latter conclusion indicates that the mobility of copper and gold are nearly equal.

Thermodynamic activities for copper-silver-gold are computed from binary data and adjusted to be consistent with measured tie-lines across the two-phase region which extends into the ternary diagram at 725°C. Application of these thermodynamic calculations to the diffusion data verifies the Onsager reciprocal relations to the extent that experimental uncertainties will allow.

It is found that diffusion near the critical point of the two-phase field in this system causes the composition gradients for copper and silver to approach infinity while the direct and cross coefficients become equal.

Thesis supervisor:

Robert E. Ogilvie
Associate Professor of Metallurgy
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BIOGRAPHICAL NOTE

The author was born in Charleston, West Virginia, on July 1, 1933. He completed his secondary education at The Lawrenceville School and entered Yale University in September, 1951. He was graduated with honors from Yale in June, 1956, with the degree of Bachelor of Engineering in chemical engineering. Upon graduation he was commissioned as an Ensign in the United States Naval Reserve.

From 1956 to 1960 he was assigned to the Naval Reactors Branch of the Atomic Energy Commission and the Nuclear Propulsion Branch of the Navy's Bureau of Ships. His duties consisted of the direction of design and manufacture of nuclear reactor components and the development of advanced fuel materials for naval reactors. During this time he attended the Bettis Laboratory Reactor Engineering School. He was released from active duty in the Navy in June, 1960, with the rank of Lieutenant.

From June, 1960 until September, 1960, he was employed as a materials engineer by Neutron Products, Inc., of Washington, D.C.

The author entered graduate school at MIT in September, 1960. He was awarded the degree of Master of Science in metallurgy in June, 1963. The thesis submitted for this degree was titled, "Diffusion Analysis of Phase Equilibria in Copper-Silver-Gold Alloys." Other publications by the author are included in the references at the end of this thesis.

He has been an instructor in nuclear engineering and is
currently Assistant Professor of Nuclear Materials in the departments of Nuclear Engineering and Metallurgy.
I. INTRODUCTION

Diffusion in a ternary alloy system is basically and significantly different from diffusion in binary alloys. When only two elements are present there is just one independent composition variable, and the diffusion profile of composition vs distance across a sample must change monotonically through all solid solutions bracketed by the terminal alloys. If two-phase regions are stable for compositions between the terminal values, these must appear as planar interfaces in the diffused sample, with the composition profile exhibiting sharp discontinuities. Adding a third element may alter this picture completely. Because of the additional degree of freedom in the composition, we may see composition profiles which do not change monotonically through solid solution ranges, and stable, non-planar phase interfaces. Even though two phase regions may lie between the terminal compositions of a diffusion sample on the constitution diagram, they will not necessarily appear in the diffusion profiles.

In binary diffusion only one coefficient is needed to describe the interdiffusion process. From Fick's law this coefficient relates the diffusive flux of one component to its own composition gradient. In ternary diffusion we must allow for cross interaction between the two independent species. By a linear extension of Fick's law we introduce "cross" or "off-diagonal" diffusion coefficients which relate
the flux of one component to the composition gradient of the other independent constituent. Thus we require four inter-diffusion coefficients to describe the transport process.

Mathematically, ternary diffusion is a three variable problem--two composition variables and one time-distance parameter (for infinite or semi-infinite couples). We may represent the diffused configuration in the usual manner by plotting the two composition profiles, that is, composition as a function of distance (or the time-distance parameter) across the sample. We may also plot one composition as a function of the other composition on a ternary isothermal section of the phase diagram. This representation, which is usually called the "composition path," is illustrated in Figure 1. It is impossible, without a complete knowledge of the kinetics and thermodynamics of the ternary system, to predict the position of the composition path for any given set of terminal compositions.

In this thesis we examine systematically the behavior or diffusion over the entire copper-silver-gold alloy system at 725°C. Of primary interest is the relation of the directly measurable diffusion coefficients to the more fundamental Onsager coefficients and, with the adoption of a particular model, to the atomic mobilities. This has not been done before, in fact, previous multicomponent diffusion experiments have been limited to a consideration of dilute solutions, constant coefficients or to purely metallographic studies of phase boundary configurations. Such work is reviewed in Chapter II.
Figure 1. Schematic space diagram for isothermal ternary diffusion.
In Chapter III we consider the basic descriptions of diffusive transport. In this presentation the formalism of non-equilibrium thermodynamics is surveyed from the vantage point of the experimentalist interested in solid, metallic alloy diffusion. This is a somewhat different approach from the available textbook treatments. In addition, we develop a picture of solid diffusion in terms of atomic mobilities as an extension of Darken's proposal for binary systems. At the end of Chapter III we present solutions of the diffusion equations which may be used to evaluate the experimental coefficients.

All analyses of diffusion samples in this thesis were made with the electron beam microanalyzer. The application of this instrument to the quantitative analysis of multicomponent alloys was developed by the author, and a discussion of the accuracy of the method is given in Chapter IV. Experimental results are presented also in Chapter IV.

In Chapter V the experimental measurements are discussed in relation to the phenomenology developed in Chapter III. The necessary thermodynamic properties have been calculated from binary data and adjusted to agree with measured ternary phase equilibria. (These calculations are summarized in Appendix B.)

The extent of experimental work required to study any aspect of ternary diffusion is many times greater than that needed to obtain the same information for binary diffusion. As a result, the present work is limited to a consideration
of interdiffusion only and at a single temperature. There are many questions left unanswered and new avenues for investigation indicated by the work reported herein. Some recommendations for future experiments are listed in Chapter VI.
II. REVIEW OF MULTICOMPONENT DIFFUSION EXPERIMENTS

Experiments designed to measure multicomponent diffusion coefficients have been infrequent, particularly for solid-state diffusion. A comprehensive review by Miller\(^{(58, 59)}\) to test the Onsager reciprocal relations for isothermal diffusion includes only liquid systems. For nine of the ten systems reported, Onsager's relations are verified within the experimental error of the data, and it is suggested that the coefficients for the tenth system are questionable. Verification of the ORR is reported more recently\(^{(74, 75)}\) for two additional liquid systems.

Regarding diffusion in solids, there have been many studies of the effect of a third element on the interdiffusion coefficient of a binary system; that is, the data are not analyzed as ternary diffusion with four coefficients but as quasi-binary systems. An interesting example is that of Mehl and Rhines\(^{(55)}\) who diffused pure copper against copper-Ni\(_2\)Si alloys. They report that the diffusion of silicon is slowed by the presence of nickel to the point where these two elements diffused in copper as Ni\(_2\)Si. This indicates a strong negative cross effect of nickel on silicon. Other quasi-binary studies are summarized by Guy and Smith\(^{(26)}\).

Turning to experiments with ternary systems which have been treated as truly multicomponent diffusion, we may distinguish between those in which the primary concern was examination of the microstructure and those in which the
diffusion coefficients were computed. The first are of interest because they have led to qualitative "rules" describing the composition path and phase boundary relations to be expected in multicomponent samples. The latter studies bear directly, of course, on the phenomenology of diffusion to be discussed in Chapter III.

**Metallographic Studies**

One of the first experiments of this kind was carried out by Clark and Rhines for the system Al-Mg-Zn\(^{(10)}\). A series of Mg-Zn alloys were diffused against pure aluminum at 335°C. The resulting phase distributions were extremely complicated since the system contains twelve stable phases at that temperature. By metallographic examination they were able to plot the composition paths on the ternary isothermal section and systematize the configuration of these paths.

Other phase studies have been reported by Kirkaldy and Fedak\(^{(39)}\) for Fe-Ni-Cr and Cu-Zn-Sn and by Castleman and Seigle\(^{(7)}\) for Cu-Zn-Ni. The phase relations, phase boundary morphology, and composition path configurations which are observed have been generalized by Kirkaldy and Brown\(^{(38)}\). Their "theorems" incorporate the earlier "rules" of Clark and Rhines and the modifications suggested by Kirkaldy\(^{(37)}\) and Meijering\(^{(57)}\). Of direct interest to the present thesis is the first "rule" which states that "diffusion penetration curves (for semi-infinite samples) can be mapped onto the ternary isotherm for all times as stationary lines." This representation was illustrated in Figure 1. The diffusion
line, which is a three variable function, \( f(n_1, n_2, x/\sqrt{t}) \),
may be projected onto the \( n-x \) planes and the \( n_1-n_2 \) plane.
Since the \( n-x \) profiles are both functions of \( x/\sqrt{t} \), it follows
that the "composition path", which is the curve on the \( n_1-n_2 \)
plane, is time invariant. This has been demonstrated experimentally by the author\(^{76}\).

Analytic Studies

Darken's experiment for diffusion in Fe-C-Si alloys,
published in 1949\(^{15}\), is an excellent example of the demonstration of cross effects in diffusion. This experiment satisfies the requirements which have since been summarized by Kirkaldy, Zia-Ul-Haq, and Brown\(^{45}\) for magnifying the cross effects, namely, that at least one of the solute concentration differences be large and that the direct coefficients be appreciably different (silicon diffuses in iron much more slowly than carbon). Darken's data were first analyzed as a multicomponent system by Kirkaldy\(^{31}\). The coefficients for the Fe-C-Si experiment were later modified to \( D_{CC}^{Fe} = 4.8 \times 10^{-7} \), \( D_{SiSi}^{Fe} = 4.6 \times 10^{-11} \) and \( D_{CSi}/D_{CC}^{Fe} = 0.162 \) by Kirkaldy and Brown\(^{16}\). Darken type experiments for Fe-C-Co alloys have been run by Chandok, Hirth, and Dulis\(^{8}\), and although cobalt produces a striking redistribution of carbon (which was initially constant on both sides of the couples), they do not calculate the cross coefficients.

Several experimental measurements of cross coefficients are reported from Professor Kirkaldy's group. These are
summarized by Kirkaldy and Brown (38) and may be separated into two classifications: interstitial-substitutional additions to gamma iron and purely substitutional alloys. In the former class are data for Fe-C-Si, Fe-C-Mn, Fe-C-Ni, Fe-C-Cr, and Fe-C-Co. In the latter class are Cu-Mn-Al (41, 52), Zn-Cu-Al (45) and Sn-Zn-Cu (38).

For the five systems of ternary austenite alloys the measurements have confirmed the relation \( \frac{D_{12}^3}{D_{11}^3} = k_1 n_1 \) where \( n_1 \) is the atom fraction of carbon and \( k_1 \) is a constant. This relation is derived from the assumption that there is negligible interaction between the interstitial and the substitutional components in these alloys. Kirkaldy's work provides considerable experimental verification of the diffusion models which are discussed in the next chapter.

No general conclusions can as yet be drawn about the diffusion coefficients in substitutional diffusion. The experiments on Cu-Mn-Al, Zn-Cu-Al and Sn-Zn-Cu cited above include relatively few measurements and limited solubility ranges. It is the purpose of this thesis to examine a substitutional system in a more general fashion.

Recently, Guy and Leroy (24) have reported the measurement of intrinsic diffusion coefficients in Ni-Co-Cr alloys. In this work, incremental ternary diffusion couples are prepared with a marked interface. The markers must be located at a certain composition in the diffusion zone (see discussion in Chapter III), and this requires the trial diffusion of several samples with slightly varied terminal compositions. The intrinsic coefficients are evaluated from
a measurement of the total flow of each component past the marker interface. This method of analysis has been described by Guy and Philibert$^{(25)}$. Leroy has stated$^{(50)}$ that the work will be extended to include measurement of thermodynamic activities so that the intrinsic coefficients may be related to fundamental mobilities.
III. THE PHENOMENOLOGY OF MULTICOMPONENT DIFFUSION

If we introduce a chemical concentration variation into an isolated material system and then allow this system to remain at constant temperature and pressure and in mechanical equilibrium, we will observe as time goes on that the composition variations gradually disappear. This is the nature of diffusion. The earliest statement of the kinetics of transport by diffusion is Fick's first law which says that the diffusive flux (rate of transport of atoms or molecules through a unit cross sectional area) divided by the concentration gradient is constant; that is

$$ J = -D \frac{\partial c}{\partial x} \quad (III-1) $$

where $J$ is the diffusive flux (mass units/sec-cm$^2$) in the direction $x$, $c$ is the concentration (mass units/cm$^3$), and $D$ is a constant called the "diffusivity." The negative sign is used since it was observed that diffusion always occurred in such a way as to reduce the magnitude of the gradient—matter, like heat, was seen to flow "downhill."

This law, which was originally formulated from observations of diffusion in gases, has been applied to the motion of matter in gases, liquids and solids. It has been found, however, that the original supposition that the diffusivity was constant is not true. In general, and particularly in solids, the coefficient $D$ depends on the composition of the material. It is also now evident that this simple equation accurately describes diffusive transport only in systems
consisting of two elements. For diffusion where three or more components are present we shall have to consider a more general statement of Fick's first law. Moreover, we now know that the concentration gradient is not the fundamental driving force for diffusion, and we must develop a new formulation in terms of thermodynamic properties of the diffusing substances.

The extension of Fick's law to multicomponent systems was made by Onsager\(^{(62)}\) in 1945. He proposed, most generally, that if there are a total of \(s\) diffusing species then we may consider the motion of each to be linearly dependent on all gradients, or

\[
J_i = -\sum_{k=1}^{s} D_{ik} \frac{\partial c_k}{\partial x} \quad (i=1,\ldots,s) \quad (III-2)
\]

In this statement there are \(s^2\) coefficients relating the flux of component \(i\) to the concentration gradient of component \(k\). Generally we may impose two conditions of the form

\[
\sum_{i=1}^{s} a_i J_i = 0 \quad (III-3)
\]

and

\[
\sum_{k=1}^{s} b_k \frac{\partial c_k}{\partial x} = 0 \quad (III-4)
\]

which permit us to eliminate one of the gradients and one of the fluxes from Equation (III-2). We therefore reduce the coefficient matrix to an \(s-1\) square array defined by the equations

\[
J_i = -\sum_{k=1}^{s-1} D_{ik}^{s} \frac{\partial c_k}{\partial x} \quad (i=1,\ldots,s-1) \quad (III-5)
\]
For a binary system there is only one coefficient so that Fick's law is still applicable, but we have four coefficients for a ternary system, nine for a quarternary, and so on.

It should already be apparent that we have several choices to make in arriving at Equation (III-5). Equations (III-3) and (III-4) define certain frames of reference and these will be discussed in detail in a later section. In Equation (III-5) we have left out the gradient of component \( s \) (usually called the "solvent" whether it is the major constituent or not), and the values of the coefficients depend on which element we choose to eliminate. (Following the suggestion of Mason\(^{(52)} \) we use a superscript to designate this choice.) The conversion from one "solvent" basis to another may be made from the relation available from Equations (III-2), (III-4) and (III-5), namely

\[
D^S_{ik} = D^I_{ik} - \frac{b_k}{b_s} D^I_{sk}
\]

The conversions for a ternary system are listed in Appendix A.

The generalization of Fick's law by Onsager introduces a significant new feature into the study of diffusion—the presence of "cross effects." In a ternary system, for example, the flux of element \( i \) will depend not only on its own gradient but also on the gradient of element \( j \). The coefficients \( D^S_{ik} \) where \( i \neq k \) are called "cross" or "off-diagonal" coefficients, and it has been found, as reviewed in the previous chapter and as reported later herein for Cu-Ag-Au, that they are often
quite sizable. To understand the origin of these cross effects it is necessary to develop the diffusion equations from a more fundamental standpoint. In the next section we will review the thermodynamics of transport processes and then consider specifically the diffusion equations on an experimental basis. Finally we shall discuss the possible atomic nature of diffusion in crystalline solids.

Nonequilibrium Thermodynamics

Although it had been anticipated well before, it is Darken's report in 1949\(^{(15)}\) of diffusion in Fe-C-Si which is often quoted as the first indication that the chemical composition gradient is not the fundamental driving force in solid diffusion. This by now classic experiment was at odds with previous metallurgical experience since it showed an "uphill" transport of carbon against its own composition gradient.

In 1931, Onsager\(^{(61)}\) established the basis for the "modern" formulation of diffusion equations in terms of the chemical potential gradients. He proposed that the diffusive flux could be written as the linear summation of the potential gradients,

\[
J_i = -\sum_{k=1}^{s} L_{ik} \nabla \mu_k \quad (i=1, \ldots, s) \quad (III-7)
\]

(Onsager's formulation was more general than this, but we shall confine our discussion to isothermal, isobaric systems in mechanical equilibrium.) This equation defines an entirely
new set of coefficients, and following the suggestion of Kirkwood, Baldwin et al.\textsuperscript{(46)} we shall call these "fundamental" coefficients to distinguish them from the "practical" coefficients of Fick's law.

Onsager examined the properties of this system of equations from the viewpoint of classical thermodynamics and concluded that, provided the fluxes and forces were properly defined, the matrix of fundamental coefficients would be symmetrical, that is, for \( i \neq k \),

\[ L_{ik} = L_{ki} \quad \text{(III-8)} \]

This equation, known as the "Onsager Reciprocal Relations" (ORR), was based, not on a thermodynamic theorem, but on the "reasonable assumption that molecular dynamical systems, like those known to our macroscopic experience, possess symmetry in past and future."\textsuperscript{(63)} This assumption is Onsager's principle of "microscopic reversibility."

The application of these ideas to multicomponent diffusion appeared to lie dormant for a period of years, prompting Onsager to state in 1945, "It is a striking symptom of the common ignorance in this field that not one of the phenomenological schemes which are fit to describe the general case of diffusion is widely known."\textsuperscript{(62)} Perhaps as a result of this prompting, the development of nonequilibrium thermodynamics moved rapidly from then on, and through the efforts of Casimir, Prigogine, de Groot, and others, a formalism was established. There are two modern textbooks which treat the subject, de Groot and Mazur\textsuperscript{(18)} and Fitts\textsuperscript{(21)}, and we shall
give here only an outline of the important principles.

**Basic Principles**

"The purpose of nonequilibrium thermodynamics is to extend classical thermodynamics to include systems in which transport processes are taking place." *(F1)* Its basis is the second law of thermodynamics which states that "the internal entropy production due to an irreversible process in a system is positive definite." *(F3)* Beyond this, there are certain postulates which must be stated. These are:

"**Postulate I.** For a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the nonequilibrium system are the same functions of the local state variables as the corresponding equilibrium properties." *(F21)*

"**Postulate II.** The fluxes or currents are linear, homogeneous functions of the forces." *(F35)*

"**Postulate III.** If linear relations are written for the set of conjugated fluxes and forces which appear in (the equation for the rate of entropy production) and if the resulting phenomenological coefficients are well defined, then the matrix of these phenomenological coefficients is symmetric." *(F36)*

These three postulates may be substantiated from considerations of statistical thermodynamics in the same way as the second law is treated. **Postulate I,** which allows us

*This designation refers to page numbers in Fitts*(21).
to describe transport properties in terms of classical thermodynamic quantities, is essentially valid if the system locally is not too far removed from equilibrium. This applies to solid state diffusion as illustrated by Kirkaldy (36): "Take for example a solid state diffusion couple which starts initially at time zero with an infinite gradient at the weld and which is diffused for one second. In a typical case this will have a gradient at the weld of $10^4$ atom fractions per cm. This appears to be a very extreme gradient, but in fact, on the atomic scale, the concentration changes by only one atom in 10,000 per lattice parameter. This system already has attained a high degree of local equilibrium."

Postulates II and III are restatements of Onsager's principles. While Postulate II is indefinite about the definition of fluxes and forces, and indeed we have a wide selection, Postulate III is quite specific. In order to apply the ORR we must consider the fluxes and forces which are so chosen that they generate the rate of entropy production. Additional restrictions on the forces and fluxes are discussed in a later section.

Taking the time derivative of the first law of thermodynamics and solving for the rate of entropy change in a unit volume, we have (F30)

$$\frac{T}{V} \frac{dS}{dt} = \frac{1}{V} \frac{dE}{dt} + \frac{P}{V} \frac{dV}{dt} - \sum_{i=1}^{N} \mu_i \frac{dc_i}{dt}$$  \hspace{1cm} (III-9)

in which $S$, $E$, and $V$ are the integral molar entropy, internal energy and volume, respectively, $P$ is the pressure, $\mu_i$ is the chemical potential (partial molar Gibbs free energy), $c_i$ is
the molar density of component \( i \), \( T \) is the local thermodynamic temperature, and \( t \) is time. For an isothermal, isobaric system in mechanical equilibrium the quantities on the right side of Equation (III-9) may be evaluated in terms of the entropy flux and mass fluxes with the result that (F30)

\[
\frac{T}{V} \frac{dS}{dt} = -TV \cdot J_s - \sum_{i=1}^{S} J_i^M \cdot \nabla \mu_i \tag{III-10}
\]

where \( J_s \) is the entropy flux and \( J_i^M \) is the molar flux relative to the local center of mass.

If we write a continuity equation for entropy in the volume element,

\[
\frac{1}{V} \frac{dS}{dt} + \nabla \cdot J_s = \sigma \tag{III-11}
\]

where \( \sigma \) is the local rate of entropy generation and \( J_s \) is the entropy flux, then we see by comparison of Equations (III-10) and (III-11) that for this system

\[
T \sigma = - \sum_{i=1}^{S} J_i^M \cdot \nabla \mu_i \tag{III-12}
\]

That is, we have identified the local rate of entropy production as the linear summation of the products of a set of fluxes, \( J_i^M \), and forces, \( -\nabla \mu_i \). Fluxes and forces which appear in this manner in the equation for entropy production are said to be "conjugated." A general statement of (III-12) is

\[
T \sigma = \sum_{i} Q_i \cdot \chi_i \tag{III-13}
\]
Fluxes and Forces

Having developed the entropy production equation we may now write the phenomenological relations from Postulate II for conjugated fluxes and forces:

$$\mathbf{J}_i = \sum_k \mathbf{L}_{1k} \gamma_i$$

(III-14)

Postulate III then says that the matrix of coefficients is symmetrical, i.e.,

$$\mathbf{L}_{1k} = \mathbf{L}_{ki}, \quad i \neq k$$

(III-8)

There is, however, an additional restriction which must be observed in order for the ORR to be valid. It is possible to construct more than one set of conjugated fluxes and forces which will satisfy Equation (III-13). The ORR do not apply to any set, but only to certain sets for which the coefficients defined by (III-14) are unambiguous. This has been pointed out by several authors, (28, 29, 58, 59) hence the requirement in Fitt's statement of Postulate III that the ORR are valid "if the resulting phenomenological coefficients are well defined."

Hooymann and de Groot (29) have stated this restriction as follows: "Since in the proof of the Onsager relations the fluxes as well as the forces are assumed to be independent, this formalism should be applied with care if linear dependencies exist amongst the fluxes or amongst the forces....A linear dependency for only one of the two classes of variables give rise to additional relations amongst the phenomenological coefficients which leave the symmetry of the coefficient scheme unimpaired. However, when both classes of variables,
fluxes and forces, are dependent the phenomenological coefficients are not uniquely defined, and the validity of the Onsager relations can no longer be guaranteed." Consider the latter case, which is the usual situation arising in experimental measurements. We have linearly dependent forces and fluxes given by

$$\sum_{i=1}^{s} p_i J_i = 0 \quad (\text{III-15})$$

and

$$\sum_{i=1}^{s} q_i x_i = 0 \quad (\text{III-16})$$

The entropy production written in terms of independent quantities is

$$T\sigma = \sum_{i=1}^{s-1} J_i \cdot \left( x_i + \frac{p_i}{p_s} \sum_{j=1}^{s-1} \frac{q_j}{q_s} x_j \right) \quad (\text{III-17})$$

and the appropriate phenomenological equations are

$$J_{i}^{p} = \sum_{k=1}^{s-1} L_{ik} \left( x_k + \frac{p_k}{p_s} \sum_{j=1}^{s-1} \frac{q_j}{q_s} x_j \right) \quad (i=1, \ldots, s-1) \quad (\text{III-18})$$

(The superscript p is used to indicate the imposition of Equation (III-15).) We have properly chosen the fluxes and forces so that the ORR apply to the matrix $L_{ik}$. We could however, have written the flux equations as

$$J_{i}^{p} = \sum_{k=1}^{s-1} L'_{ik} x_k \quad (i=1, \ldots, s-1) \quad (\text{III-19})$$

The relation between the two coefficient matrices defined above is

$$L'_{ik} = L_{ik} + \frac{q_k}{q_s} \sum_{j=1}^{s-1} \frac{p_j}{p_s} L_{ij} \quad (i, k=1, \ldots, s-1) \quad (\text{III-20})$$
It is apparent from Equation (III-20) that in general

\[ L'_{ik} \neq L'_{ki}. \]

**Basic Definitions of Fluxes and Forces**

Coleman and Truesdell (11) have pointed out that requiring the fluxes and forces in the linear equations

\[ J_i = \sum L_{ik} \chi_k \]  \hspace{1cm} (III-14)

to generate the entropy production

\[ T\sigma = \sum_i J_i \cdot \chi_i \]  \hspace{1cm} (III-13)

is not a sufficient condition to produce a symmetric coefficient matrix. In fact, they have demonstrated that for every set of fluxes and forces which obey Equations (III-13) and (III-14) and the ORR, there exist infinitely many choices of forces and fluxes which obey Equations (III-13) and (III-14) but which do not obey the ORR. They conclude that "in phenomenological theories based on (Equations (III-13) and (III-14) above), there is no content in the statement that (the matrix) \( L_{ij} \) is or is not symmetric....Until the forces and fluxes in any particular case are physically identified by some property more specific than their mere entry into the bilinear form (of Equation (III-13)), application of Onsager's theorem is precarious."

The crucial point then, is in the way that the forces and fluxes are to be physically identified. The fundamental statement of Onsager's theorem is spelled out by Coleman and Truesdell as follows:

"If each flux \( J_i \) is the time derivative of a thermo-
dynamic variable $a_1$,

$$J_1 = \mathfrak{S}_1$$  \hspace{1cm} (III-21)

and if each $a_1$ is an even function* of the velocities of the atoms constituting the system and enters into an equation of the form

$$S = \frac{1}{2} \sum_{i=1}^{s} \sum_{k=1}^{s} g_{ik} a_i a_k$$  \hspace{1cm} (III-22)

where $S$ is the entropy of the system (to within a time independent constant), and if further, the forces $X_k$ have so been chosen that

$$X_k = \left( \partial S / \partial a_k \right) = \sum_{i=1}^{s} g_{ik} a_i$$  \hspace{1cm} (III-23)

then, the matrix $L_{ik}$ of the phenomenological coefficients (in Equation (III-14) is symmetric."

Taking the time derivative of Equation (III-22).

$$\dot{S} = \sum_{i=1}^{s} \sum_{k=1}^{s} g_{ik} \dot{a}_i a_k$$  \hspace{1cm} (III-24)

and substituting Equations (III-21) and (III-23), we obtain the bilinear form of the entropy production as in Equation (III-13). Thus the entropy production equation follows as a necessary consequence of the proper identification of fluxes and forces, but it alone is not sufficient to guarantee the validity of Equations (III-21) and (III-22).

The fundamental statement of the ORR as given above is of course generally recognized\(^{(17, 18, 21)}\). It is not, however, possible to demonstrate the validity of Equations (III-21)

*Other cases may be treated (see de Groot and Mazur\(^{(18)}\), pg. 35 ff).
and (III-22) from the phenomenological theory, and we must assume that the fluxes and forces satisfy these relations. It is on this basis that Fitts, for example, lists the ORR as a "postulate" rather than a "theorem." The validity of Postulate III for diffusion and heat flow is based on statistical-mechanical theories of transport so that we may consider the treatment given in the preceding section as well-founded from a microscopic viewpoint. (F40)

**Experimental Diffusion Coefficients**

In this section we consider the relationship between experimentally measured diffusion coefficients and the phenomenological theory. In particular, we shall derive the necessary restrictions on the values of the practical coefficients which are a consequence of nonequilibrium thermodynamics.

**Definition of the Practical Coefficients**

Consider that we construct a diffusion couple from two homogeneous alloys and anneal this sample for a certain length of time at a certain temperature. We may always (in solids, at least) select the dimensions, times and temperatures so that the total extent of measurable diffusion is much less than the sample dimensions, and we may therefore consider this to be an infinitely long sample. We measure the composition profile along the diffusion direction and apply a suitable analysis (see later section) to compute the diffusion coefficients.

In this process we are in effect measuring physical distances along the sample with respect to fixed "laboratory"
or "cell" coordinates, and we may take the origin of these coordinates to be fixed at one end of the sample. If there is no change in the total volume of the sample during diffusion (i.e., no volume change on mixing, hence constant partial molar volumes) then the cell-fixed reference is equivalent to the volume-fixed reference frame (diffusion relative to the local center-of-volume). If there is a change in the total volume, we may correct the cell-fixed reference to the volume-fixed reference in the manner described by Kirkwood, Baldwin et al (46) or Sauer and Freise (66).

Accordingly, we define the experimental or practical coefficient matrix by

\[ J^V = - \sum_{k=1}^{s-1} D^S_{ik} \frac{\partial c_k}{\partial x} \]  

(III-25)

Here \( J^V \) is the molar flux relative to the volume-fixed reference which is defined by

\[ \sum_{i=1}^{s} \nabla_i J^V_i = 0 \]  

(III-26)

\( \nabla_i \) being the partial molar volume, and \( c_k \) is the molar density, (gram atoms per unit volume in the case of alloy diffusion).

The superscript \( s \) on the coefficient indicates that we have eliminated component \( s \) from the equations. This is accomplished using the relations

\[ \sum_{k=1}^{s} c_k \nabla_k = 1 \]  

(III-27)

and

\[ \sum_{k=1}^{s} c_k d\nabla_k = 0 \]  

(III-28)
(at constant pressure and temperature). These together give us that

\[ \sum_{k=1}^{s} \frac{V_k}{\mathcal{V}_k} \frac{\delta c_k}{\delta x} = 0 \quad (\text{III-29}) \]

**Onsager Relations for the D-Matrix**

The L-matrix coefficients for the volume-fixed reference are defined by

\[ J^V_i = - \sum_{k=1}^{s-1} L^V_{1k} \frac{\delta \mu^V_k}{\delta x} \quad (i=1, \ldots, s-1) \quad (\text{III-30}) \]

Since the chemical potential may be completely specified in terms of \( s-1 \) concentrations, we may write

\[ \frac{\delta \mu^V_k}{\delta x} = \sum_{m=1}^{s-1} f_{km} \frac{\delta c_m}{\delta x} \quad (\text{III-31}) \]

where we have introduced the notation

\[ f_{km} = \left( \frac{\partial \mu^V_k}{\partial c_m} \right)_{c_i \neq c_m, c_s} \quad (\text{III-32}) \]

Substitution of Equation (III-31) into (III-30) and comparison with Equation (III-25) yields

\[ D^S_{ik} = \sum_{m=1}^{s-1} L^V_{im} f_{mk} \quad (i=1, \ldots, s-1) \quad (\text{III-33}) \]

From the previous summary of the requirements for the ORR, it is apparent that the volume-fixed coefficients defined by Equation (III-30) are not appropriate. The forces and fluxes are both linearly dependent because of Equation (III-26) and the Gibbs-Duhem relation

\[ \sum_{k=1}^{s} c_k \frac{\delta \mu^V_k}{\delta x} = 0 \quad (\text{III-34}) \]
The entropy production should properly be written from Equation (III-17) as

\[
T\sigma = - \sum_{i=1}^{s-1} J_i^V \cdot \left( \frac{\partial \mu_i}{\partial x} + \frac{V_i}{V_s} \sum_{k=1}^{s-1} \frac{c_k}{c_s} \frac{\partial \mu_k}{\partial x} \right)
\]

(III-35)

which gives

\[
J_i^V = - \sum_{k=1}^{s-1} L_{ik} \left( \frac{\partial \mu_k}{\partial x} + \frac{V_k}{V_s} \sum_{m=1}^{s-1} \frac{c_m}{c_s} \frac{\partial \mu_m}{\partial x} \right)
\]

(III-36)

and from Equation (III-20),

\[
L_{ik}^V = L_{ik} + \frac{c_k}{c_s} \sum_{m=1}^{s-1} \frac{V_m}{V_s} L_{im}
\]

(III-37)

The matrix \(L_{ik}^V\) should be symmetric by virtue of Postulate III given previously, but the matrix \(L_{ik}\) will not be except for very dilute solutions \((c_1 \ll c_s)\) where the two sets are approximately identical. To develop an equation by which we may examine the ORR, we solve Equations (III-33) and (III-37) for the \(L_{ik}\) and impose the symmetry conditions in terms of the practical coefficients. The resulting ORR for a ternary system \((c_2)\) are:

\[
aD_{12} + bD_{22} = cD_{11} + dD_{21}
\]

(III-38)

\[
ad - bc \neq 0
\]

where

\[
a = \left(1 + \frac{c_1V_1}{c_3V_3}\right) f_{11} + \frac{c_2V_1}{c_3V_3} f_{21}
\]

\[
b = \frac{c_1V_2}{c_3V_3} f_{11} + \left(1 + \frac{c_2V_2}{c_3V_3}\right) f_{21}
\]
\[ c = \left( 1 + \frac{c_1 v_1}{c_3 v_3} \right) f_{12} + \frac{c_2 v_1}{c_3 v_3} f_{22} \]

\[ d = \frac{c_1 v_2}{c_3 v_3} f_{12} + \left( 1 + \frac{c_2 v_2}{c_3 v_3} \right) f_{22} \]

Other Thermodynamic Relations

Kirkaldy, Weichart and Zia-Ul-Haq\textsuperscript{(44)} have derived other properties of the D-matrix. These are inequality relations which result from the second law of thermodynamics and the criteria for stability of solutions. The conclusions are given here without elaboration.

The second law which states that the internal entropy production be positive definite, requires that the Onsager L-matrix be positive definite. The stability conditions of a solution require that the Hessian of the Gibbs free energy,

\[ F_{ij} = \frac{\delta^2 F}{\delta N_i \delta N_j} = \frac{\delta^2 \mu_i}{\delta N_j} \]

\((N_i, N_j \text{ are mole numbers})\), also be positive definite. Kirkaldy et al. have shown that as a consequence of these conditions the eigenvalues of the D-matrix must be real and positive.

If the coefficients are constant, the necessary and sufficient conditions for a ternary system are

\[ D_{11} + D_{22} \geq 0 \]

\[ D_{11}D_{22} - D_{12}D_{21} \geq 0 \]

\[ (D_{11} + D_{22})^2 \geq 4(D_{11}D_{22} - D_{12}D_{21}) \]

It is interesting to note that there is no basic requirement that each direct coefficient be positive, only the sum must
be so.

Sundelöf\(^{(70)}\) has examined the behavior of the D-matrix at the critical point of mixing. Based on the requirement that the determinant of chemical potential derivatives vanishes at the critical point, i.e.,

\[ |f_{ik}| = 0 \quad (i, k=1,\ldots,s-1) \]

it follows that the determinant of the practical coefficients also vanishes:

\[ |D^S_{ik}| = 0 \quad (i, k=1,\ldots,s-1) \]

This holds for coefficients which may be defined for any flux reference frame. In addition, Sundelöf shows that the fluxes individually vanish at the critical point. This conclusion is not a necessary condition and is discussed further in Chapter V.

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**Atomic Mobilities and Intrinsic Diffusion**

The following discussion relating the multicomponent diffusion coefficients to "intrinsic" coefficients and atomic mobilities is developed more extensively in a recent paper by
Ziebold and Cooper(77).

Darken(14) proposed the concept of "intrinsic" diffusion to explain the motion of markers in solid diffusion samples of binary systems. Subsequently, Bardeen and Herring(4) and LeClaire(48) developed phenomenological equations for vacancy diffusion and extended Darken's analysis to multicomponent systems. They assumed that the flux of one component relative to a fixed lattice could be written without including cross effects between the diffusing species when the driving forces are taken to be the chemical potential gradients. This assumption has been examined from statistical models of diffusion by Bardeen and Herring(4), Le Claire(49), and Kirkaldy et al.(43, 47), among others. It is concluded that the supposition of negligible interactions between different species, while not exact, is nevertheless a close approximation, especially for dilute solutions. Oishi(60) has extended Darken's equation for ideal ternary solutions, showing how the phenomenological coefficients are related to the self-diffusion coefficients, and Cooper(12) has treated multicomponent diffusion in non-ideal solutions and ionic solutions in the same manner.

In the following paragraphs, the proposal of Bardeen and Herring is extended to multicomponent diffusion for fluxes relative to the local center of volume, which is the usual experimental frame of reference. We will show that the extension of the mobility model to the volume-fixed frame gives rise to cross coefficients in the fundamental matrix which are necessary to cancel the net volume flux. It will
be seen that these coefficients are consistent with the Onsager reciprocal relations and with the experimental data of Kirkaldy (for dilute solutions). Finally, we shall derive the analogous Darken equations for general multicomponent systems and comment on the implications of the model for measurements of multicomponent diffusion.

**Fundamental Coefficients and Mobilities**

On the assumption that there is no interaction between different diffusing species except to produce a net mass flow relative to the local center of volume, we may write the molar flux of one component relative to the local center of volume as:

\[-J_i^V = c_i B_i \nabla \mu_i + c_i u \quad (i=1, \ldots, s) \quad (III-39)\]

where $B_i$ is the atomic mobility, and $u$ is the lattice velocity* relative to the local center of volume. Since we have chosen our coordinate reference frame to be the local center of volume, then the net volume flux must be zero; that is, we apply Equation (III-26):

\[\sum_{i=1}^{s} \nabla_i J_i^V = 0 \quad (III-26)\]

We use this condition to eliminate the relaxation velocity from Equation (III-39), and by the application of the Gibbs-Duhem relation to reduce the expression to independent

---

*We use the term "lattice velocity" because this is a commonly used expression for crystalline metals. However, the concept is more generally applicable, and $u$ is sometimes called the "relaxation velocity" or the net mass flow.
potential gradients only, we obtain:

\[-J^V_i = \sum_{k=1}^{s-1} L^V_{ik} \nabla \mu_k \quad (i=1, \ldots s-1) \quad (III-40)\]

where the matrix of fundamental coefficients in the volume-fixed reference is related to the mobilities by

\[L^V_{ik} = \delta_{ik} c_k B_k - c_k c_k (\nabla B_k - \nabla S) \quad (i, k=1, \ldots s-1) \quad (III-41)\]

\[\delta_{ik}\] being the Kronecker delta function. The response of component \(i\) to the gradient force of component \(k\) thus depends on the mobility of \(k\) (since our net volume flux must be zero) and of the "solvent" \(s\) (since we have taken \(\mu_s\) to be dependent on all the others). The cross coefficients arise solely from the selection of frames of reference but cannot be taken to be zero unless \(\nabla B_k = \nabla B_s\) for all \(k\), which is unlikely, or unless the solution is very dilute \((c_i, c_k \ll c_s)\).

To test the Onsager reciprocal relations we must choose the proper combination of fluxes and forces. One procedure, which is somewhat different than that of the preceding section but which is equally valid, is to use a solvent-fixed reference frame (diffusion fluxes are measured relative to the component \(s\)), and the individual chemical potential gradients. The coefficients for this system are defined by:

\[-J^S_i = \sum_{k=1}^{s-1} L^S_{ik} \nabla \mu_k \quad (i=1, \ldots s-1) \quad (III-42)\]

where \(J^S_i\) is now the molar flux of component \(i\) relative to the "solvent" \(s\). The relation between the coefficients in the
volume-fixed and solvent-fixed systems may be shown to be:

\[ L^S_{1k} = L^V_{1k} + \frac{c_1}{c_s} \sum_{m=1}^{s-l} \bar{V}_m L^V_{m,k} \quad (i,k=1,\ldots,s-1) \]  

(III-43)

The two sets of coefficients are identical only for very dilute solutions. Substituting Equation (III-41) into (III-43) relates the solvent based coefficients to the mobilities as:

\[ L^S_{1k} = \delta_{ik} c_k B_k + c_1 c_k B_s/c_s \quad (i,k=1,\ldots,s-1) \]  

(III-44)

It is immediately apparent that the matrix of coefficients is symmetrical, that is, \[ L^S_{1k} = L^S_{k1} \], as required by the Onsager relations. This is to be expected since the assumption made in Equation (III-39) is that, relative to the lattice-fixed frame, the cross coefficients of the dependent matrix are all zero. Thus in the lattice-fixed frame Onsager's relations are trivially satisfied, and it has been shown\(^{77}\) that if symmetric coefficients can be found for the dependent forces and fluxes in any reference system, then the reciprocal relations are satisfied.

**Practical Coefficients and Mobilities**

The matrix of practical coefficients defined by

\[ -J^V_i = \sum_{k=1}^{s-l} D^S_{1k} \bar{V}_c_k \quad (i=1,\ldots,s-1) \]  

(III-25)

is related to the fundamental matrix by

\[ D^S_{1k} = \sum_{m=1}^{s-l} L^V_{1m} f^m_{mk} \quad (i, k=1,\ldots,s-1) \]  

(III-33)

as we have shown before. Substituting Equation (III-41) into
(III-25) we obtain

\[ D_{ik}^S = \sum_{m=1}^{s-1} \left[ \delta_{im} B_m - c_i (V_m B_m - V_s B_s) \right] c_m f_{mk} \]

\[ (i, k=1, \ldots, s-1) \quad (III-45) \]

This is the multicomponent extension of "Darken's equation" for binary diffusion. ("Darken's equation" was actually written much earlier by Onsager and Fuoss.(63).) It will be more easily recognized if we adopt the common assumption that the integral molar volume is everywhere constant. (This requires constant and equal partial molar volumes.) For this case, Equation (III-45) reduces to

\[ D_{ik}^S = \sum_{m=1}^{s-1} \left[ \delta_{im} B_m - n_i (B_m - B_s) \right] n_m f_{mk} \sqrt{V} \]

\[ (III-46) \]

where \( n_i \) and \( n_m \) are atom fractions and \( V \) is the molar volume. Introducing the auxiliary definitions

\[ D_i \equiv B_i RT \]

\[ (III-47) \]

and

\[ g_{ik} \equiv \left( \frac{\partial \log a_i}{\partial \log n_k} \right) n_m = n_k, n_s \]

\[ (III-48) \]

in which \( a_i \) is the activity of component \( i \), we obtain

\[ D_{ik}^S = \sum_{m=1}^{s-1} \left[ \delta_{im} D_m - n_i (D_m - D_s) \right] \frac{n_m}{n_k} g_{mk} \]

\[ (III-49) \]

the usual form in which "Darken's equation" is expressed.

(The complete statement of Equation (III-49) for a ternary system is given in Appendix A).

**Intrinsic Diffusion Coefficients**

Kirkaldy(33), and Guy and Smith(26), have defined "intrin-
sic" coefficients, $i_k$, for multicomponent systems as those which describe diffusion relative to the lattice:

$$-J^V_1 = \sum_{k=1}^{s-1} \mathcal{J}_{ik} \nabla c_k + c_1 V$$ (III-50)

where $V$ would be measured as the velocity of Kirkendall markers. This is a linear extension of Darken's equation for binary systems. Eliminating the marker velocity $V$ by summing the volume fluxes to zero, we obtain:

$$-J^V_1 = \sum_{k=1}^{s-1} \left[ \sum_{m=1}^{s} (\delta_{im} - c_1 \nabla_m) \mathcal{G}_{mk} \right] \nabla c_k$$ (III-51)

$$\quad (i=1, \ldots s-1)$$

We may determine the value of these intrinsic coefficients under the assumption that the basic interaction between diffusing species is all accounted for by the lattice velocity, that is, by using the model developed in the preceding sections. By comparing Equations (III-25) and (III-51), it is apparent that:

$$D_{ik} = \sum_{m=1}^{s} (\delta_{im} - c_1 \nabla_m) \mathcal{G}_{mk}$$ (I, k=1, \ldots s-1) (III-52)

Comparison of Equations (III-45) and (III-52) indicates that the intrinsic coefficients may be expressed in terms of the atomic mobilities and thermodynamic factors:

$$\mathcal{G}_{ik} = c_i B_i f_{ik}$$ (III-53)

Comparing Equations (III-46) and (III-53) we see that the intrinsic coefficients are identical to the dilute solution approximation of the practical diffusion coefficients. This is consistent with Darken's use of intrinsic coefficients for binaries.
The Number of Independent Coefficients

The relations developed above are most significant when we consider the number of independent coefficients necessary to describe multicomponent diffusion. For a system of $s$ components there are $\frac{s(s-1)}{2}$ independent coefficients if we utilize the ORR. On the other hand, the model which is based on atomic mobilities relates the diffusion coefficients to $s$ mobilities so that there can be only $s$ independent coefficients (as suggested by Darken\(^{(16)}\) in 1950).

Consider the following values:

$$s = 2 \ 3 \ 4$$
$$s(s-1)/2 = 1 \ 3 \ 6$$

For a binary system only one fundamental coefficient is defined, hence the two mobilities must be related (as they are by Darken's equation). For a ternary system there are three mobilities and three diffusivities, and each set is completely determined by the other. For the same reason, however, it is impossible to test the mobility model for a ternary system from interdiffusion measurements alone. A direct test can be made by measuring the self-diffusion coefficients with tracer methods if we identify the tracer coefficients with the $D_1$ as is usually done\(^{(69)}\), that is

$$D_1^* = D_1 = B_1RT \quad (\text{III-54})$$

and apply them to Equation (III-45) or (III-49). The quaternary system, for which there are six coefficients and only four mobilities, requires that there be two additional relations among the practical coefficients; this is the
lowest order system for which there can be a direct test by chemical diffusion measurements.

We also note that Guy and Smith's proposal requires $s(s-1)$ intrinsic diffusion coefficients and they presumed them all to be independent. It becomes clear from Equation (III-50) that the intrinsic coefficients are related through thermodynamic quantities, specifically $f_{1k}$. When these have been measured, it is unnecessary to obtain the double marker movements which they suggest to describe ternary diffusion.

Critique of the Mobility Model

We have discussed here a model for multicomponent diffusion in which the primary diffusion is described in terms of atomic mobilities, and cross effects between different diffusing species arise from the requirement that the net volume flux vanish. The assumptions necessary to the development of this model are first, that the relaxation velocity always be great enough to cancel the net flux; second, that the mobilities remain unchanged by the introduction of chemical gradients; and third, that there is no coupling mechanism between species other than that caused by the relaxation velocity.

The first assumption is equivalent to assuming for substitutational diffusion that the vacancy flux is large enough to compensate for differences in the atomic mobilities, that is, there is no resistance to the production or disappearance of vacancies. (Hydrodynamic flow is an alternative source of a relaxation velocity that is more likely for non-crystalline
substances.) The second assumption is necessary for all treatments of diffusion, and in the usual cases it causes no difficulty. It would become a poor approximation only at extremely steep gradients.

The third assumption, that of zero cross coupling in the lattice-fixed frame, requires further comment. First of all, we must distinguish between the cases of interstitial and substitutional diffusion. Kirkaldy and Purdy(43) present a derivation of the coefficients for ternary systems in which one solute is interstitial and the other is substitutional. Their treatment, which follows the statistical analysis of Seitz(68), shows that neglect of the off-diagonal fundamental coefficients in the lattice-fixed frame is equivalent to considering only nearest neighbor interactions among the solutes and first-order terms in a Taylor's series expansion of the flux as a function of the lattice spacing. On this basis they show that

\[
\frac{D_{12}}{D_{11}} \approx 6 \frac{E_{12} - E_{31}}{kT} n_1
\]

\[
\frac{D_{21}}{D_{22}} \approx 6 \frac{E_{12} - E_{31}}{kT} n_2
\]

(III-55)

where \(E_{ij}\) are the nearest neighbor interaction energies(42) and \(n_i\) are the atom fractions. (Component 1 is interstitial.)

This result may be expected to hold quite well for diffusion of the interstitial component which is moving via different sites than the substitutional components, and indeed there is considerable experimental verification of the first
of Equations (III-52), as discussed in Chapter II. For the
substitutional component, however, the second of Equations
(III-52) should be limited to dilute solutions. A further
consideration of substitutional diffusion is available from
Lane and Kirkaldy(47). On the basis of transition-state
kinetics applied to the vacancy diffusion model, the flux of
component \( _1 \) relative to a fixed lattice is

\[
J^L_1 = -c_1 \frac{\lambda^2 P_1}{RT} \nabla \mu_1
\]

(III-56)

where \( \lambda \) is the lattice spacing and \( P_1 \) is the average jump
frequency of \( _1 \) atoms. This is the relation that was assumed
_a priori_ in writing Equation (III-39) if we identify the
mobility with \( \lambda^2 P_1/RT \). Le Claire(49) examines the diffusion
process with random walk calculations, and his conclusion is
again that the off-diagonal coefficients will be zero.

The developments outlined above assume that atom-vacancy
interchanges are not correlated and we must modify the con-
cclusions when we consider that the direction of one jump of
an atom is not independent of the direction of its previous
jumps. Based on the random walk model, Le Claire(49) states
that correlation of jumps will appear only as a modification
of the diagonal coefficients; it can in no way appear wholly
in cross-terms. This is contrary to the conclusion of Bardeen
and Herring(4) that the whole correlation effect would be
contained in cross terms. Lane and Kirkaldy(47) suggest that
this effect would introduce nonzero, off-diagonal coefficients
which could be derived from their analysis of diffusion by an
exchange mechanism. Finally, Manning(51), who considers in
detail the effect of correlated motion on binary diffusion, concludes that the vacancy flow will introduce cross coefficients as well as altering the direct terms.

The experimental test of whether the off-diagonal, lattice-fixed coefficients are actually zero or not will be difficult. It will require not only diffusion and activity data, but also the measurement of marker movement so that the coefficients may be related to the fixed lattice framework. It will be shown in the next section that the multicomponent coefficients can be calculated only at certain points in a diffusion couple and the chances of having markers at the proper location are almost zero. Guy and Smith(26) have suggested the use of incremental couples for marker studies, but it has been pointed out by Kirkaldy(37) that in order to see measurable cross effects the terminal composition step must be as large as possible. Hence the accurate measurement of marker motion and the accurate measurement of cross-coefficients seem to be mutually exclusive.

It seems that the only practicable approach is to measure the self-diffusion coefficients by means of radioactive tracers and to test the validity of Equation (III-45). This requires the identification of the mobility with the tracer diffusion coefficient, Equation (III-53), and in view of the recent criticism of this relation by Vignes and Birchenall(72) the situation becomes even less hopeful. One may be forced to quaternary systems where specifying the six practical coeffi-
cients in terms of four mobilities yields two relations which may be tested solely by chemical diffusion measurements.

**Solutions of the Diffusion Equations**

In this section mathematical solutions of the multicomponent diffusion equations will be developed with emphasis on solutions from which the diffusion coefficients may be evaluated. In general, the coefficients are dependent on the composition, particularly where samples include a wide composition range. Solutions for constant coefficients are of interest, however, since they yield at least a qualitative picture of the diffusion path configuration. The constant coefficient solutions are strictly applicable to samples involving only small changes in composition.

With the infinite diffusion sample, we measure the component distributions after a certain diffusion time. The basic equation to be exploited is Fick's second law, the continuity equation, which states that (for one-dimensional flow)

\[
\frac{\partial c_i}{\partial t} + \frac{\partial J_i}{\partial x} = 0
\]  

(III-57)

Utilizing the expressions for diffusion flux in a multicomponent system we have a set of equations

\[
\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left[ \sum_{k=1}^{s-1} D_{ik} \frac{\partial c_i}{\partial x} \right] \quad (i=1, \ldots, s-1) \]  

(III-58)

Integration of these equations to solve for the molar density may be performed either if we take the coefficients to be
constant or if we suitably arrange the boundary conditions so that the equation may be transformed to an ordinary differential equation.

**Constant Coefficients**

The continuity equations for a ternary system under the condition of constant coefficients are

\[
\frac{\partial c_1}{\partial t} = D_{11} \frac{\partial^2 c_1}{\partial x^2} + D_{12} \frac{\partial^2 c_2}{\partial x^2} \tag{III-59}
\]

\[
\frac{\partial c_2}{\partial t} = D_{21} \frac{\partial^2 c_1}{\partial x^2} + D_{22} \frac{\partial^2 c_2}{\partial x^2}
\]

Fujita and Gosting\(^{(23)}\) and Kirkaldy\(^{(32)}\) have solved these equations for the common boundary conditions of an initial step change in concentration in a sample which is infinite in extent, that is

\[
\begin{align*}
\text{for } t &= 0 \quad \begin{cases} 
  c_1 = c_{1}^{-}, c_2 = c_{2}^{-} \text{ for } x < 0 \\
  c_1 = c_{1}^{+}, c_2 = c_{2}^{+} \text{ for } x > 0
\end{cases} \tag{III-60} \\
\text{for } t &> 0 \quad \begin{cases} 
  c_1 = c_{1}^{-}, c_2 = c_{2}^{-} \text{ for } x = -\infty \\
  c_1 = c_{1}^{+}, c_2 = c_{2}^{+} \text{ for } x = +\infty
\end{cases}
\end{align*}
\]
The solution for constant coefficients subject to these boundary conditions is:

\[ c_1 = \overline{c}_1 + A_{11}\text{erf}\left(\frac{x}{2\sqrt{u_1}t}\right) + A_{12}\text{erf}\left(\frac{x}{2\sqrt{u_2}t}\right) \]

\[ c_2 = \overline{c}_2 + A_{21}\text{erf}\left(\frac{x}{2\sqrt{u_1}t}\right) + A_{22}\text{erf}\left(\frac{x}{2\sqrt{u_2}t}\right) \]  \hspace{1cm} (III-61)

in which

\[ A_{11} = \frac{1}{2\pi} \left[ D_{12}^3 \Delta c_2 - (D_{22}^3 - D_{11}^3 - D') \Delta c_1 / 2 \right] \]

\[ A_{12} = (\Delta c_1 - 2A_{11}) / 2 \]

\[ A_{21} = \frac{1}{2\pi} \left[ D_{21}^3 \Delta c_1 - (D_{11}^3 - D_{22}^3 - D') \Delta c_2 / 2 \right] \]

\[ A_{22} = (\Delta c_2 - 2A_{21}) / 2 \]

\[ u_1 = D_{11}^3 - (D_{11}^3 - D_{22}^3 - D') / 2 \]

\[ u_2 = D_{22}^3 + (D_{11}^3 - D_{22}^3 - D') / 2 \]

\[ D' = \sqrt{(D_{11}^3 - D_{22}^3)^2 + 4D_{12}^3D_{21}^3} \]

\[ \overline{c}_1 = (c_1^+ + c_1^-) / 2 \]

\[ \overline{c}_2 = (c_2^+ + c_2^-) / 2 \]

\[ \Delta c_1 = c_1^+ - c_1^- \]

\[ \Delta c_2 = c_2^+ - c_2^- \]

Castleman and Froot(6) have discussed certain restrictions on the coefficient values which are necessary for non-negative solutions of the above equation. Note that the solution is similar to the familiar expression for binary systems except that sums of error functions are involved. Kirkaldy has
shown(34) that this is quite generally true for any set of boundary conditions. The statement of his formal solution is that, "if \( c = f(x,y,z,Dt) \) is a solution of the binary diffusion equation \( \frac{\partial c}{\partial t} = D\nabla^2 c \) for a given boundary condition, then

\[
c_i = a_{i0} + \sum_{k=1}^{s-1} a_{ik}f(x,y,z,u_k t) \tag{III-62}
\]

with

\[
u_k = \sum_{j=1}^{s-1} D_{ij} a_{jk}/a_{ik}
\]

is a solution of \( \frac{\partial c_i}{\partial t} = \sum_{k=1}^{s-1} D_{ik} \nabla^2 c_k \) for the \( i \)-th component of an \( s \)-component system subject to the same formal boundary condition." This facilitates the solution for other boundary conditions, for example the thin plane source which is often employed in tracer diffusion.

Use of Equation (III-61) to evaluate the coefficients involves a trial and error selection of values until a fit is obtained. An alternate approach given by Baldwin, Dunlop and Gosting(2) makes use of moments of the concentration gradients. The \( r \)-th moment of the gradient of component \( i \) at time \( t \) is defined as

\[
(m_r)_i \equiv \frac{1}{c_i^+ - c_i^-} \int_{-\infty}^{\infty} x^r \frac{\partial c_i}{\partial x} \, dx = \frac{1}{c_i^+ - c_i^-} \int_{c_i^-}^{c_i^+} x^r \, dc_i \tag{III-63}
\]

for the infinite couple. Using the boundary conditions given in Equation (III-60), the odd moments vanish; this condition defines the origin of the \( x \) coordinate when applied to the first moment. We compute the coefficients from graphical
evaluations of the second and fourth moments and the relations:

\[
D_{11}^3 t = \frac{(1/2)(m_2)_1(m_2)_2 - (1/6)(m_4)_1}{(m_2)_2 - (m_2)_1}
\]  
(III-64)

\[
D_{12}^3 t = \frac{(1/6)(m_4)_1 - (1/2)(m_2)_1(m_2)_1}{(m_2)_2 - (m_2)_1} \left( \frac{c_1^+ - c_1^-}{c_2^+ - c_2^-} \right)
\]

Similar expressions for \(D_{22}\) and \(D_{21}\) are obtained by interchanging the subscripts.

As stated earlier, the assumption of constant coefficients is approximately correct only when incremental couples are used. However, they also provide a useful estimation of the concentration paths at the ends of a sample where the terminal compositions are approached. Differentiating Equations (III-61) with respect to \(x\) gives

\[
\frac{\partial c_1}{\partial x} = \frac{A_{11}}{\sqrt{\pi u_1 t}} e^{-x^2/4u_1 t} + \frac{A_{12}}{\sqrt{\pi u_2 t}} e^{-x^2/4u_2 t}
\]

\[
\frac{\partial c_2}{\partial x} = \frac{A_{21}}{\sqrt{\pi u_1 t}} e^{-x^2/4u_1 t} + \frac{A_{22}}{\sqrt{\pi u_2 t}} e^{-x^2/4u_2 t}
\]

(III-65)

As \(x\) becomes much larger in magnitude than \(u_1 t\) and \(u_2 t\) the exponential quantities may be factored out with the approximate result that

\[
\frac{\partial c_2}{\partial c_1} = \frac{\partial c_2}{\partial x} \frac{\partial x}{\partial c_1} = \frac{A_{21}\sqrt{u_2} + A_{22}\sqrt{u_1}}{A_{11}\sqrt{u_2} + A_{12}\sqrt{u_1}} = \frac{\Delta c_2}{\Delta c_1} \left( \frac{1 + \frac{2A_{21}}{\Delta c_2} \left( \sqrt{u_2} / u_1 - 1 \right)}{1 + \frac{2A_{11}}{\Delta c_1} \left( \sqrt{u_2} / u_1 - 1 \right)} \right)
\]

(III-66)
which is exact at the limits \( x = \pm \infty \). Note first of all that the slopes are identical at either terminal composition. In fact, the solution for constant coefficients is symmetrical about \( x = 0 \) so that this is true for any symmetrical positive and negative values of \( x \) as is apparent from Equations (III-65).

If we restrict our attention to terminal conditions where one component is zero (that is, composition paths which begin on a binary side) then we may utilize Equation (III-66) to estimate coefficients which are otherwise inaccessible. Along the binary 1-3 side \( c_2 \) is everywhere zero. Since the flux of component 2 must be zero it follows that \( D_{21}^3 \) is also zero along this side. Further, by analyzing binary couples of components 1 and 3 we may evaluate \( D_{11}^3 \) which is simply the interdiffusion coefficient for the binary system. Thus we know two of the four coefficients. We may then make use of Equation (III-66) to estimate the remaining coefficients, \( D_{12}^3 \) and \( D_{22}^3 \), from the terminal slopes \( \partial c_2 / \partial c_1 \) for two samples which originate at the same point. In similar fashion, we may estimate \( D_{21}^3 \) and \( D_{11}^3 \) along the binary 2-3 side.

**Variable Coefficients**

Computation of concentration-dependent coefficients from experimental composition profiles for multicomponent systems may be carried out by an extension of the Matano analysis\(^{\text{(53)}}\) which has often been applied to binary diffusion data. This was suggested by Kirkaldy\(^{\text{(31)}}\) and Mason\(^{\text{(52)}}\) and discussed further by Kirkaldy, Lane and Mason\(^{\text{(40)}}\). Quite commonly\(^{\text{(13,69)}}\), the Matano analysis is based on the assumption that the
integral molar volume is constant throughout the sample, but Baluffi (3), Sauer and Freise (66), and Kirkwood, Baldwin et al. (46) have published general analyses wherein volume changes on mixing are considered. In the following paragraphs the Matano analysis is developed with the assumption of constant integral molar volume. The errors resulting from this simplification are discussed in a later section.

We consider a coordinate system originated at any plane within the sample. Considering the boundary conditions of Equation (III-60) with an initial discontinuity at some position \(x_o\), we may make the Boltzmann transformation to the single variable

\[
\lambda = (x-x_o)/\sqrt{t} 
\]  
(III-67)

The continuity equations are transformed to ordinary differential equations

\[
-(1/2)\lambda \frac{dn_1}{d\lambda} = \frac{d}{d\lambda} \left[ D_{11} \frac{dn_1}{d\lambda} + D_{12} \frac{dn_2}{d\lambda} \right] 
\]  
(III-68)

\[
-(1/2)\lambda \frac{dn_2}{d\lambda} = \frac{d}{d\lambda} \left[ D_{21} \frac{dn_1}{d\lambda} + D_{22} \frac{dn_2}{d\lambda} \right] 
\]

The composition variable has been changed to the atom fraction, \(n_1 = c_1/\sum c_i\), since we are considering that the partial molar volumes are constant and equal (i.e., constant integral molar volume).

Integrating with respect to \(\lambda\) and using the condition that the gradients are zero at the origin, we obtain

\[
\int_{n_1}^{n_2} \lambda dn_1 = -2 \left[ D_{11} \frac{dn_1}{d\lambda} + D_{12} \frac{dn_2}{d\lambda} \right] 
\]  
(III-69)
This gives
\[ \int_{n_1^-}^{n_1^+} \lambda dn_1 = 0 \quad (III-70) \]

Transforming back to the laboratory coordinates for some fixed time \( t \) we have
\[ -\frac{1}{2t} \int_{n_1^-}^{n_1^+} (x-x_0) dn_1 = D_{11} \frac{dn_1}{dx} + D_{12} \frac{dn_2}{dx} \quad (III-71) \]
and
\[ \int_{n_1^-}^{n_1^+} (x-x_0) dn_1 = 0 \quad (III-72) \]

From Equation (III-72) the position \( x_0 \) is found to be
\[ (n_1^+ - n_1^-)x_0 = \int_{n_1^-}^{n_1^+} x dn_1 \quad (III-73) \]

Similarly, from the second of Equations (III-68) we would obtain
\[ (n_2^+ - n_2^-)x_0 = \int_{n_2^-}^{n_2^+} x dn_2 \quad (III-74) \]

The agreement between the values of \( x_0 \) determined from these two equations provides an experimental check of the consistency of the composition data.

To evaluate the two coefficients, \( D_{11} \) and \( D_{12} \), from Equation (III-69) requires that we have two samples with different terminal compositions but with a common composition
somewhere in the diffusion zone. In other words, solutions may be obtained only at points of intersection of the composition paths. It is advantageous to handle Equation (III-69) in a modified form obtained by dividing both sides by $\frac{dn_1}{d\lambda}$.

Letting

$$\Phi_1 = -\frac{1}{2} \frac{d\lambda}{dn_1} \int_{n_1^-}^{n_1^+} \lambda dn_1$$

Equation (III-69) becomes

$$D_{11} + D_{12} \frac{dn_2}{dn_1} = \Phi_1$$

Equation (III-75)

Equation (III-76) becomes

$$D_{11} + D_{12} \frac{dn_2}{dn_1} = \Phi_1$$

The functions $\Phi_1$ and $\frac{dn_2}{dn_1}$ are determined graphically or numerically from the experimental curves.

Equation (III-76) provides an improved analysis of the data for two reasons. First, the functions $\Phi_1$ may be evaluated for the whole sample and then smoothed on a plot of $\Phi_1$ against $n_1$. Second, the function $\frac{dn_2}{dn_1}$ may be determined from the ratio of gradients taken from the $n_1^- - \lambda$ plots and checked against the value measured directly from the $n_1^- - n_2$ plot. In practice this latter graph provides smoothing of the composition data since no distance errors are involved when the compositions of all elements are analyzed simultaneously (as with the electron microanalyzer).

Equation (III-76) still involves the measurement of gradients $\frac{dn_1}{d\lambda}$ which are included in the function $\Phi_1$. An alternate solution is obtained by integrating Equation (III-76) over composition:

$$\int_{n_1^-}^{n_1^+} \Phi_1 dn_1 = -\frac{1}{2} \int_{n_1^-}^{n_1^+} \left[ \frac{d\lambda}{dn_1} \int_{n_1^-}^{n_1^+} \lambda dn_1 \right] dn_1$$

Equation (III-77)
Integration by parts of the right hand side of this expression gives
\[ -\lambda \int \Phi_1 dn_1 = \lambda \int \lambda dn_1 - \int \lambda^2 dn_1 = \Psi_1 \] (III-78)

The function \( \Psi_1 \) may often be slowly varying with composition, and the evaluation of \( \Phi_1 \) from
\[ \Phi_1 = -\frac{1}{2} \frac{d\Psi_1}{dn_1} \] (III-79)
rather than from Equation (III-75) would reduce the error incurred from the measurement of slopes. In addition, integrating the data before measuring the slopes should reduce the experimental scatter. The integral form of Equation (III-78) is particularly amenable to numerical analysis of the data with a digital computer.

Some thought was given in this work to the possibility of computer solution of the diffusion equations. In the preceding sections it has been shown that when the four coefficients are variable they may be evaluated only from pairs of couples and only at the single point of intersection on the composition plane. In order to measure the coefficients over any appreciable composition range a large number of samples is required. To make more efficient use of the experimental data it should be possible to approximate the coefficients with suitable composition functions and generate the composition curves. Comparison of the generated and measured curves then provides a means of adjusting the fit to obtain the desired interpolations. For practical purposes
this procedure would require the use of a computer.

Unfortunately, it is almost impossible a priori to select suitable composition functions for the diffusion coefficients. A search of the literature on binary diffusion has shown that, in the general case where composition is allowed to vary widely, the composition dependence of the diffusion coefficients may take almost any mathematical form. One might hope that the fundamental coefficients or the mobilities would be less extreme in their behavior and more easily adaptable to approximations. The difficulty here, of course, is the lack of thermodynamic data required to relate the measurable practical coefficients to the fundamental coefficients.

One particular requirement on the coefficient functionality which would be of use in this respect is that the cross-coefficients $D_{ik}^S$ must vanish on the binary side where $n_i = 0$ (70). As suggested by Mason (52), we might take $D_{ik}^S = d_{ik}n_i$, where $d_{ik}$ is a constant. This constant could be evaluated from the point solution at an intersection and then used to obtain a continuous solution for the diagonal coefficient $D_{ii}^S$ from the composition profile.

The generation of composition curves from assumed values of the coefficients could be done by adapting the analysis of Fujita (22) or of Philip (64) for semi-infinite couples (fixed surface composition). A solution for the infinite couple with initial composition discontinuity has been given by Kirkaldy, Lane, and Mason (40). Either approach
would involve iterative procedures to fit the generated curves to measured composition profiles. It is reported, however, that these computations converge rapidly so that an inordinate amount of computer time would not be required.
IV. EXPERIMENTAL MEASUREMENTS AND CALCULATIONS

Sample Preparation and Diffusion

Most of the materials used in this work were supplied on loan by Engelhardt Industries, Inc. They prepared by induction melting and casting four copper-gold alloys, four silver-gold alloys (20, 40, 60 and 80 weight percent for each series), and six ternary alloys. (The ternary alloys were used as calibration standards only.) The as-received materials were cold swaged and annealed for twenty-four hours or more at a temperature 50 to 75 degrees below the melting point to induce recrystallization and grain growth. Examination of polished sections indicated the grain diameter to be on the order of one-half millimeter (500 microns) or more after this treatment. Thus the undesirable interference of grain boundary diffusion should be negligible.

The alloys were prepared from high purity copper, silver and gold. Spectrographic analyses of these materials, given in Table 1, reveal only minor trace impurities, chiefly iron and calcium. The alloy compositions were determined in the as-cast condition and after swaging and annealing. The analyses given in Table 2 for the final materials were unchanged from those of the cast alloys. These analyses were made independently for the major constituents and indicate that the total impurity level is below 0.3 weight percent for the silver-gold alloys and below 0.05 weight percent for the copper-gold alloys. No evidence of segregation has been found by microanalysis of these materials.
Table 1.
Spectrographic Analysis of Copper, Silver, and Gold
(Analysis by Baker and Co., Inc.)

<table>
<thead>
<tr>
<th>Element</th>
<th>Report for</th>
<th>Element</th>
<th>Report for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ag</td>
<td>Au</td>
</tr>
<tr>
<td>Al</td>
<td>ft</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>As</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ca</td>
<td>st</td>
<td>st</td>
<td>st</td>
</tr>
<tr>
<td>Cd</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cr</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>t</td>
<td>st</td>
<td>st</td>
</tr>
<tr>
<td>Ga</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ir</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>t</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo</td>
<td>nr</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

st - strong trace
0 - not detected
nr - not reported
t - trace
ft - faint trace
Table 2.

Analysis of Binary Alloys after Swaging and Annealing

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Cu</th>
<th>Au</th>
<th>sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>5C</td>
<td>4.44</td>
<td>95.5</td>
<td>99.94</td>
</tr>
<tr>
<td>20C</td>
<td>20.18</td>
<td>79.82</td>
<td>100.00</td>
</tr>
<tr>
<td>40C</td>
<td>39.96</td>
<td>60.07</td>
<td>100.03</td>
</tr>
<tr>
<td>60C</td>
<td>59.92</td>
<td>40.12</td>
<td>100.04</td>
</tr>
<tr>
<td>80C</td>
<td>79.44</td>
<td>20.65</td>
<td>100.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Ag</th>
<th>Au</th>
<th>sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>5S</td>
<td>4.93</td>
<td>95.2</td>
<td>100.13</td>
</tr>
<tr>
<td>20S</td>
<td>19.58</td>
<td>80.17</td>
<td>99.75</td>
</tr>
<tr>
<td>40S</td>
<td>40.37</td>
<td>59.33</td>
<td>99.70</td>
</tr>
<tr>
<td>60S</td>
<td>59.30</td>
<td>40.58</td>
<td>99.88</td>
</tr>
<tr>
<td>80S</td>
<td>80.05</td>
<td>19.92</td>
<td>99.97</td>
</tr>
</tbody>
</table>
In addition to the 20, 40, 60 and 80 weight percent binary alloys supplied by Engelhardt Industries, a 5 weight percent alloy in each binary set was prepared by arc melting a ten gram button (melted three times) which was then cold rolled and annealed. It was suspected that these alloys might be somewhat inhomogeneous but duplicate analyses from extreme portions of the buttons agree to better than 0.2 weight percent. The average analysis is given in Table 2. Microanalysis of the actual pieces used in diffusion samples showed a minor segregation--on the order of a 5% (relative) fluctuation from the average over a 100 micron distance.

After swaging and annealing, the alloys were sectioned into discs approximately 3/8" diameter and 1/16 inch thick. These were polished metallographically down to Linde "B" alumina (0.01 micron) and assembled into diffusing couples. The sample list of couples is given in Table 3. The samples were actually diffused two at a time by assembling sandwiches of three discs (Table 4). The couples were bonded for two hours at 500°C in a vacuum while being held under mechanical pressure between bolted iron discs. Initially the bonds were examined metallographically, but subsequently it was found that inability to break the bond by hand was sufficient indication of a sound weld.

Some difficulty was experienced in diffusing the couples in which pure silver was against the 95%Au/5%Cu and the pure gold (samples 10 and 11). These couples showed sound bonds before diffusion, but they broke apart when sectioned for analysis after diffusion. It became evident from an examina-
Table 3.

**Assembly List of Diffusion Samples**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Code</th>
<th>at% Cu* on Cu side</th>
<th>at% Ag* on Ag side</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C/G</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>C/5S</td>
<td>100.0</td>
<td>8.65</td>
</tr>
<tr>
<td>3</td>
<td>C/20S</td>
<td>100.0</td>
<td>30.9</td>
</tr>
<tr>
<td>4</td>
<td>C/40S</td>
<td>100.0</td>
<td>55.4</td>
</tr>
<tr>
<td>5</td>
<td>C/60S</td>
<td>100.0</td>
<td>72.8</td>
</tr>
<tr>
<td>6</td>
<td>C/S</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>7</td>
<td>60C/S</td>
<td>82.3</td>
<td>100.0</td>
</tr>
<tr>
<td>8</td>
<td>40C/S</td>
<td>67.4</td>
<td>100.0</td>
</tr>
<tr>
<td>9</td>
<td>20C/S</td>
<td>44.0</td>
<td>100.0</td>
</tr>
<tr>
<td>10</td>
<td>5C/S</td>
<td>12.6</td>
<td>100.0</td>
</tr>
<tr>
<td>11</td>
<td>a/S</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>12</td>
<td>80C/80S</td>
<td>92.3</td>
<td>88.0</td>
</tr>
<tr>
<td>13</td>
<td>40C/40S</td>
<td>67.4</td>
<td>55.4</td>
</tr>
<tr>
<td>14</td>
<td>20C/20S</td>
<td>44.0</td>
<td>30.9</td>
</tr>
<tr>
<td>15</td>
<td>80C/40S</td>
<td>92.3</td>
<td>55.4</td>
</tr>
<tr>
<td>16</td>
<td>20C/40S</td>
<td>44.0</td>
<td>55.4</td>
</tr>
<tr>
<td>17</td>
<td>20C/5S</td>
<td>44.0</td>
<td>8.65</td>
</tr>
</tbody>
</table>

*Balance of composition on each side is gold.*
### Table 4.
**Diffusion Times and Temperatures**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Code</th>
<th>Time at Temp</th>
<th>Recorded Temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>hours $\sqrt{sec}$</td>
<td>average range</td>
</tr>
<tr>
<td>1</td>
<td>C/G/C</td>
<td>48.0 416</td>
<td>725.3 3.5</td>
</tr>
<tr>
<td>2,3</td>
<td>5S/C/20S</td>
<td>60.75 468</td>
<td>725.5 4.4</td>
</tr>
<tr>
<td>4,5</td>
<td>60S/C/40S</td>
<td>60.0 465</td>
<td>722.3 2.0</td>
</tr>
<tr>
<td>6</td>
<td>C/S</td>
<td>48.0 416</td>
<td>724.7 6.1</td>
</tr>
<tr>
<td>7,8</td>
<td>60C/S/40C</td>
<td>61.5 471</td>
<td>727.0 6.0</td>
</tr>
<tr>
<td>9</td>
<td>20C/S</td>
<td>48.0 416</td>
<td>727.4 5.0</td>
</tr>
<tr>
<td>10,11</td>
<td>5C/S/G</td>
<td>51.25 430</td>
<td>725.3 6.6</td>
</tr>
<tr>
<td>12,15</td>
<td>80S/80C/40S</td>
<td>48.0 416</td>
<td>724.8 6.3</td>
</tr>
<tr>
<td>13,16</td>
<td>40C/40S/20C</td>
<td>48.0 416</td>
<td>726.6 5.7</td>
</tr>
<tr>
<td>14,17</td>
<td>20S/20C/5S</td>
<td>48.0 416</td>
<td>722.9 4.8</td>
</tr>
</tbody>
</table>
tion of all the diffused samples that the porosity produced in the diffusion zone is increasingly prominent as the compositions approach the silver-gold binary. It is concluded that, although samples 10 and 11 could be diffused and sectioned while held in a picture frame, any data obtained from these samples would be essentially worthless because of the extensive porosity formation. Consequently, these samples have not been analyzed.

Diffusion times and temperatures are listed in Table 4. The samples were diffused in the vacuum furnace diagrammed in Figure 2. This furnace, which was originally constructed for activity measurements from a design by Clancy\(^9\), is advantageous since it permits placing a thermocouple directly in contact with the diffusion sample. In operation, the sample was placed in the tube with the furnace withdrawn, the system was flushed several times with purified helium and finally pumped down to about 5 x 10^{-5} \text{ mm Hg}. The furnace, which was at the desired temperature, was then moved over the sample. A typical recording from the thermocouple on the sample, Figure 3, indicates that the sample reached a steady temperature after about 30 minutes. Since diffusion times were always 48 to 60 hours this heating time is short. Cooling from temperature when the furnace was removed was made even faster by immediately flushing the tube with purified helium.

Temperature readings were taken periodically with a microvolt Rubicon potentiometer. The temperatures listed in Table 4 give the average of all readings and the range between
FIGURE 2. VACUUM DIFFUSION FURNACE
the minimum and maximum recorded values. In general the readings were within two degrees of the average and the ranges listed reflect isolated readings which probably include reading errors.

**Microanalysis of Samples**

**Instrumentation**

All measurements of the diffusion sample composition profiles were made with an Applied Research Laboratories (ARL) electron beam microanalyzer. The use of this instrument for analysis of copper-silver-gold diffusion samples has been described previously by the author\(^{(76)}\), and only the modifications which were made in the course of the present work will be described here. These modifications consisted of the installation of improved counting instrumentation so as to increase the sensitivity of the measurements.

The electron microanalyzer uses a focused, high energy beam of electrons to excite characteristic x-radiation from the sample being analyzed. It is ideally suited for examination of diffusion samples since the volume of material analyzed is on the order of a cubic micron \((10^{-12} \text{ cubic centimeters})\), and the sample may be traversed in small steps under the beam to generate the entire composition-distance profile. The ARL instrument has provision for simultaneous recording of three x-ray signals and has a beam diameter at the sample of about one micron. For x-ray analysis the area analyzed is somewhat larger than the incident beam because of electron diffusion
below the sample surface. In the present work the effective x-ray spot size is about three microns.

The sensitivity of the analysis depends entirely on the arrangement of the x-ray spectrometers and their associated instrumentation. In the ARL instrument as originally supplied, x-ray signals were recorded by collecting on a capacitor the charge produced from proportional detectors. This scheme is not amenable to energy discrimination of the x-rays nor to statistical analysis of the data. Furthermore, it is susceptible to noise since any pulse from the detector, no matter how small, will be accumulated into the integrated charge. These problems are reflected in a low-peak background ratio (ratio of x-ray line intensity to continuous spectrum background), particularly for the AgL and AuL lines used in the present work.

For these reasons it was decided to modify the ARL instrument by adding counting scalers with pulse height analyzers. Unfortunately, it was found that the signals from the ARL proportional detectors were too low to operate satisfactorily with the counting circuits, and new detectors had to be installed. Because space is limited in the x-ray spectrometers, point anode flow proportional detectors were designed. These detectors, described in Appendix C, provide a sufficiently large pulse to drive scaling equipment and have an energy resolution comparable to the original ARL detectors, but they definitely have a non-linear count rate dependence. Even when the count rate from a pure element
standard is limited to four or five thousand counts per second, the error due to non-linearity at 1000 cps (corresponding roughly to 20% composition) approaches ten percent. For the present work, experimental calibration curves have been used, and these will account for the counter error if the microanalyzer is adjusted so that the maximum intensity is always the same.

In spite of the difficulties encountered with detector non-linearity, the improvement in peak/background ratio, which has been made possible primarily by the addition of pulse height analyzers, is striking. The values listed in Table 5 are increased three times or more over those attained previously. The largest gain was made for the AgLα line which is up by a factor of five. Energy discrimination with a pulse height analyzer is most important for long wavelength lines where multiple order reflections of shorter lines contribute significantly to the background.

The detectability limits listed in Table 5 have been computed from the equation derived in Appendix D. The listed values represent the sampling procedure which has been followed in the analysis of diffusion samples; that is, three repeated measurements of sample and background with a 25 second point count on each. Although this is not as large a sample as one would take for trace analysis, the indicated detectability limits are quite low because of the large peak-background ratios. (The limiting values are computed for a confidence level of 95%)
Table 5.

Spectrometer Performance for Copper, Silver, Gold Analyses

<table>
<thead>
<tr>
<th>Line</th>
<th>Spectrometer</th>
<th>Peak Intensity*</th>
<th>Background Measured on</th>
<th>P/B Ratio</th>
<th>Detectable Limit, wt%**</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuKα</td>
<td>11&quot;, SiO₂</td>
<td>3600</td>
<td>Ni</td>
<td>630</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ag</td>
<td>570</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Au</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>AgLα</td>
<td>4&quot;, ADP</td>
<td>4500</td>
<td>Cu</td>
<td>150</td>
<td>0.064</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Au</td>
<td>200</td>
<td>0.096</td>
</tr>
<tr>
<td>AuLα</td>
<td>4&quot;, LiF</td>
<td>4500</td>
<td>Cu</td>
<td>260</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ag</td>
<td>150</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt</td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>

*ARL microanalyzer, 30KV, 0.05 microamperes specimen current on pure copper.

**See text for definition of detectability limit.
Calibration

As discussed previously by Ziebold and Ogilvie(78), several problems arise in converting the x-ray measurements to chemical composition. The origins of these difficulties are the interaction of the electron beam with the sample, the absorption of x-rays within the sample, and the secondary fluorescence of one element by x-ray emission from another element in the sample. The most reliable procedure for surmounting the problem is to measure a series of calibration standards of known chemical composition. Calibration curves for the copper-gold and silver-gold alloys are given in Table 6 and in Figure 4. In the table, $K$ is the standard intensity relative to the pure element intensity, both corrected for background. These curves were measured with the point anode detectors and include the effects of detector non-linearity. This is illustrated in the figures by comparison with curves previously obtained with the ARL detectors.

In addition to the eight binary alloys, six ternary alloys were used for calibration standards. Because some of these were two-phase or revealed microsegregation they were analyzed by enlarging the electron beam and transversing the sample while making a point count. This technique effectively measures the average composition. In the present case it was found to be satisfactorily reproducible. The ternary calibration values are given in Table 6. The calibration standards were measured a total of 35 times which was sufficient to establish reliable statistics of the sampling. The errors
Table 6.

Measured Relative Intensities for Calibration Standards.

(All values are corrected for background.)

Copper-Gold Alloys

<table>
<thead>
<tr>
<th>wt% Cu</th>
<th>100K (CuKα)</th>
<th></th>
<th>wt% Au</th>
<th>100K (AuLα)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>19.5 ± 0.1</td>
<td>40.0</td>
<td>60.0</td>
<td>48.0 ± 0.3</td>
</tr>
<tr>
<td>40.0</td>
<td>40.5 ± 0.2</td>
<td>59.9</td>
<td>40.1</td>
<td>28.5 ± 0.2</td>
</tr>
<tr>
<td>59.9</td>
<td>61.1 ± 0.2</td>
<td>79.4</td>
<td>20.6</td>
<td>12.7 ± 0.1</td>
</tr>
<tr>
<td>79.4</td>
<td>80.6 ± 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Silver-Gold Alloys

<table>
<thead>
<tr>
<th>wt% Ag</th>
<th>100K (AgLα)</th>
<th>40.4</th>
<th>75.4 ± 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.6</td>
<td>8.01 ± 0.04</td>
<td>59.5</td>
<td>53.1 ± 0.3</td>
</tr>
<tr>
<td>40.5</td>
<td>20.2 ± 0.1</td>
<td>40.6</td>
<td>32.6 ± 0.1</td>
</tr>
<tr>
<td>59.4</td>
<td>37.7 ± 0.2</td>
<td>19.9</td>
<td>15.1 ± 0.1</td>
</tr>
<tr>
<td>80.1</td>
<td>62.7 ± 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Copper-Silver-Gold Alloys

<table>
<thead>
<tr>
<th>weight %</th>
<th>100 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>5.36</td>
<td>14.9</td>
</tr>
<tr>
<td>10.0</td>
<td>30.0</td>
</tr>
<tr>
<td>15.0</td>
<td>44.9</td>
</tr>
<tr>
<td>10.0</td>
<td>9.97</td>
</tr>
<tr>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>29.9</td>
<td>30.0</td>
</tr>
</tbody>
</table>
FIGURE 4B. AG-AU CALIBRATION
(30 KV, 52.5°)

- "MINITRON" DETECTOR
- POINT ANODE DETECTOR

RELATIVE INTENSITY

AG.Lα

AU.Lα

WEIGHT PERCENT GOLD
listed in Table 6 are the standard deviation of the mean and they reflect the distribution of the mean value for repeated sets of similar measurements.

Analysis of multicomponent alloys may be simplified by making an analytical fit to the calibration curves. It has been found(79) by an examination of the calibration data for several binary alloy systems that these curves may be expressed within experimental error as

\[
\frac{1-K_1}{K_1} = a_{12} \frac{1-W_1}{W_1}
\]  

(IV-1)

where \(K_1\) is the relative intensity (relative to the pure element) from element \(l\) in a binary alloy having the weight fraction composition \(W_1\). The conversion parameter \(a_{12}\) is for the measurement of a particular characteristic line emitted by element \(l\) in the binary alloy. We assume that the same expression will apply for a multicomponent alloy, but with an average conversion parameter taken as the weight fraction average of the binary parameters involved. That is, for an alloy containing elements 1, 2, 3,...,\(N\), the conversion for element \(l\) is

\[
\frac{1-K_1}{K_1} = \bar{a}_{1}(N) \frac{1-W_1}{W_1}
\]  

(IV-2)

where

\[
\bar{a}_{1}(N) = \frac{a_{12}W_2 + a_{13}W_3 + \ldots a_{1N}W_N}{W_2 + W_3 + \ldots W_N}
\]  

(IV-3)
This relationship was tested with the six ternary copper-silver-gold alloys in the following manner. For each \( K \) value of the binary and ternary alloys (Table 6) an \( a \) value was computed from Equation (IV-2). A least squares fit was made to Equation (IV-3) to determine the six parameters. The resulting values are given in Table 7. The parameters computed in this manner for Cu-Au and Ag-Au were then compared with the parameters computed using only the binary data and Equation (IV-1). Differences between the two sets were 0.8\% for Cu, 1.3\% for Ag and 4.3\% for Au. These differences are well within the experimental errors involved.

Compositions computed from the measured parameters are compared with the known compositions in Table 8. In most cases the errors are no greater than the variations in the intensity measurements, and, except for low compositions, the errors are less than 3\%. However, the agreement between known and calculated compositions is not as close for data taken with the point anode detectors as for previously determined measurements of the same standards\(^{76}\). This is attributed to the detector non-linearity. Because of this effect, it must be noted that the calibration data are correct only for the particular instrument used and only when the pure element intensities are the same as given in Table 5.

Further evidence that Equation (IV-2) represents a valid conversion for x-ray data is obtained by comparing diffusion sample analyses from independent measurements and will be discussed in the next section. In a recent paper\(^{80}\)
Table 7.
Conversion Parameters for Copper-Silver-Gold Alloys
(Point anode detector, 30KV, 52.5° spectrometer angle)

Conversion to weight fraction composition

<table>
<thead>
<tr>
<th>Binary Alloy</th>
<th>Line Measured</th>
<th>CuKα</th>
<th>AgLα</th>
<th>AuLα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Ag</td>
<td></td>
<td>1.265</td>
<td>1.517</td>
<td></td>
</tr>
<tr>
<td>Cu-Au</td>
<td></td>
<td>1.000</td>
<td></td>
<td>1.667</td>
</tr>
<tr>
<td>Ag-Au</td>
<td></td>
<td></td>
<td>2.672</td>
<td>1.329</td>
</tr>
</tbody>
</table>

Conversion to atom fraction composition

<table>
<thead>
<tr>
<th>Binary Alloy</th>
<th>Line Measured</th>
<th>CuKα</th>
<th>AgLα</th>
<th>AuLα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Ag</td>
<td></td>
<td>2.148</td>
<td>0.894</td>
<td></td>
</tr>
<tr>
<td>Cu-Au</td>
<td></td>
<td>3.100</td>
<td></td>
<td>0.538</td>
</tr>
<tr>
<td>Ag-Au</td>
<td></td>
<td></td>
<td>4.879</td>
<td>0.728</td>
</tr>
</tbody>
</table>
Table 8.
Standard Compositions Computed from Measured Parameters
(Compositions in atom percent)

<table>
<thead>
<tr>
<th>Copper-Gold Alloys</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Copper</td>
</tr>
<tr>
<td></td>
<td>Known</td>
</tr>
<tr>
<td>44.0</td>
<td>42.9</td>
</tr>
<tr>
<td>67.4</td>
<td>67.8</td>
</tr>
<tr>
<td>82.3</td>
<td>83.0</td>
</tr>
<tr>
<td>92.3</td>
<td>92.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Silver-Gold Alloys</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silver</td>
</tr>
<tr>
<td></td>
<td>Known</td>
</tr>
<tr>
<td>30.9</td>
<td>29.8</td>
</tr>
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<td>55.4</td>
<td>55.3</td>
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<tr>
<td>72.8</td>
<td>74.7</td>
</tr>
<tr>
<td>88.0</td>
<td>89.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Copper-Silver-Gold Alloys</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Copper</td>
</tr>
<tr>
<td></td>
<td>Known</td>
</tr>
<tr>
<td>12.8</td>
<td>11.7</td>
</tr>
<tr>
<td>21.4</td>
<td>20.8</td>
</tr>
<tr>
<td>27.6</td>
<td>27.4</td>
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<tr>
<td>41.1</td>
<td>23.3</td>
</tr>
<tr>
<td>39.1</td>
<td>39.6</td>
</tr>
<tr>
<td>49.5</td>
<td>51.2</td>
</tr>
</tbody>
</table>
Ziebold and Ogilvie consider this method from a theoretical standpoint and show that it is a close approximation when no secondary fluorescence is produced. Within a limited range of composition (above roughly 10% by weight) it is valid even when strong secondary fluorescence is present.

**Experimental Results**

**Composition Profiles**

Compositions were obtained from x-ray data using the analytical expression discussed in the preceding section. The x-ray emission from all three elements was measured at all points. Only two of the three sets of data are needed to fix a ternary composition, therefore the calculations were repeated three times taking the x-ray data in pairs. That is, the composition was computed from CuKα and AgLα, then AgLα and AuLα, then AuLα and CuKα. This yields three entirely independent determinations of the composition at each point analyzed. All computations were done at the MIT Computation Center using a program developed by J. T. Goldstein and the author(76).

A comparison of the three determinations is presented in Figure 5. These two illustrations are typical of the two basic types of diffusion sample--pure copper against a Ag-Au alloy and pure silver against a Cu-Au alloy. There is no consistent error in any trace which can be attributed to the method of converting x-ray data. In most cases the agreement between the three sets of determinations is within the scatter
FIGURE 5A. COMPARISON OF DETERMINATIONS FROM:

- CU K$_a$ & AU L$_a$
- CU K$_a$ & AG L$_a$
- AG L$_a$ & AU L$_a$

(SAMPLE 3)

COMPOSITION - ATOM PERCENT

PENETRATION - MICRONS

COPPER

GOLD

SILVER
FIGURE 5B. COMPARISON OF DETERMINATIONS FROM:

○ CU Kα & AU Lα
× CU Kα & AG Lα
△ AG Lα & AU Lα

(SAMPLE 9)
of data points themselves. In some cases, one is shown in Figure 5b, there is some discrepancy between the values determined by difference and the other two values. In every case (except at low concentrations where the difference values are usually scattered) this error is associated with a steep gradient. It is possible that this may reflect the effect of having an electron beam of finite size which integrates the composition over a small volume. The resulting error would be more pronounced in steep gradients, although in the samples analyzed this effect should be small. This has been discussed previously by the author(76).

At least three traces were taken across the diffusion zone of each sample. The data were plotted for each trace, as shown in Figure 5, and the best curve drawn. The plots for each trace were overlayed to obtain the average curve for a sample. In every case the agreement between traces was well within the scatter of the data. A typical example is shown in Figure 6. The final composition-penetration profiles are presented in Figure 7.

As explained previously, the data may also be plotted on a ternary section to show the "composition path." In such a plot nearly all of the kinetic information is lost, but it is a concise method of comparing the diffusion behavior in relation to the phase diagram. In addition, the derivative \( \frac{dn_2}{dn_1} \) measured from the composition path is an independent quantity which may be used in the Matano or double integration analysis. The composition paths are given in Figure 8. Two
FIGURE 6. COMPARISON OF REPEATED TRACES (SAMPLE 3)
FIGURE 7. COMPOSITION - PENETRATION

TIME - DISTANCE PARAMETER - MICRONS

(SCALE ORIGIN IS MATANO INTERFACE)
FIGURE 8B. DIFFUSION PATHS AT 720°
illustrations are given—the triangular coordinate plot is the more familiar method of presentation, but the rectangular coordinate plot is more illustrative of the derivative functions $\frac{dn_2}{dn_1}$.

**Computation of Coefficients**

As discussed in Chapter III, the four interdiffusion coefficients may be determined only at the points of intersection of the composition paths. These points are labelled in Figure 8. Two of the four coefficients may be evaluated at extreme points where one of the composition gradients becomes zero. Five such extremes are also listed in Figure 8. Solutions for the diffusion coefficients are obtained from equations of the form

$$\Phi_1 = D_{11}^3 + D_{12}^3 \frac{dn_2}{dn_1} = -\frac{1}{2} \frac{d\lambda}{dn_1} \int_{n_1^+}^{n_1} \lambda dn_1$$

To make the most use of the data, the integral and derivative functions were evaluated over the entire diffusion zone of each sample and smoothed graphically.

The copper and silver composition profiles were plotted as a function of $\lambda = x/\sqrt{t}$ on 50 x 50 centimeter paper. The integrals were measured with a planimeter to better than 1% accuracy. The slopes $\frac{dn_1}{d\lambda}$ and $\frac{dn_2}{d\lambda}$ were measured with a mirror device, but even with repeated determinations the error was no less than about 10%. The derivative function $\frac{dn_2}{dn_1}$ was taken as an average of the slope determined directly.
from the $n_2/n_1$ plot and the ratio value

$$\frac{dn_2}{dn_1} = \frac{dn_2/d\lambda}{dn_1/d\lambda}$$

The experimental coefficients are presented in Table 9 and Figure 9. A detailed discussion of the results is given in Chapter V.

Sources of Error

Errors involved in the determination of the compositions have been discussed in a previous section. In general it can be said that the compositions are accurate to about 0.5 atom percent. Other errors which must be considered are those involved in diffusion time and temperature, porosity effects, and the Matano analysis.

The errors in diffusion time and temperature are exceedingly small. If we assume an activation energy of 60 kilocalories per gram atom (the maximum reported by Seith (67) for diffusion of copper, silver, and gold), the heating and cooling curve of Figure 3 represents a time error of less than 5 minutes. This is 0.2% of the total time at temperature and is entirely negligible. Similarly, the fluctuations of 2 degrees in the temperature represent a 6% change in the diffusion coefficient. However, since the fluctuations are roughly sinusoidal in time about the reported average, the error is essentially cancelled. The maximum difference in the average temperature for different samples is 2.5°C. This is equivalent to a 7% change in the coefficient for an assumed activation energy of 60 kilocalories per gram atom.
### Table 9. Measured Diffusion Coefficients

(1 = Cu, 2 = Ag, 3 = Au)

<table>
<thead>
<tr>
<th></th>
<th>(100n_1)</th>
<th>(100n_2)</th>
<th>(D_{11}^3)</th>
<th>(D_{22}^3)</th>
<th>(D_{12}^3)</th>
<th>(D_{21}^3)</th>
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<td>0.04</td>
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<td>0.70</td>
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<td>EE</td>
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Units: \(cm^2/sec \times 10^{10}\)
FIGURE 9A. COPPER DIRECT COEFFICIENT

$D_{11}^3 \times 10^{12}$ CM$^2$/SEC.

($1 = \text{CU, } 2 = \text{AG, } 3 = \text{AU}$)

- INTERSECTION
- EXTREME
FIGURE 9B. SILVER DIRECT COEFFICIENT

$D_{22}^3 \times 10^{12}$ CM$^2$/SEC.

(1 = CU, 2 = AG, 3 = AU)
FIGURE 9C. COPPER CROSS COEFFICIENT

\[100 \frac{D_{12}^3}{D_{11}^3}\]

(1 = CU, 2 = AG, 3 = AU)

○ SEE TEXT
● INTERSECTION
□ EXTREME
FIGURE 9D. SILVER CROSS COEFFICIENT

100 D21 / D22

(CONTOURS SHOW FUNCTION 100 f21 / f22)

(1 = CU, 2 = AG, 3 = AU)

● INTERSECTION
□ EXTREME
Porosity effects in the diffusion samples are more serious. It has already been stated that the diffusion samples of pure silver against gold-rich alloys (samples 10 and 11) were discarded for this reason. Even in sample 9, where pure silver was diffused against the 56% Au-Cu alloy, the effect of porosity is evident in the composition profile. This appears as a sharp drop in the curve at the high silver end of the diffusion zone in Figure 5b which results in an abnormally low value of the diffusion coefficient at that composition. The pronounced porosity effect in silver-gold diffusion has been reported previously and discussed by Le Claire (48). Porosity is also evident in the pure copper against gold-silver alloy couples by metallographic examination, but is much less extensive and shows only a minor effect on the measured coefficient.

The effect of porosity can be reduced by diffusing samples with only small differences in the terminal compositions. For multicomponent samples, however, this makes it nearly impossible to measure cross effects. One expects the cross coefficients to be comparitively small, and steep composition gradients are required to accentuate the cross interactions. This seems to present an inherent difficulty in obtaining accurate multicomponent diffusion coefficients.

In carrying out the Matano analysis, we have assumed that the integral molar volume of the copper-silver-gold system is not a function of composition. This introduces two errors; first, it neglects volume changes on mixing, and
second, it assumes that the partial molar volumes are all equal. The binary solid solutions of Cu-Au, Ag-Au, and Cu-Ag show only slight deviations from Vegard's law (see Barrett\(^5\), page 221). The neglect of volume changes on mixing is therefore not a significant error. On the other hand, the lattice parameter for pure copper is about 12% less than that for pure silver and gold (the latter two being about equal) which means that the molar volumes will differ by about 36%. This makes no difference in the measured practical coefficients since these are nearly always determined from atom fraction plots. That is, the coefficient is defined in terms of the gram molar flux rather than the molar volume flux. (Lane and Kirkaldy\(^47\) designate this the "number-fixed" frame of reference.) The error results when we attempt to relate the practical coefficients to the fundamental coefficients or mobilities. If the practical coefficient is defined for the number-fixed reference, then Equation (III-33) must be modified to include the partial volumes. In addition, the Onsager relations expressed in terms of the practical coefficients, Equation (III-38), include the partial volumes. In the absence of data on the partial volumes for the ternary system, we have assumed them to be equal. This introduces some error, but in view of the uncertainties in the thermodynamic properties, which are discussed in the next chapter, and the added complexity of the computations, it is not considered worthwhile to account for the differences in the partial molar volumes.

The greatest single source of error in computing the
diffusion coefficients lies in the measurement of composition gradients. This is true, of course, in the analysis of binary systems, but the error is compounded in ternary systems. The determination of the coefficients requires solving two simultaneous equations. Depending on the relative values of the gradients for the two intersecting samples, an error of 10% in the slopes can quite easily result in an error of 100% in the coefficients. The worst case will result when the two composition paths intersect at a small angle (points H, K, and N in Figure 8, for example) because the values \( \frac{dn_2}{dn_1} \) will be nearly the same for the two samples. This situation can only be improved after the fact by diffusing new samples with a new set of terminal compositions selected to give a more nearly perpendicular intersection.
V. DISCUSSION OF RESULTS

Configuration of Diffusion Paths

Figure 8 illustrates the major difficulty encountered in any study of ternary diffusion over a wide composition range--namely, the fact that one does not know \textit{a priori} where the composition paths will intersect. For a limited range of compositions where we may assume the coefficients to be constant, the path may be calculated for estimated values of the coefficients. It is evident from the shape of the curves shown in Figure 7 that the coefficients in copper-silver-gold are quite variable with composition. As originally planned, this thesis was to focus attention on the high gold, solid solution range of the ternary system. Referring to Figure 8, it is seen that the intersections are nearly all either close to the binary sides or close to the boundary of the two-phase field. Unfortunately, the diffusion coefficients are least accurate near the binary sides and the thermodynamic calculations are least accurate near the miscibility gap. It was not expected that the diffusion paths would show such a pronounced curvature as to keep the intersections away from the central portion of the diagram.

The intersections and extreme points which have been used to calculate the coefficients are listed in Figure 5. The other points of intersection could not be used since they lie too close to the terminal end of a sample where the derivative and integral functions are quite inaccurate. In all,
however, twenty-eight usable points were obtained. This is a rather small number for the purposes of fairing in the contours but does permit the development of a qualitative picture of the dependence of the coefficients on composition. Better coverage of the system will be obtained only by starting with ternary alloys selected to cover the high gold portion of the diagram.

It may be thought that the composition path at its terminal compositions will always bend away from the most rapidly diffusing component. This is generally true, but the statement must be qualified to include the effect of the overall driving force. For example, compare the terminal directions of samples 13 and 16 in Figure 8. The path for sample 13 bends away from the copper corner, but the path for sample 16 bends away from the silver corner (relative to a straight line joining the terminal points). The two samples differ basically in that the overall change in gold content goes with the change in copper in one case and opposes the change in copper in the other case. This is a generally observed result — the path bends away from the silver corner when the gold content decreases in the same direction as decreasing copper and away from the copper corner when the gold decreases in the same direction as decreasing silver.

Experimental Coefficients

The measured practical diffusion coefficients are summarized in Table 9 and Figure 9. They are discussed in turn in the following paragraphs.
The direct coefficient for copper*, $D_{11}^3$, appears to be nearly insensitive to the silver concentration, at least for alloys which have a low silver content. The contours shown in Figure 9a have been drawn parallel to the lines of constant copper composition for the low silver region of the system. This behavior is indicated from the measured integral function

$$\Phi_1 = D_{11}^3 + D_{12}^3 \frac{dn_2}{dn_1}$$

which is shown for the copper-rich samples in Figure 10. It can be seen in the figures that the derivative $\frac{dn_2}{dn_1}$ is nearly zero at the high copper end of these samples, and consequently, the integral function equals $D_{11}^3$. Because the $\Phi_1$ curves have essentially the same value above 70% copper, the direct coefficient cannot be a strong function of the silver content in this range. This is supported further by the behavior of the curves as the copper content goes to zero. At this limit the cross coefficient, $D_{12}^3$, must vanish, and again the integral function is equal to the direct coefficient. Since the curves tend to the same intercept value, the direct copper coefficient must be nearly constant along the silver-gold binary side. The contours for $D_{11}^3$ have been closed off in the center of the diagram as indicated by the few data points available.

The scatter in the direct coefficients for silver, $D_{22}^3$, is too great for any but the faintest indication of the

*Throughout this section, subscripts 1 and 2 refer to copper and silver, respectively. The superscript 3 refers to gold which is arbitrarily selected as the dependent component or "solvent." Numerical values of the coefficients depend on the choice of "solvent," and relations for converting from one basis to another are tabulated in Appendix A.
composition dependence shown in Figure 9b. The binary silver-gold sample could not be used because of the severe porosity produced in the diffusion zone, and information along this side, which would be of help in drawing the contours, will have to be obtained from incremental couples. It is indicated, however, that the coefficient is nearly constant along this side, and this is consistent with previously reported values for the binary silver-gold\(^{(67)}\).

The cross coefficient for copper is shown as the ratio \(\frac{D_{12}^3}{D_{11}^3}\) in Figure 9c. Following the conclusion that the direct coefficient is not a function of the silver content, we may determine the cross coefficient from the relation

\[
\frac{dn_2}{dn_1} D_{12}^3 = \Phi_1(n_1, n_2) - \Phi_1(n_1, 0)
\]

where the value of \(\Phi_1(n_2=0)\) is the coefficient for binary copper-gold. We may now compute the cross coefficient along the entire diffusion path rather than at intersections only. The values determined in this way are shown in Figure 9c and are generally consistent with the intersection values. The cross coefficient reaches its largest values for compositions near the center of the system. At the copper corner the cross coefficient tends to negative values, and near the silver-gold side it approaches zero. Both of these results are consistent with the thermodynamic considerations which are developed in a later section.

Figure 9d presents the cross coefficient for silver, \(\frac{D_{21}^3}{D_{22}^3}\). The contours are drawn from thermodynamic calculations
and are seen to agree closely with the behavior of the measured diffusion coefficients. This is discussed further in a later section.

To digress briefly from the problem of ternary diffusion, we consider further the binary copper-gold data. As a preliminary to the work of this thesis, diffusion in the binary systems was measured at 750°C. The coefficients in copper-gold for the two temperatures 750°C and 725°C are compared in Figure 11. The maximum value occurs at 45% copper for the higher temperature and at 50% copper for the lower temperature. This trend is confirmed by higher temperature measurements reported by Seith(67), but is contrary to the measurements of Austin and Richard(1) which do not show a maximum. The copper-gold system exhibits a minimum melting temperature of 889°C at 45% copper, so that one would expect to see a maximum diffusion coefficient at this composition. If we assume a value of 60 kilocalories per gram atom for the activation energy, reducing the temperature by 25°C will lower the diffusion coefficient by a factor of two. This is the right order of magnitude for the observed change in copper-gold alloys containing up to 50% copper. For alloys richer in copper than 50%, however, the indicated activation energy is much smaller. This is the range of composition which includes the ordered phases CuAu and Cu$_3$Au, and it is evident that a quite different diffusion behavior exists, even though the temperatures involved here are well above the critical temperature for stability of the ordered phases. This point will become evident again when we consider the thermodynamic properties.
FIGURE II. DIFFUSION COEFFICIENTS IN Cu-Au

$D_t \times 10^{10}$ cm$^2$/sec.

750 °C

725 °C

ATOM PERCENT COPPER
Test of the Onsager Relations

Expressed in terms of the practical coefficients, and assuming that the molar volumes are constant, the Onsager reciprocal relations take the form

\[
\begin{align*}
\left[ g_{22} + \frac{1-n_2}{n_2} g_{12} \right] D_{11}^3 + \left[ \frac{1-n_1}{n_2} g_{22} + \frac{n_1}{n_2} g_{12} \right] D_{21}^3 &= \\
\left[ g_{11} + \frac{1-n_1}{n_1} g_{21} \right] D_{22}^3 + \left[ \frac{1-n_2}{n_1} g_{11} + \frac{n_2}{n_1} g_{21} \right] D_{12}^3 &=
\end{align*}
\]

where the thermodynamic factors are defined as

\[
\gamma_{ik} = \frac{\partial \ln a_i}{\partial \ln n_k} n_j = n_k, n_s
\]

(i, k=1, ... s-1)

The thermodynamic factors have been calculated in the manner described in Appendix B. Values for the compositions at which the diffusion coefficients have been measured are listed in Table 10, and the Onsager relations are tested in Table 11. It is seen that the agreement between the two sides of the above equation is reasonably close only for the points well removed from the boundaries of the miscibility gap (points F through N). The thermodynamic calculations, while dependable for the high gold solid solution range, are fairly inaccurate near the miscibility gap. It is considered that this uncertainty accounts for the failure of the Onsager relations. Nevertheless, it can be said that for the points where there is the greatest confidence in both the diffusion coefficients and in the thermodynamic calculations, the Onsager relations are verified.
**Table 10.**

Calculated Thermodynamic Factors

\(1 = \text{Cu, } 2 = \text{Ag, } 3 = \text{Au}\)

<table>
<thead>
<tr>
<th></th>
<th>100(n_1)</th>
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<th>(g_{11})</th>
<th>(g_{22})</th>
<th>(g_{12})</th>
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<tr>
<td>A</td>
<td>2.1</td>
<td>86.9</td>
<td>0.904</td>
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Table 11.

Test of the Onsager Relations

(1 = Cu, 2 = Ag, 3 = Au)

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<td>-1.4</td>
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</table>

* See page 98.
Calculation of Fundamental Coefficients

Based on the mobility model discussed in Chapter III (i.e., zero cross coefficients for volume diffusion relative to a fixed lattice) and assuming constant molar volumes, the practical coefficients may be written in terms of self-diffusion coefficients as

\[ D_{11}^3 = \left[ D_1 - n_1 (D_1 - D_3) \right] g_{11} - n_2 (D_2 - D_3) g_{21} \]
\[ D_{12}^3 = \left[ D_1 - n_1 (D_1 - D_3) \right] \frac{n_1}{n_2} g_{12} - n_1 (D_2 - D_3) g_{22} \]
\[ D_{22}^3 = \left[ D_2 - n_2 (D_2 - D_3) \right] g_{22} - n_1 (D_1 - D_3) g_{12} \]
\[ D_{21}^3 = \left[ D_2 - n_2 (D_2 - D_3) \right] \frac{n_2}{n_1} g_{21} - n_2 (D_1 - D_3) g_{11} \]

It is immediately apparent that we may write simple relations for the cross-coefficients if any two of the self-diffusion coefficients are approximately equal. Thus, if \( D_2 = D_3 \), then

\[ \frac{D_{12}^3}{D_{11}^3} = \frac{g_{12} n_1}{g_{11} n_2} = \frac{f_{12}}{f_{11}} \]
and if \( D_1 = D_3 \), then

\[ \frac{D_{21}^3}{D_{22}^3} = \frac{g_{21} n_2}{g_{22} n_1} = \frac{f_{21}}{f_{22}} \]

These relations are also approximately applicable when the solutions are dilute in components 2 and 1 respectively.

The expressions are tested from the measured coefficients and calculated thermodynamic factors in Table 12. The test is successful for the silver coefficients in copper-rich solutions (lower portion of the table). The range of agreement falls in
### Table 12.

**Test of the Cross Coefficients**

(1 = Cu, 2 = Ag, 3 = Au)

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<th>100n₂</th>
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<th>100f₁₂</th>
<th>100D₂₁</th>
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<td>-239</td>
<td>5</td>
<td>4.3</td>
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</table>
the high copper solutions and so cannot be attributed to the
dilute solution approximation. The conclusion, then, is that
the self-diffusion coefficients for copper and gold are nearly
equal in solutions which contain less than about 20 atom
percent silver.

This result is confirmed by copper-gold data. For the
binary alloys
\[
\frac{D_{11}^3}{g_{11}} = D_1 - n_1(D_1 - D_3)
\]
This function is shown in Figure 12. The curve is nearly
constant for alloys with less than 50 atom percent copper
and shows a slow variation for the copper-rich alloys. The
curve indicates again that diffusion in the copper-gold system
is quite different for alloys above and below the 50% composition level, although it must be noted that there is some
uncertainty in the calculated thermodynamic factor at the
high copper end of the system (see Appendix B).

Using the observed correlation of \(D_{21}^3/D_{22}^3\) with the
thermodynamic factors \(f_{21}/f_{22}\), we may calculate the dependence
of the silver coefficients over a wide range of the ternary
system. The contours in Figure 9d show the function \(f_{21}/f_{22}\).
Although the correlation is closely followed only for the
silver-poor solutions, the thermodynamic function does seem
to predict the maximum which occurs near the silver-gold side
of the diagram.

The thermodynamic ratio does not correlate at all with
the ratio \(D_{12}^3/D_{11}^3\) for copper except to predict the negative
values of the cross coefficient at the copper corner.
FIGURE 12. COEFFICIENT AND THERMODYNAMIC FACTOR FOR Cu-Au (SAMPLE 1)
Since there are only three mobility coefficients but four interdiffusion coefficients, there is a redundant equation among the relations between the two sets of coefficients. We may use this redundancy to test the validity of the mobility model. The relations as given above are inverted to the form

\[ D_1 - D_3 = \frac{D_{22}^3 g_{21}/n_1 - D_{21}^3 g_{22}/n_2}{g_{11}^3 g_{22}^2 - g_{12}^2 g_{21}} \]

\[ D_2 - D_3 = \frac{D_{11}^3 g_{12}/n_2 - D_{12}^3 g_{11}/n_1}{g_{11}^3 g_{22}^2 - g_{12}^2 g_{21}} \]

\[ D_3(I) = \frac{D_{11}^3 + D_{12}^3}{g_{11}^3 + g_{12}^3 n_1/n_2} + \frac{n_2 g_{21} + n_1 g_{22}}{g_{11}^3 + g_{12}^3 n_1/n_2} (D_2 - D_3) - (1-n_1)(D_1 - D_3) \]

\[ D_3(II) = \frac{D_{22}^3 + D_{21}^3}{g_{22}^3 + g_{21}^3 n_2/n_1} + \frac{n_1 g_{12} + n_2 g_{11}}{g_{22}^3 + g_{21}^3 n_2/n_1} (D_2 - D_3) - (1-n_2)(D_2 - D_3) \]

The last two equations are independently obtained and are used to check the model in Table 13. As with the Onsager relations, the agreement is closest only for the points well removed from the miscibility gap, and even here the test is none too successful. It is interesting to note, however, that the two sets of values calculated for the self-diffusion coefficient of gold show a regular pattern ranging from large to small in different directions as the composition is varied from the silver corner to the copper corner.

It is tempting to attribute this pattern to the thermodynamic calculations since the copper activities are least accurate near the silver corner and vice versa. We might then assume that the model is correct and average the self-diffusion
### Table 13.

**Calculated Self-Diffusion Coefficients**

(1 = Cu, 2 = Ag, 3 = Au)

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<td>-2.2</td>
<td>0.54</td>
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<td>3.9</td>
<td>0.0</td>
<td>-1.6</td>
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<td>-1.04</td>
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<td>-0.99</td>
<td>0.26</td>
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<td>1.1</td>
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</table>
coefficients as shown in Table 13. Except for the very end points, the average value is nearly constant. This is an intriguing result, and is supported by data for the binary copper-gold and silver-gold diffusion. (In the latter case the reported interdiffusion coefficient is nearly constant\(^{(67)}\), and the solutions are not far removed from ideal thermodynamic behavior.)

**Diffusion Near the Critical Point**

Referring to Figure 8, one sees that the diffusion path for sample 15 passes just over the top of the miscibility gap and the path for sample 4 cuts through the gap via a tie-line just below the top. The gradients in sample 15 are extremely steep, but careful metallographic and microprobe examination of this sample after 240 hours of diffusion has shown that the compositions are continuous. Samples 4 and 15, therefore, bracket the critical point of mixing at 725°C, and the critical point must lie in the vicinity of 29%Au-38%Cu-33%Ag.

The composition, integral, and derivative functions for sample 15 are shown in Figure 13. These data are interpreted by recalling the conditions for diffusion near the critical point which were derived by Sundelöf\(^{(70)}\) and summarized in Chapter III. It was argued that, since the entropy production is zero at the critical point, the determinant of the coefficient matrix must vanish, that is

\[
|D| = D_{11}^3 D_{22}^3 - D_{12}^3 D_{21}^3 = 0
\]

Sundelof states further that the diffusion fluxes individually
FIGURE 13. DIFFUSION FUNCTIONS
FOR SAMPLE 15.
vanish. This condition is obtained from the inverted flux equations, which are

\[-\frac{dn_1}{d\lambda} = \frac{(D_{22}^3 J_1 - D_{21}^3 J_2)}{|D|}\]

\[-\frac{dn_2}{d\lambda} = \frac{(D_{11}^3 J_2 - D_{21}^3 J_1)}{|D|}\]

Contrary to Sundelöf's conclusion, it is not necessary that the fluxes vanish individually; only the sum of terms in the numerators above need to be zero when the determinant is zero. It is unrealistic to suppose that the fluxes are zero, for then a sample containing the critical concentration would have a plane across which there could be no mass transport. Diffusion could not occur in such a sample, and it would not be possible to produce a diffusion path cutting exactly through the critical point.

The analysis of sample 15 indicates the following behavior near the critical point in copper-silver-gold. It appears that the gradient of gold \( \frac{dn_3}{d\lambda} \) is tending to zero and the slope \( \frac{dn_2}{dn_1} \) is tending to the value \(-1\). Let us assume that this is the case at the critical point so that the fluxes may be written

\[J_1 = -(D_{11}^3 - D_{12}^3)\frac{dn_1}{d\lambda}\]

\[J_2 = -(D_{22}^3 - D_{21}^3)\frac{dn_2}{d\lambda}\]

Furthermore, when \( \frac{dn_2}{d\lambda} \) is zero, the integral functions are

\[\Phi_1 = D_{11}^3 - D_{12}^3\]

\[\Phi_2 = D_{22}^3 - D_{21}^3\]
Figure 13 shows that these functions are a minimum when the path is closest to the critical point, and suggests that they may be zero if the path should actually contain the critical point. The data indicate, therefore, that at the critical point

\[ D_{11}^3 - D_{12}^3 = D_{22}^3 - D_{21}^3 = 0 \]

which will cause the determinant to vanish. At that point the gradients of copper and silver would have to be infinite in order for the fluxes to remain finite. Diffusion through the critical point may thus be pictured as a transition between solution behavior where all gradients are finite and the phase interface behavior where the compositions are discontinuous.

Professor J. W. Cahn has suggested to the author that any diffusion path through the critical point will lie tangent to the miscibility gap at that point. This is indicated by the path of sample 15, but the slope \( \frac{dn_2}{dn_1} \) may not be -1 since the tie-lines point to a critical composition somewhat to the right (in Figure 8A) of the point of tangency of constant gold content. As a result, the above analysis based on the assumption that \( \frac{dn_3}{d\lambda} = 0 \) at the critical point would not be strictly applicable. It is a close approximation, however, to conclude that the differences \( D_{11}^3 - D_{12}^3 \) and \( D_{22}^3 - D_{21}^3 \) are vanishingly small at the critical point in this alloy system.

Conclusions

It has been the purpose of this thesis to review the phenomenological descriptions of multicomponent diffusion and
to present the results of a general investigation of the entire copper-silver-gold system.

From the standpoint of experimental procedures, it has been shown that microanalysis of ternary samples may be carried out using a simple expression for the conversion of x-ray intensity to composition. The accuracy of this method has been demonstrated by the analysis of standard alloys and by the reproducibility of composition determinations using different x-ray lines.

The four interdiffusion coefficients have been measured at 725°C throughout the range of solid solutions except at the high gold corner. The network of data points has not been as useful as originally designed because the composition paths show a more pronounced curvature than anticipated. The points of intersection have fallen close to either the binary sides or the miscibility gap. Near the binary sides the measurement of the diffusion coefficients becomes inaccurate and near the miscibility gap the thermodynamic calculations become uncertain.

Nevertheless, it is possible to deduce the general dependence of the coefficients on composition. The direct copper coefficient is nearly independent of silver content for alloys low in silver and the direct silver coefficient appears to be nearly constant along the binary solution sides. The behavior of the cross coefficient for copper is uncertain, but the cross coefficient for silver correlates well with the thermodynamic properties, particularly for solutions containing less than 20% silver.
In the range of solid solutions for which there is the greatest confidence in both the diffusion data and thermodynamic calculations, the Onsager reciprocal relations have been verified. Computations of the atom mobilities have been less successful although there is strong evidence that the self-diffusion coefficients for copper and gold are nearly equal. There is an indication that these coefficients may be constant over an appreciable range of composition near the copper-gold binary side.

Finally, there has been an opportunity to examine the nature of diffusion near a two-phase critical point. It is shown that the diffusion path tends to lie tangent to the gap at the critical point, and for the copper-silver-gold system the differences $D_{11}^3 - D_{12}^3$ and $D_{22}^3 - D_{21}^3$ tend to vanish. This causes the copper and silver gradients $(dn_1/d\lambda$ and $dn_2/d\lambda)$ to become extremely steep for a diffusion path near the critical composition.
VI. RECOMMENDATIONS FOR FUTURE WORK

The present work has indicated several areas of interest for future work. These are outlined below.

Incremental Samples
Incremental couples should be diffused to establish the coefficients near the silver-gold binary side. In addition, couples consisting initially of at least one ternary alloy should be examined in order to fill in the unknown regions near the center of the ternary system. These must be selected to provide large gradients without excessive porosity. Ternary alloys containing about 50% gold and diffused against pure gold or gold-rich binary alloys should be suitable. Such samples could utilize effectively the data reported in this thesis.

Activity Measurements
It is strongly urged that the thermodynamic activities be measured in the copper-silver-gold system. Emphasis should be placed on the terminal solutions at either side of the miscibility gap. These regions provide the greatest departures from ideal behavior and include the compositions where the greatest amount of diffusion data have been accumulated.

Radioactive Tracer Measurements
It is also strongly recommended that the self-diffusion coefficients be determined with radioactive tracers. This information, together with the diffusion data contained in this thesis and the activity measurements proposed above,
will provide a direct test of the mobility model.

**Temperature Dependence**

The temperature dependence of the diffusion coefficients must be known before the mechanism of diffusion can be understood. Although a great deal of work along this line has been done for binary systems, ternary data are essentially non-existent. Of particular interest would be the behavior of the cross coefficients in relation to the thermodynamic properties.

**Numerical Analysis**

The experimental calculations associated with ternary diffusion are formidable. It is distressing that the coefficients may be obtained by direct solution only at points of intersection of the composition paths. The use of a computer offers the possibility of developing the phenomenological relations to the point where they may be used to extract the maximum amount of information from the experimental data. It would be advantageous to apply such an approach to the present work even though at this stage the thermodynamic properties are not precisely known.
APPENDIX A. SUMMARY OF PHENOMENOLOGICAL RELATIONS
FOR A THREE COMPONENT SYSTEM WITH CONSTANT MOLAR VOLUME.

Relations of practical coefficients for different solvents:

\[
\begin{align*}
D_{11}^2 &= D_{11}^3 - D_{12}^3 \\
D_{13}^2 &= -D_{12}^3 \\
D_{31}^2 &= D_{22}^3 + D_{12}^3 - D_{11}^3 - D_{21}^3 \\
D_{33}^2 &= D_{22}^3 + D_{12}^3
\end{align*}
\]

\[
\begin{align*}
D_{22}^1 &= D_{22}^3 - D_{21}^3 \\
D_{23}^1 &= -D_{21}^3 \\
D_{32}^1 &= D_{11}^3 + D_{21}^3 - D_{22}^3 - D_{12}^3 \\
D_{33}^1 &= D_{11}^3 + D_{21}^3
\end{align*}
\]

Conversion from D-matrix to L-matrix:

\[
\begin{align*}
D_{11}^3 &= L_{11} \left[ \frac{1}{n_3} + \frac{n_1}{n_3} f_{11} + \frac{n_2}{n_3} f_{21} \right] + L_{12} \left[ \frac{n_1}{n_3} f_{11} + \left( \frac{n_2}{n_3} f_{21} + 1 \right) \right] \\
D_{12}^3 &= L_{11} \left[ \frac{1}{n_3} + \frac{n_1}{n_3} f_{12} + \frac{n_2}{n_3} f_{22} \right] + L_{12} \left[ \frac{n_1}{n_3} f_{12} + \left( \frac{n_2}{n_3} f_{22} + 1 \right) \right] \\
D_{21}^3 &= L_{22} \left[ \frac{1}{n_3} + \frac{n_1}{n_3} f_{21} + \frac{n_2}{n_3} f_{22} \right] + L_{21} \left[ \frac{n_2}{n_3} f_{21} + \left( \frac{n_1}{n_3} f_{11} + 1 \right) \right] \\
D_{22}^3 &= L_{22} \left[ \frac{1}{n_3} + \frac{n_2}{n_3} f_{22} + \frac{n_1}{n_3} f_{12} \right] + L_{21} \left[ \frac{n_2}{n_3} f_{22} + \left( \frac{n_1}{n_3} f_{12} + 1 \right) \right]
\end{align*}
\]

Onsager Reciprocal Relations:

\[
\begin{align*}
D_{22}^3 \left[ g_{11} + \frac{1-n_1}{n_1} g_{21} \right] + D_{12}^3 \left[ \frac{1-n_2}{n_1} g_{11} + \frac{n_2}{n_1} g_{21} \right] = \\
D_{22}^3 \left[ g_{22} + \frac{1-n_2}{n_2} g_{12} \right] + D_{21}^3 \left[ \frac{1-n_1}{n_2} g_{22} + \frac{n_1}{n_2} g_{12} \right]
\end{align*}
\]
Relation of D-matrix to Mobilities:

\[
D_{11}^3 = \left[ D_1 - n_1(D_1 - D_3) \right] g_{11} - n_2(D_2 - D_3)g_{21}
\]

\[
D_{12}^3 = \left[ D_1 - n_1(D_1 - D_3) \right] \frac{n_1}{n_2} g_{12} - n_1(D_2 - D_3)g_{22}
\]

\[
D_{21}^3 = \left[ D_2 - n_2(D_2 - D_3) \right] \frac{n_2}{n_1} g_{21} - n_2(D_1 - D_3)g_{11}
\]

\[
D_{22}^3 = \left[ D_2 - n_2(D_2 - D_3) \right] g_{22} - n_1(D_1 - D_3)g_{12}
\]
APPENDIX B. CALCULATION OF THERMODYNAMIC FUNCTIONS

Correlation Formulae

In the absence of thermodynamic data for the ternary Cu-Ag-Au system it has been necessary to compute the required functions from binary data. In this procedure use has been made of the measured tie-lines across the miscibility gap which extends into the ternary section from the Cu-Ag side so that a limited amount of ternary information has been accomodated.

The calculation of ternary activities requires choosing suitable correlation functions for the binary data. In an earlier attempt at this problem\(^{(76)}\), the author demonstrated that calculations based on a regular solution model, similar to those of Meijering\(^{(56)}\), could not account quantitatively for the configuration of the miscibility gap. It was evident that a more complicated description would be required.

A general representation of the thermodynamic properties of solutions is given by Redlich and Kister\(^{(65)}\). Their equations make use of the series expansion for the excess integral molar free energy suggested by Guggenheim (see Wagner\(^{(73)}\), page 48). For binary solutions the series is

\[
F^E = RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2) = n_1 n_2 \sum_{k=0}^{m} A_k (n_1 - n_2)^k \quad (B-1)
\]

in which \(n_1\) and \(n_2\) are the mole fractions and \(\gamma_1\) and \(\gamma_2\) are the activity coefficients. It is desirable to work with this function in fitting data, rather than the individual activity
coefficients, since the two activities are redundant by virtue of Duhem's equation. Redlich and Kister recommend, in fact, the use of the function $\log \left( \frac{\gamma_1}{\gamma_2} \right)$ which is one degree lower in composition dependence than the integral excess free energy.

For a binary solution, the correlation function may be written

$$Q_{12} = \frac{(f^E)_{12}}{RT} = n_1 n_2 \left[ B_{12} + C_{12}(n_1 - n_2) + D_{12}(n_1 - n_2)^2 + \ldots \right] \quad (B-2)$$

The series for a ternary system is then represented by

$$Q = Q_{12} + Q_{23} + Q_{31} + n_1 n_2 n_3 \left[ C + D_1(n_2 - n_1) + D_2(n_3 - n_1) + \ldots \right] \quad (B-3)$$

where $Q_{12}$, $Q_{23}$ and $Q_{31}$ are the appropriate functions for the binary sides and are to be evaluated at the ternary composition $(n_1, n_2, n_3)$. The procedure is to determine the constants $B_{12}$, $B_{23}$, $B_{31}$, $C_{12}$, etc., from binary data and then determine the constants $C$, $D_1$, $D_2$, etc., from ternary data. In treating the binary data it is recommended that the function

$$\log \frac{\gamma_1}{\gamma_2} = \frac{dQ_{12}}{dn_1} = B_{12}(n_2 - n_1) + C_{12}(6n_1 n_2 - 1) + D_{12}(n_2 - n_1)(1 - 8n_1 n_2) + \ldots \quad (B-4)$$

be used. This function provides a means for checking the consistency of the data since

$$\int_0^1 \log(\frac{\gamma_1}{\gamma_2})dn_1 = 0 \quad (B-5)$$
The mechanics for performing the computations efficiently are described by Redlich and Kister.

For the case at hand, we need the thermodynamic factors

\[ g_{11} = \left( \frac{\partial \log a_1}{\partial \log n_1} \right) n_2 \] and \[ g_{12} = \left( \frac{\partial \log a_1}{\partial \log n_2} \right) n_1 \]

and similar factors in terms of the activity of component 2. These are developed from the integral function \( Q \) by means of the relation

\[ \ln \chi_1 = Q + (1-n_1) \left( \frac{\partial Q}{\partial n_1} \right) n_2/n_3 \tag{B-6} \]

Since

\[ dQ = \left( \frac{\partial Q}{\partial n_1} \right) n_2 + \left( \frac{\partial Q}{\partial n_2} \right) n_1 \tag{B-7} \]

it follows that

\[ \left( \frac{\partial Q}{\partial n_1} \right) n_2/n_3 = \left( \frac{\partial Q}{\partial n_1} \right) n_2/n_3 + \left( \frac{\partial Q}{\partial n_2} \right) n_1/n_3 \]

\[ \text{or} \quad \left( \frac{\partial Q}{\partial n_1} \right) n_2/n_3 = \left( \frac{\partial Q}{\partial n_1} \right) n_2/n_3 \]

\[ - \frac{n_2}{1-n_1} \left( \frac{\partial Q}{\partial n_2} \right) n_1 \tag{B-8} \]

Combining Equations (B-6) and (B-8), the desired thermodynamic factors may be calculated from

\[ \left( \frac{\partial \ln \chi_1}{\partial n_1} \right) n_2 = (1-n_1) \left( \frac{\partial^2 Q}{\partial n_1^2} \right) n_2 - n_2 \left( \frac{\partial^2 Q}{\partial n_1 \partial n_2} \right) \tag{B-9} \]

\[ \left( \frac{\partial \ln \chi_1}{\partial n_2} \right) n_1 = (1-n_1) \left( \frac{\partial^2 Q}{\partial n_1 \partial n_2} \right) - n_2 \left( \frac{\partial^2 Q}{\partial n_2^2} \right) n_1 \]
Table B-1.

Equations for Activity Coefficients

\( 1 = \text{Cu}, 2 = \text{Ag}, 3 = \text{Au}; r = n_1/n_2, s = n_2/n_3 \)

\[
\ln \frac{\gamma_1}{(1-n_1)^2} = R_o + 2R_1n_1 + 3R_2n_1^2
\]

\[
R_o = \frac{RB_{12}+B_{13}}{r+1} - \frac{r^2C_{12}+C_{13}}{(r+1)^2} - \frac{r}{(r+1)^2} \left[ B_{23}+2C_{23} \frac{r-1}{r+1} - C - \frac{r^2D_{12}+rD}{r+1} \right]
\]

\[
R_1 = \frac{rC_{12}+C_{13}}{r+1} + \frac{r^2C_{12}+C_{13}}{(r+1)^2} - \frac{r}{(r+1)^3} \left[ (r-1)C_{23}+(r+1)C+2r(2r+1)D_{12} + (3r+1)D \right]
\]

\[
R_2 = \frac{r(2r+1)}{(r+1)^3} \left[ (2r+1)D_{12}+D \right]
\]

\[
\ln \frac{\gamma_2}{(1-n_2)^2} = S_o + 2S_1n_2 + 3S_2n_2^2
\]

\[
S_o = \frac{sB_{21}+B_{23}}{s+1} - \frac{s^2C_{21}+C_{23}}{(s+1)^2} - \frac{s}{(s+1)^2} \left[ B_{13}+2C_{13} \frac{s-1}{s+1} - C - \frac{s^2D_{21}-sD}{s+1} \right]
\]

\[
S_1 = \frac{sC_{21}+C_{23}}{s+1} + \frac{s^2C_{21}+C_{23}}{(s+1)^2} - \frac{s}{(s+1)^3} \left[ (s-1)C_{13}+(s+1)C+2s(2s+1)D_{21} - (3s+1)D \right]
\]

\[
S_2 = \frac{s(2s+1)}{(s+1)^3} \left[ (2s+1)D_{21}-D \right]
\]
Table B-2. Equations for Thermodynamic Factors

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<th>Variable</th>
<th>Coefficient for $g_{11}$</th>
<th>Value*</th>
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<tr>
<td>1</td>
<td>1</td>
<td>1.000</td>
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*From Table B-5.
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<td>$B_{13}+B_{23}-B_{12}+2(C_{12}-2C_{23}-4C_{13}-C\text{-D})$</td>
<td>1.014</td>
</tr>
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*From Table B-5.
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<td>0</td>
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<tr>
<td>$n_1n_2$</td>
<td>$B_{23} + B_{13} - B_{21} + 2(C_{21} - 2C_{13} - 4C_{23} - C + D)$</td>
<td>-2.342</td>
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<td>$2(B_{23} - 9C_{23})$</td>
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<tr>
<td>$n_1n_2^2$</td>
<td>$2(C_{21} + 3C_{13} + C_{23} + C - 2D_{21} + D)$</td>
<td>-8.002</td>
</tr>
<tr>
<td>$n_1n_2^2$</td>
<td>$-4(C_{21} - C_{13} - 3C_{23} - C + D)$</td>
<td>-3.772</td>
</tr>
<tr>
<td>$n_2^3$</td>
<td>$12C_{23}$</td>
<td>-2.412</td>
</tr>
<tr>
<td>$n_1^4$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1n_2^3$</td>
<td>$-3(D_{21} + D)$</td>
<td>-2.07</td>
</tr>
<tr>
<td>$n_1n_2^3$</td>
<td>$12D_{21}$</td>
<td>8.28</td>
</tr>
<tr>
<td>$n_1n_2^3$</td>
<td>$-9(D_{21} - D)$</td>
<td>-6.21</td>
</tr>
<tr>
<td>$n_1^4$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*From Table B-5.
Table B-2 (continued)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Coefficient for $g_{21}$</th>
<th>Value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1$</td>
<td>$B_{21} - B_{13} - B_{23} + 2(C_{13} + C_{23})$</td>
<td>4.228</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1^2$</td>
<td>$2(B_{13} - C_{21} - 6C_{13} - C_{23} - C - D)$</td>
<td>6.016</td>
</tr>
<tr>
<td>$n_1n_2$</td>
<td>$B_{23} + B_{13} - B_{21} + 2(C_{21} - 2C_{13} - 4C_{23} - C + D)$</td>
<td>-2.342</td>
</tr>
<tr>
<td>$n_2^2$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1^3$</td>
<td>$3(4C_{13} + D_{21} + D)$</td>
<td>-9.210</td>
</tr>
<tr>
<td>$n_1^2n_2$</td>
<td>$4(C_{21} + 3C_{13} + C_{23} - 2D_{21} + C + D)$</td>
<td>-16.004</td>
</tr>
<tr>
<td>$n_1n_2^2$</td>
<td>$-2(C_{21} - C_{13} - 3C_{23} + 3D_{21} - C - 5D)$</td>
<td>-6.026</td>
</tr>
<tr>
<td>$n_2^3$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1^4$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$n_1^3n_2$</td>
<td>$-9(D_{21} + D)$</td>
<td>-6.21</td>
</tr>
<tr>
<td>$n_1^2n_2^2$</td>
<td>$12D_{21}$</td>
<td>8.28</td>
</tr>
<tr>
<td>$n_1n_2^3$</td>
<td>$-3(D_{21} - D)$</td>
<td>-2.07</td>
</tr>
<tr>
<td>$n_1^4$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*From Table B-5.
Fitting the Binary Data

Thermodynamic data for Cu-Ag, Ag-Au and Cu-Au are tabulated by Hultgren et al. (30). There seems to be good agreement among the various sources of these data. The Ag-Au system (2-3) follows subregular solution behavior and the tabulated functions are

\[
\frac{-F_2^E}{(1-n_2)^2} = 5650 - 1.375T - 1600(1-n_2)
\]

\[
\frac{-F_3^E}{(1-n_3)^2} = 4850 - 1.375T - 1600n_3
\]

The desired constants, \(B_{23}\) and \(C_{23}\), are calculated directly from these equations. The values for 1000°K are listed in Table B-5.

Properties for Cu-Au (1-3) are given by Hultgren et al. at 720°K. This system is complicated by the ordered phases, but extrapolation in the range of 720°K to 1000°K can be made assuming the integral molar enthalpy and entropy are constant. This was checked by the data for CuAu and Cu\(_3\)Au which are listed at various temperatures. The error in free energy at 1000°K was only 2% for the constant enthalpy and entropy extrapolation. The tabulated activity coefficients at 720°K and the extrapolated values at 1000°K are listed in Table B-3.

Plots of \(\ln \gamma/(1-n)^2\) and \(\ln(\gamma_1/\gamma_3)\) for Cu-Au are shown in Figure B-1. It is seen that for the high Cu solutions there is a departure from the subregular behavior for which the functions \(\ln \gamma/(1-n)^2\) will be linear. The departure is
### Table B-3.

Tabulated Activity Coefficients for Cu-Ag and Cu-Au.

#### Copper-Silver

<table>
<thead>
<tr>
<th>$n_{Cu}$</th>
<th>Tabulated at 1052°K*</th>
<th>Extrapolated to 1000°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>0</td>
<td>15.24</td>
<td>1.000</td>
</tr>
<tr>
<td>0.02</td>
<td>13.50</td>
<td>1.001</td>
</tr>
<tr>
<td>0.04</td>
<td>11.98</td>
<td>1.005</td>
</tr>
<tr>
<td>0.06</td>
<td>10.66</td>
<td>1.011</td>
</tr>
<tr>
<td>0.08</td>
<td>9.52</td>
<td>1.020</td>
</tr>
<tr>
<td>0.10</td>
<td>8.50</td>
<td>1.031</td>
</tr>
<tr>
<td>0.12</td>
<td>7.62</td>
<td>1.045</td>
</tr>
<tr>
<td>0.141</td>
<td>6.81</td>
<td>1.063</td>
</tr>
<tr>
<td>0.951</td>
<td></td>
<td>1.011</td>
</tr>
<tr>
<td>0.96</td>
<td></td>
<td>1.007</td>
</tr>
<tr>
<td>0.98</td>
<td></td>
<td>1.002</td>
</tr>
<tr>
<td>1.00</td>
<td></td>
<td>1.000</td>
</tr>
</tbody>
</table>

#### Copper-Gold

<table>
<thead>
<tr>
<th>$n_{Cu}$</th>
<th>Tabulated at 720°K*</th>
<th>Extrapolated to 1000°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Au</td>
</tr>
<tr>
<td>0</td>
<td>0.137</td>
<td>1.000</td>
</tr>
<tr>
<td>0.1</td>
<td>0.127</td>
<td>1.004</td>
</tr>
<tr>
<td>0.2</td>
<td>0.137</td>
<td>0.986</td>
</tr>
<tr>
<td>0.3</td>
<td>0.166</td>
<td>0.926</td>
</tr>
<tr>
<td>0.4</td>
<td>0.218</td>
<td>0.799</td>
</tr>
<tr>
<td>0.5</td>
<td>0.301</td>
<td>0.610</td>
</tr>
<tr>
<td>0.6</td>
<td>0.429</td>
<td>0.395</td>
</tr>
<tr>
<td>0.7</td>
<td>0.622</td>
<td>0.197</td>
</tr>
<tr>
<td>0.8</td>
<td>0.885</td>
<td>0.070</td>
</tr>
<tr>
<td>0.9</td>
<td>1.007</td>
<td>0.034</td>
</tr>
<tr>
<td>1.0</td>
<td>1.000</td>
<td>0.049</td>
</tr>
</tbody>
</table>

*Reference 30.*
most pronounced for the copper data, but in this case the functions become rather inaccurate (because $1-n_1$ is small). An inconsistency is noted since the function $\log(\gamma_1/\gamma_3)$ does not satisfy Equation B-5. Making a least squares fit to the points up to $n_{\text{Cu}} = 0.6$ gives the dashed curves shown in Figure B-1. The function $\log(\gamma_1/\gamma_3)$ more closely obeys Equation B-5. Since attention will be focused on the properties of high Au solutions, it is concluded that the subregular solution fit is adequate. The constants $b_{13}$ and $c_{13}$ are given in Table B-5.

At 1000°K the binary Cu-Ag (1-2) exhibits solutions only over the range 0-3% Cu and 0-11.5% Ag. These values, from Hansen (27), are in agreement with the present work at the copper end, but at the silver end the limiting value determined from Cu//Ag diffusion couple is 13.5% Ag. The discrepancy is not significant in view of the difficulty in extrapolating the diffusion curves to the phase interface, and Hansen's solubility limit is used in computing the activities. Hultgren lists the thermodynamic properties for Cu-Ag at 1052°K, as shown in Table B-3. The minor extrapolation to 1000°K was made assuming constant enthalpy and entropy.

Fitting of the activity data for Cu-Ag is somewhat inaccurate unless many terms are used. The objection to using a high order fit, other than algebraic complexity, is that the derivative functions, $g_{12}$, may become increasingly inaccurate due to small oscillations of the curves. For this reason the fit using the series of Redlich and Kister was confined to
three constants. The function $\ln(\gamma_1/\gamma_2)$ is shown in Figure B-2. The fit was made both by the method suggested by Redlich and Kister (where adjustment is made to certain characteristic points) and by a least squares fit. Although the least squares fit to $\ln(\gamma_1/\gamma_2)$ appeared to be close, the agreement on an activity plot was not. Because the fit using characteristic points gives a somewhat better activity curve than the least squares method, the former values were used. The constants $B_{12}$, $C_{12}$ and $D_{12}$ are listed in Table B-5.

**Ternary Calculations**

Activities in the ternary section were first computed from the binary constants alone. Since tie-lines across the gap represent lines of constant activity of all three constituents, we seek to have the activity contours run parallel to the tie-lines. Measured tie-line end points are listed in Table B-4. The fit using only binary data nearly satisfies the requirement, but to improve the configuration, we need to add terms which will swing the lines away from the Cu-Ag side in the region near the silver corner. This effect should increase as $n_3$ increases since a larger correction is needed near the top of the gap. The desired correction terms are therefore

$$n_1 n_2 n_3 \left[ C + D(n_2 - n_1) \right]$$

to follow the series expansion given by Redlich and Kister. The adjustment of $C$ and $D$ was essentially trial and error. In making the fit it was found that when a non-zero value for
### Table B-4.
**Measured Ternary Tie-Line Compositions**

<table>
<thead>
<tr>
<th>Copper-Rich End</th>
<th>Silver-Rich End</th>
</tr>
</thead>
<tbody>
<tr>
<td>at% Cu</td>
<td>at% Ag</td>
</tr>
<tr>
<td>97.0</td>
<td>3.0</td>
</tr>
<tr>
<td>80.8</td>
<td>6.7</td>
</tr>
<tr>
<td>78.3</td>
<td>8.3</td>
</tr>
<tr>
<td>71.0</td>
<td>11.2</td>
</tr>
<tr>
<td>56.0</td>
<td>18.0</td>
</tr>
<tr>
<td>50.0</td>
<td>22.5</td>
</tr>
</tbody>
</table>
Table B-5.
Parameters for Series Expansion of Activity Coefficients

<table>
<thead>
<tr>
<th>System</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper-Silver</td>
<td>$b_{12} = b_{21} = 2.53$</td>
</tr>
<tr>
<td></td>
<td>$c_{12} = -c_{21} = 0.10$</td>
</tr>
<tr>
<td></td>
<td>$d_{12} = d_{21} = 0.69$</td>
</tr>
<tr>
<td>Copper-Gold</td>
<td>$b_{13} = b_{31} = -2.433$</td>
</tr>
<tr>
<td></td>
<td>$c_{13} = -c_{31} = -0.940$</td>
</tr>
<tr>
<td>Silver-Gold</td>
<td>$b_{23} = b_{32} = -1.547$</td>
</tr>
<tr>
<td></td>
<td>$c_{23} = -c_{32} = -0.201$</td>
</tr>
<tr>
<td>Copper-Silver-Gold</td>
<td>$C = 0.5$</td>
</tr>
<tr>
<td></td>
<td>$D = 0$</td>
</tr>
</tbody>
</table>
D was used, the iso-activity lines showed too much curvature across the gap. Hence this term was dropped.

The final configuration is shown in Figures B-3, 4, and 5, and the constants are listed in Table B-5. Numerical values of the series coefficients for the \( g_{11} \) and \( g_{12} \) functions are given in Table B-2.
FIGURE B-3. CALCULATED COPPER ACTIVITY AT 1000 °K
TABULATED DATA:
- CU-AG
- CU-AU
FIGURE B-4. CALCULATED SILVER ACTIVITY AT 1000 °K
TABULATED DATA:
• AG-CU
FIGURE B-5. CALCULATED ACTIVITIES OF COPPER AND SILVER AT 1000 °K
APPENDIX C. DESIGN AND PERFORMANCE OF POINT ANODE PROPORTIONAL DETECTORS

In the course of installing scalers to read x-ray signals from the ARL microanalyzer, it was found that the standard ARL detectors ("Minitrons") did not provide a sufficiently strong signal at the vacuum wall connectors. (There is approximately six feet of cable between the vacuum wall connectors and the detectors.) This could be corrected either by installing preamplifiers close to the detectors (inside the vacuum chamber) or by changing to a different detector design. At the time of modifying the instrument it was decided to take the latter course as being the simpler, although it now appears that the installation of preamplifiers may be a more satisfactory solution.

Because the ARL spectrometers limit the physical size of detectors to about 1-1/4 inch in a direction parallel to the line of x-rays coming from the crystal, a point anode, end window geometry was used for the new detector. Proportional detectors of this type are described by Mathieson and Sanford\(^{(54)}\) A unit based on their design and compatible with the ARL spectrometer is shown in Figure C-1. The anode is a number 10 sewing needle press fit into a steel shank. The critical dimension in this design is the spacing between the point and the window, which should be between 29 and 30 mm for the design shown.

The pulse amplitude resolution of this detector was checked with the unit installed on the MIT microanalyzer
BRASS TUBES (GAS FLOW)

BRASS CAP

1/4 MIL "MYLAR" WINDOW

"TEFLON" CAP

#10 SEWING NEEDLE

29 MM

STEEL SHANK

BRASS BODY (GOLD PLATED)

TWICE ACTUAL SIZE

FIGURE C-1. POINT ANODE PROPORTIONAL DETECTOR
where a short cable to the preamplifier could be used. A comparison of the point detector differential pulse height curve with curves from a coaxial detector (designed for the MIT microanalyzer) and an ARL "Minitron" is given in Figure C-2. The point detector has a resolution nearly as good as the "Minitron", but has a somewhat higher background level. It should be noted, however, that the desired increase in signal strength has been accomplished. In the curves shown, the peak is placed at the same baseline level—the lower voltage and amplifier gain required for the point detector is therefore indicative of a considerably higher pulse amplitude. This is illustrated again in Figure C-3 which is a comparison of pulse height curves with the detectors installed in the ARL microanalyzer (long cable between detector and preamplifier). Here it is evident that the high voltage and high gain needed with the "Minitron" is amplifying the noise level considerably.

In spite of the improvement in pulse amplitude, the point detectors are not completely satisfactory because of a non-linear count rate dependence. Counter linearity may be checked by taking the electron beam current absorbed in the specimen as proportional to the true x-ray intensity emitted. A plot of integral count rate (pulse height analyzer "wide open") against specimen current indicates the response of the observed count rate to the true count rate. Curves for the point anode detectors installed in the ARL are given in Figure C-4. The difference in count rates between these
FIGURE C-2. PULSE HEIGHT CURVES (SHORT CABLE)

COAXIAL DETECTOR
Ni Kα (3rd ORDER)
V = 1370 VOLTS
G = 1
ΔE = 0.5 VOLT

ARL MINITRON
Ni Kα (3rd ORDER)
V = 2000 VOLTS
G = 0.5
ΔE = 0.5 VOLT

POINT ANODE
Ni Kα (3rd ORDER)
V = 1500 VOLTS
G = 0.5
ΔE = 0.5 VOLT

BASE LINE-VOLTS
FIGURE C-3. PULSE HEIGHT CURVES (LONG CABLE)

ARL MINITRON
FE. Kα (1st ORDER)
V = 1986 VOLTS
G = 1.0
ΔE = 0.5 VOLT

525 CPS

POIN T ANODE
FE. Kα (3rd ORDER)
V = 1481 VOLTS
G = 0.23
ΔE = 0.5 VOLT

83 CPS

POIN T ANODE
SU Kα (1st ORDER)
V = 1457 VOLTS
G = 0.74
ΔE = 0.5 VOLT

470 CPS

22% FWHM

47% FWHM

BASE LINE - VOLTS
FIGURE C-4. DETECTOR RESPONSE (HIGH RANGE)

INTERVAL COUNT RATE - 10^3 CPS

DETECTOR #2 (AU L\alpha)

DETECTOR #1 (CU K\alpha)

DETECTOR #3 (AG. L\alpha)

SPECIMEN CURRENT - MICROAMPERES
curves results from the different geometries and crystals associated with each detector.

To amplify the behavior at low count rates, the ratio of observed intensity to specimen current is plotted in Figure C-5. If the detector is linear this ratio will be constant. There is considerable uncertainty because of the difficulty in measuring the specimen current (which is on the order of $10^{-7}$ amperes), nevertheless these detectors show definite non-linear characteristics at low count rates. There is no readily apparent explanation for the nature of these plots.
FIGURE C-5. DETECTOR RESPONSE (LOW RANGE)

DETECTOR #1 (CU. Kα)

DETECTOR #2 (AU. Lα)

DETECTOR #3 (AG. Lα)

COUNT RATE / SPECIMEN CURRENT (RELATIVE SCALE)

INTEGRAL COUNT RATE – 1000 COUNTS/SEC.
APPENDIX D. TRACE DETERMINATIONS IN MICROANALYSIS

In a recent paper, Theisen\(^{(71)}\) demonstrated that it is possible to extend x-ray microanalysis to the domain of trace determination. His paper is the first to consider the errors involved in trace microanalysis on a rigorous statistical basis, and it is of direct practical interest. In the following discussion Theisen's treatment is expanded and the significant features are discussed.

If we are concerned with low concentration analysis, the x-ray calibration curve (relative intensity vs. concentration) becomes a linear function. Suppose that we measure the intensity emitted from a known calibration standard of composition \(C_c\). For any other composition between zero and \(C_c\) the fixed-time count observed will be

\[
C_x = \frac{N_x - N_B}{N_c - N_B} C_c
\]

where \(N_x\), \(N_B\) and \(N_c\) are the mean counts determined for the unknown, its background, and the calibration sample, respectively. (It is assumed here that the background is constant for the limited range of composition involved.) It is apparent that the detectability limit is governed by the minimum value of the difference \(N_x - N_B\) which can be measured with statistical significance.

The analysis of the difference of two means is a common problem in statistics\(^{(20)}\). We are specifically interested here in the test of whether the difference is zero or not.
This may be done by using "Student's" distribution which gives, in terms of known statistics of the sample, the probability of exceeding the observed difference of the means by repeated random sampling. Consider that we measure the sample and its background \(n\) times (the same counting time interval is used for each measurement). The statistics we require are:

Means: \(\overline{N}_x = \frac{\sum(N_x)}{n}\) and \(\overline{N}_B = \frac{\sum(N_B)}{n}\)

Estimate of total variance: \(s^2 = \frac{\sum(N_x - \overline{N}_x)^2 + \sum(N_B - \overline{N}_B)^2}{2(n-1)}\)

"Student's" distribution factor: \(t = \frac{(\overline{N}_x - \overline{N}_B)\sqrt{1/2n}}{s}\)

Degrees of freedom: \(f = 2(n-1)\)

"Student's" distribution gives the frequency of occurrence of \(t\) for a particular number of degrees of freedom, \(f\). Tables of the distribution generally give the probability that \(t\) will be exceeded. A portion of Fisher's (20) tabulation is given as Table D-1. Since \(t\) is proportional to the difference of means, then we may specify through the value of \(t\) a confidence level for the determination of \(\overline{N}_x - \overline{N}_B\). Customarily the level is chosen as 5\% or 1\%, which means that when \(t\) has the value corresponding to these levels, we would expect to exceed the measured \(\overline{N}_x - \overline{N}_B\) in only 5\% (or 1\%) of repeated random samples. Thus we have a high degree of confidence that our measurement is actually greater than zero.

From the above discussion we see that the detectability limit depends on the specified confidence level (through \(t\))
and the statistics of the sample (through $s$). The limit is given by

$$(N_x - N_B)_{DL} = \frac{st}{\sqrt{1/2n}}$$

Combining this with the expression for the conversion of point count to composition, the "detectability limit" is

$$C_{DL} = \frac{C_c}{N_c - N_B} \frac{st}{\sqrt{1/2n}}$$

Carrying through a similar analysis we could obtain essentially the same expression for the sensitivity of our analysis to determine deviations from a certain value. The relative error in low level determinations is then

$$\epsilon = \frac{C_{DL}}{C_x}$$

We may define the "analytical limit" as the minimum composition which can be determined with a specified relative error. Thus the analytical limit is

$$C_{AL} \approx \frac{C_{DL}}{\epsilon} = \frac{C_c}{\epsilon(N_c - N_B)\sqrt{1/2n}}$$

For the purpose of relating the detectability limit to spectrometer performance, it is desirable to generalize the above by specifying the factor $C_c/(N_c - N_B)$ in terms of peak intensity and peak/background ratios. It has been shown\(^{(79)}\) that we may specify the x-ray calibration curve by the relation

$$\frac{C}{K} = a + (1-a)C$$

where $K$ is the intensity relative to the pure element and $a$
is the conversion parameter. For the calibration standard,

\[ K_c = \frac{N_c - N_B}{N_o - N_B} = \frac{N_c - N_B}{N_o (1 - N_B/N_o)} \tag{D-7} \]

where \( N_o \) is the count from the pure element reference standard and is equal to \( N_o \tau \), where \( N_o \) is the standard intensity and \( \tau \) is the count time interval. The ratio \( N_o/N_B \) is the "peak-to-background" ratio, which we will designate \( R \).

Combining Equations (D-3), (D-6) and (D-7), we have

\[ C_{DL} = \frac{ast}{I_o \tau (1 - 1/R)} \tag{D-8} \]

The rms deviation of the low level measurements, \( s \), may be computed from the individual measurements, or we may use the estimate from Poisson statistics (see, for example, Evans\(^{(19)}\) page 750 ff.), that

\[ s = \sqrt{N_B} \tag{D-9} \]

which will be the minimum attainable.

With this approximation to the true variance, the detectability limit is

\[ C_{DL} = \frac{at}{\sqrt{1/2n\tau I_o R}} \tag{D-10} \]

This is the most useful form for estimating the capabilities of a particular experimental setup. Note that the detectability limit depends directly on the x-ray conversion parameter. This means, for example, that the limit is lower for the analysis of copper in gold than for silver in gold.
In the latter case, there is a strong absorption effect resulting in a large a value. Further, the limit depends on the product of peak intensity times peak/background ratio measured on the pure elements. Nothing is gained in detectability by increasing the peak/background ratio if in the process the peak intensity is reduced by the same factor. This relation is of direct practical importance in selecting characteristic lines and adjusting the pulse height analyzer.
Table D-1.
"Student's" Distribution Factors

Listed below are values of $t$ as a function of the degrees of freedom, $f$, which will be exceeded in 5% or 1% of random samples. Values are from Fisher\(^{(20)}\).

<table>
<thead>
<tr>
<th>$f$</th>
<th>$P=5%$</th>
<th>$P=1%$</th>
<th>$f$</th>
<th>$P=5%$</th>
<th>$P=1%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.314</td>
<td>3.182</td>
<td>16</td>
<td>1.746</td>
<td>2.583</td>
</tr>
<tr>
<td>2</td>
<td>2.920</td>
<td>2.965</td>
<td>17</td>
<td>1.740</td>
<td>2.567</td>
</tr>
<tr>
<td>3</td>
<td>2.353</td>
<td>2.954</td>
<td>18</td>
<td>1.734</td>
<td>2.552</td>
</tr>
<tr>
<td>4</td>
<td>2.132</td>
<td>3.747</td>
<td>19</td>
<td>1.729</td>
<td>2.539</td>
</tr>
<tr>
<td>5</td>
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REFERENCES


50. Leroy, V., personal communication.


60. Oishi, Y., private communication.


64. Philip, J.R., "Numerical Solution of Equations of the
    Diffusion Type with Diffusivity Concentration-Dependent,"

65. Redlich, O., and Kister, A.T., "Algebraic Representation
    of Thermodynamic Properties and the Classification of

66. Sauer, F., and Freise, V., "Diffusion in Binary Systems

67. Seith, W., Diffusion of Metals, (translation as AEC
    report AEC-tr-4506).


70. Sundelöf, L.-O., "Isothermal Diffusion in Ternary Systems,"

71. Theisen, R., "Detection Limits of Electron Microprobe
    Analysis," paper presented at the ECS-AIME, Toronto,
    May, 1964 (to be published).

72. Vignes, A., and Birchenall, C.E., "The Phenomenological
    Theory of Diffusion and the Kirkendall Effect," (to be
    published).


74. Wendt, R.P., "Studies of Isothermal Diffusion at 25°C
    in the System Water-Sodium Sulfate-Sulfuric Acid and
    (1962).


