

Diffusion in solids. Part II. Diffusion in binary systems

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**DIFFUSION IN SOLIDS.
PART TWO: DIFFUSION IN BINARY SYSTEMS**

by

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TABLE OF CONTENTS

Objectives

Prerequisites

Introduction

Experimental Determination of Chemical
Diffusion Coefficients

Intrinsic Diffusion Coefficients

The Relation Between Chemical Diffusion and
Self-Diffusion

Ambipolar Diffusion

Interdiffusion in Multiphase, Binary Systems

Objectives

Upon successful completion of this module, the student should be able to:

(1) determine the chemical diffusion coefficient from a concentration profile of a binary diffusion couple, using the Matano-Boltzmann equations.

(2) describe the relation between chemical-, intrinsic- and tracer-diffusion coefficients.

(3) describe the meaning of the Kirkendall plane and the Matano plane.

Prerequisites

The reader should have completed a general chemistry course, introductory courses in differential calculus and an elementary course in thermodynamics. The reader should be acquainted with the elementary concepts of defect chemistry and should have studied Part I of this module.

GLOSSARY OF TERMS

ambipolar diffusion	diffusion of charged particles
chemical diffusion	refers to diffusion in a chemical-potential gradient
interdiffusion	is equivalent with chemical diffusion
intrinsic diffusion	describes the diffusion of the different components during chemical diffusion
tracer diffusion	refers to diffusion of a tracer isotope in very dilute concentration in an otherwise homogeneous sample without chemical potential gradients
self diffusion	is equivalent with tracer diffusion when the tracer atoms are of the same species as the non-tracer atoms
Matano plane	a mathematical plane dividing a binary diffusion couple in two halves, such that the total amount of a component that disappeared from one half equals the amount that appears in the other half
Kirkendall plane	the plane indicating the position of a marker, originally at the interface between two couple halves, after a diffusion experiment

DIFFUSION IN SOLIDS.
PART TWO: DIFFUSION IN BINARY SYSTEMS

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INTRODUCTION

In Part I of this module, we have given a phenomenological definition of diffusion coefficients using Fick's laws. We have focussed our attention mainly on the determination of tracer diffusion coefficients, D^* and we have given an interpretation of D^* in terms of atomic jumps. However, in most of the practical cases which a materials scientist will encounter, diffusion is driven by a gradient in the concentration of the diffusing elements or more generally by a gradient in the chemical potential. As discussed in Part I, the corresponding diffusion coefficient, as defined by Fick's First Law, is called chemical diffusion coefficient, or interdiffusion coefficient, \tilde{D} . In this module we will see how \tilde{D} can be evaluated experimentally and how \tilde{D} is related to the self-diffusion coefficients of the migrating elements. Next we shall trace the influence of the electrical charges when ions diffuse instead of neutral atoms.

EXPERIMENTAL DETERMINATION OF CHEMICAL
DIFFUSION COEFFICIENTS

In this section we consider the interdiffusion of two components. As a simple example we could study the interdiffusion of Cu and Ni. One then could take a piece of Cu and a piece of Ni, polish the surfaces and press these two pieces against each other. This assembly is called a diffusion couple. At time $t=0$, we place this couple in a furnace at a constant temperature and after a certain time, t , we rapidly cool the sample to room temperature. Next we measure the concentration profiles of the components Cu and Ni, e.g. with the aid of an electron probe microanalyzer. The question now is how to determine the interdiffusion coefficient \tilde{D} from the measured concentration profile.

The starting point of our discussion is Fick's First Law. For one-dimensional diffusion in the z -direction we have

$$J_i = -\tilde{D} \frac{\delta c_i}{\delta z} \quad (1)$$

where J_i is the flux of diffusing atoms i and c_i the concentration of component i . In this module, we assume that the partial molar volume \tilde{V}_i of each component is constant. The flux of atoms is then defined with respect to a fixed origin, e.g. the outer edge of the sample. Note that with the concentration c_i expressed in mol m^{-3} , distance z in m, flux J in $\text{mol m}^{-2}\text{s}^{-1}$, \tilde{D} is obtained in units m^2s^{-1} . The concentrations c_i vary with the distance z . Since the chemical diffusion coefficient \tilde{D} is concentration dependent, \tilde{D} is also a function of z . Experimentally we do not measure the atom flux but the concentration distribution at a given diffusion time. To evaluate \tilde{D} from experimentally determined concentration profiles $c_i(z,t)$, we have to solve Fick's Second Law:

$$\frac{\delta c_i}{\delta t} = \frac{\delta}{\delta z} \left(\tilde{D} \frac{\delta c_i}{\delta z} \right) \quad (2)$$

For tracer diffusion this equation could be solved under the assumption that the diffusion constant is independent of concentration. For chemical diffusion this assumption is generally not applicable. Exceptions are often found for atoms moving via the interstitial mechanism. An example of chemical diffusion where \bar{D} varies only weakly with concentration is that of carburization (or decarburization) of iron. In this system, the carbon atoms move via interstitial positions and the interaction with the iron lattice is small.

Exercise 1:

Consider a piece of iron with 100 cm^2 cross-section (assume the sample to be semi-infinite). The sample is heated in an atmosphere with constant carbon activity, e.g. in a gas mixture of CO/CO_2 or of CH_4/H_2 . After 15 hours the sample has gained 1.0g in weight. Calculate the chemical diffusion coefficient of carbon in iron. The maximum solubility of C in Fe at the diffusion temperature is 0.12 g/cm^3 .

Answer:

Due to the carbon atmosphere, a constant C surface concentration c_0 is maintained in the Fe, with c_0 equal to the saturation concentration of 0.12 g/cm^3 . For a semi-infinite sample with a constant concentration c_0 we have [Eq. (23), Part I]

$$c(z,t) = c_0 \left[1 - \operatorname{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \right]$$

with

$$\operatorname{erf} y = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-x^2) dx$$

DIFFUSION IN BINARY SYSTEMS

The flux through the surface is, according to Fick's first law

$$J = -\tilde{D}(\delta c/\delta z)_{z=0}$$

Differentiating the error function gives

$$J = \frac{\tilde{D}c_0}{(\pi\tilde{D}t)^{1/2}}$$

The total amount of carbon that diffused through the surface in t seconds is

$$M = \int_0^t \frac{\tilde{D}c_0}{(\pi\tilde{D}t)^{1/2}} dt = 2c_0 \left(\frac{\tilde{D}t}{\pi}\right)^{1/2}$$

With $M = 1/100 = 10^{-2} \text{ g/cm}^2$, $t = 15.3600 = 5.4 \cdot 10^4 \text{ s}$, and $c_0 = 0.12 \text{ g/cm}^3$, we find

$$D = 1 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$$

Alternative Answer:

In part I of this module we also gave an equation [Eq. (25)] which gives a quick estimate of the penetration depth z_p :

$$z_p^2 \approx \tilde{D}t$$

In our exercise, the penetration depth after $t = 15$ hours can be approximated: when we have 1g of carbon in a sample with 100 cm^2 cross-section and a saturation concentration of 0.12 g/cm^3 the penetration depth $z_p \approx 0.08 \text{ cm}$. Therefore $D \approx (8 \cdot 10^{-4})^2 / (15.3600) = 1.2 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$. We see that this approximation quickly leads to a value which is close to the more accurate value obtained above.

As stated earlier, in most cases of chemical diffusion, D is a function of concentration. In the following, we will therefore discuss how to solve Eq. (2)

for the general case. For this purpose a method was introduced by Matano. The assumption made by Matano is that the concentrations are a unique function of z/\sqrt{t} [compare for instance the solutions Eq. (22) and (23) discussed in Part I and also exercise 1]. This assumption is valid in many cases, but it should in fact be verified always before we use the Matano analysis. On the basis of this assumption, we introduce the new variable $\lambda = z/\sqrt{t}$. With the substitution $t = z^2/\lambda^2$ and $\delta t = -2/\lambda t \delta \lambda$. The left half of Eq. (2) can be written as

$$\frac{\delta c_i}{\delta t} = \frac{-\lambda}{2t} \frac{\delta c_i}{\delta \lambda}$$

In the right half of Eq. (2), we substitute $z = \lambda/t$, so $\delta z = \sqrt{t} \delta \lambda$.

$$\frac{\delta c_i}{\delta z} = \frac{1}{\sqrt{t}} \frac{\delta c_i}{\delta \lambda} \quad \text{and} \quad \frac{\delta}{\delta z} \left(D \frac{\delta c_i}{\delta z} \right) = \frac{1}{t} \frac{\delta}{\delta \lambda} \left(D \frac{\delta c_i}{\delta \lambda} \right)$$

With these substitutions, Eq. (2) becomes

$$-\frac{\lambda}{2} \frac{\delta c_i}{\delta \lambda} = \frac{\delta}{\delta \lambda} \left(D \frac{\delta c_i}{\delta \lambda} \right) \quad (3)$$

Consider now the case that the concentration profile of the diffusing element at a given moment is represented by Fig. 1a. At the ends of the sample, the concentrations are constant:

$$\text{for } \lambda = -\infty, c = c_i^-; \text{ for } \lambda = +\infty, c = c_i^+$$

We integrate Eq. (3) from $\lambda = -\infty$ to λ^* , i.e. from $c = c_i^-$ to $c = c_i^*$ (cf. Fig. 1b):

$$-1/2 \int_{c_i^-}^{c_i^*} \lambda dc_i = \tilde{D} \left[\left(\frac{\delta c_i}{\delta \lambda} \right)_{c=c_i^*} - \left(\frac{\delta c_i}{\delta \lambda} \right)_{c=c_i^-} \right] \quad (4)$$

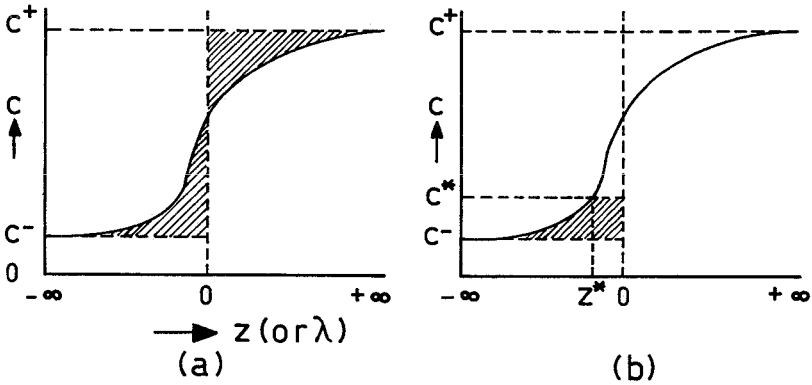


FIG. 1

Concentration profile $c(z)$ of one of the elements in a diffusion couple at a given time t . z gives the distance in the couple, λ is the variable z/\sqrt{t} . The plane $z=0$ (called Matano plane) is defined by making the shaded areas in Fig. 1a equal. The shaded area in Fig. 1b gives the value of the integral in Eq. (4); integration is carried out with respect to the c -axis.

Since

$$\left(\frac{\delta c_i}{\delta \lambda}\right)_{c=c_i^-} = 0$$

we obtain

$$\tilde{D}(c_i^*) = -1/2 \frac{\int_{c_i^-}^{c_i^*} \lambda dc_i}{(\delta c_i / \delta \lambda)_{c_i^*}} \tag{5a}$$

or

$$\tilde{D}(c_i^*) = \frac{1}{2t} \frac{\int_{c_i^-}^{c_i^*} z dc_i}{(\delta c_i / \delta \lambda)_{c_i^*}} \quad (5b)$$

Equation (5) is known as the Matano-Boltzmann equation. Using this expression, we can evaluate \tilde{D} at each point of the penetration curve.

We can only apply Eq. (5b) if we know the origin of the z -coordinate. Note that for $c_i^* = c_i^+$, Eq. (5) reduces to

$$\int_{c_i^-}^{c_i^+} \lambda dc_i = \int_{c_i^-}^{c_i^+} z dc_i = 0 \quad (6)$$

This condition defines the plane $z=0$, called the Matano plane (cf. Fig. 1a). At time $t=0$, with our restriction that the partial molar volumes \bar{V}_i are constant, this plane coincides with the contact interface between the two starting materials. It follows from this definition that the Matano plane is situated so that all atoms leaving the part $z<0$, reappear in the part $z>0$. In the case that \tilde{D} is independent of concentration, the penetration curve is symmetric with respect to the Matano plane and the concentration gradient reaches a maximum value in this plane.

Example. Suppose we want to determine \tilde{D} from the concentration profile shown in Fig. 1b, in the plane with coordinate z^* . We determine first the Matano plane using Eq. (6), as shown in Fig. 1a. Next we can apply Eq. (5b) to calculate \tilde{D} . The numerator in this equation is obtained by measuring the shaded area in Fig. 1b; note that the integration is carried out with respect to the c -axis. The denominator of Eq. (5b) is given by the slope of the concentration curve at z^* .

The parameter $\lambda(c_i)$ is very important since, at a particular temperature, it is only a function of concentration. This implies that each concentration c_i is connected with a value of z/\sqrt{t} . Therefore, a plane with a given value c_i moves through the diffusion couple in such

a way that

$$d^2 = kt \quad (7)$$

where d is the distance between the plane and the Matano interface, t the diffusion time and k a proportionality constant called the penetration constant (dimension $m^2 s^{-1}$).

INTRINSIC DIFFUSION COEFFICIENTS

The Kirkendall Effect

Let us consider in more detail the interdiffusion via a vacancy mechanism in single phase, binary metal alloys. As an example we bring metal A in close contact with metal B, and we assume that A and B form a continuous solid solution. To avoid mathematical complications we further assume:

a. The atomic volumes \bar{V}_A and \bar{V}_B are equal and independent of concentration; consequently the total volume of the couple remains constant $\bar{V}_A = \bar{V}_B = \bar{V}_M$.

b. The diffusion couple is semi-infinite i.e. the concentrations of A and B at the ends of the couple are constant. Also, the cross-section of the couple remains constant.

c. Diffusion takes place only in the direction perpendicular to the contact interface between A and B (the z -direction).

Figure 2 shows a couple where atoms A diffuse from left to right and atoms B from right to left. To mark the original interface between A and B we separate the lower parts of the couple from each other with the aid of an inert foil which acts as a diffusion barrier. In the upper part, we mark the interface with inert markers (Fig. 2a). As such, one can use small particles or thin wires, as long as they do not react with the components of the diffusion couple. Also a pore or an indentation (e.g. as made in a Vickers microhardness test) at the interface can be used as such. After a certain diffusion duration we often find a displacement of the markers with respect to

the plane of the foil (Fig. 2b). This was first demonstrated by Kirkendall and Smigelskas [1] in a diffusion couple of copper and brass, using Mo wires as markers. Therefore, the phenomenon of displacement of the marker interface relative to a fixed point outside the diffusion zone (the foil in our example) is called the Kirkendall effect. An explanation was given by Darken. He has shown that the effect occurs in all systems where diffusion takes place via the vacancy mechanism and where the two components have unequal diffusion coefficients, $D_A \neq D_B$. We call these coefficients intrinsic diffusion coefficients.

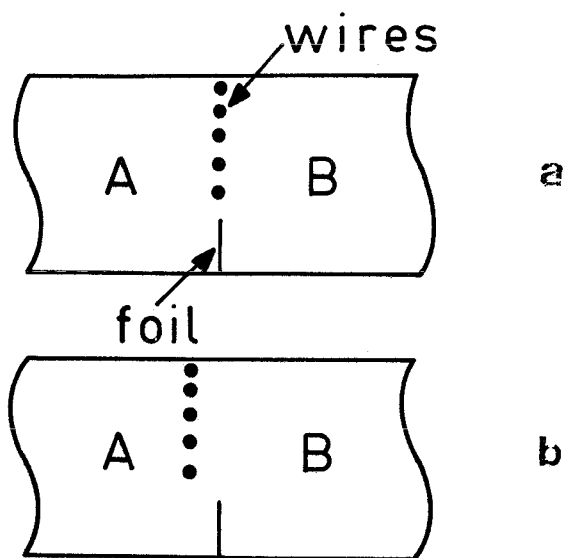


FIG. 2

Diffusion couple A vs. B. At the interface between A and B an inert metal foil and some inert markers have been inserted.

- (a) Indicates the initial marker position,
 (b) shows the marker position after diffusion.

We can illustrate the Kirkendall effect with the aid of Fig. 3. Assume that component A diffuses faster than B, i.e. the flux J_A through the interface between A and B exceeds the flux J_B through this interface. As a result

DIFFUSION IN BINARY SYSTEMS

the volume of the couple at the right-hand side of the marker plane increases, while the volume on the left decreases (see Fig. 3b). If the plane containing the markers is held in a fixed position, the couple moves to the right over a distance z_k . If the sample is brought back to its original position, the markers appear to have moved to the left over the distance z_k (see Fig. 3c); this is just what we see when we look at the markers from a fixed, external reference frame.

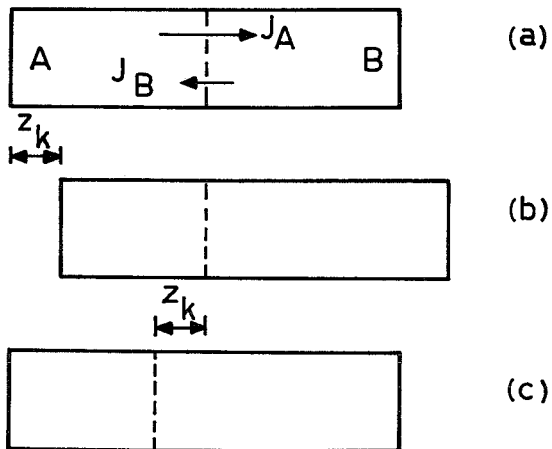


FIG. 3

The Kirkendall effect. The dotted line indicates the position of inert markers. (a) Gives the marker position at the start of the diffusion experiment, (b) and (c) give the position after diffusion. In (b) the position of the markers is thought to be fixed in space and as a result the ends of the couple are shifted. In (c) the couple is brought to its original position and as a result the marker plane is shifted.

The arrows indicate the flux of atoms, with $J_A > J_B$.

In the original experiment by Kirkendall and Smigelskas we have the following explanation. Both the Cu and the Zn atoms move over vacancies in the same lattice. However, the mobility of Cu atoms is smaller than of Zn atoms. In the Cu-rich part, the number of vacancies will

decrease and to maintain the local equilibrium concentration, new vacancies have to be created, e.g. on the surface of the sample. The opposite takes place in the Zn-rich part of the couple. The Kirkendall shift has been observed in many metal systems. The effect is often accompanied by the occurrence of porosity at the side of the diffusion zone bordering the metal with the highest diffusion rate. Referring to Fig. 3, we see that in the region left of the markers more A atoms disappeared than were replenished by B atoms. In this region, therefore, a high concentration of vacancies is created. When the vacancy concentration exceeds the thermal equilibrium concentration these vacancies can cluster and form pores.

Determination of Intrinsic Diffusion Coefficients

Let us investigate how one can obtain the intrinsic diffusion coefficients D_i , and how they are related to the chemical diffusion coefficient D . Using Fick's First Law we can write expressions for the fluxes of components A and B. We assume that there are inert markers in the original interface between the two couple halves. With respect to this (moving) plane, generally called the Kirkendall plane, we can write the fluxes as

$$J_A^K = -D_A \frac{\delta c_A}{\delta z}$$

$$J_B^K = -D_B \frac{\delta c_B}{\delta z} \quad (8)$$

where the superscript K indicates that the fluxes are evaluated in the Kirkendall plane.

The sum of the concentrations is constant, $c_A + c_B = c_T$. Therefore, $\delta c_A = -\delta c_B$.

Because $D_A \neq D_B$, the fluxes J_A^K and J_B^K will be different. If $D_A > D_B$, the number of A atoms arriving at the right-hand side exceeds the number of B atoms leaving this side. The difference in fluxes is compensated by a flux of vacancies J_V from right to left:

DIFFUSION IN BINARY SYSTEMS

$$J_V^K = -(J_A^K + J_B^K) = (D_A - D_B) \frac{\delta c_A}{\delta z} \quad (9)$$

The velocity of the marker displacement, v_K , is obtained by dividing J_V^K by the total number of atoms per unit volume

$$v_K = J_V^K / c_T = \frac{D_A - D_B}{c_T} \frac{\delta c_A}{\delta z} \quad (10)$$

In Eq. (8) we have defined the fluxes with respect to a moving coordinate system. Let us next consider the fluxes with respect to the Matano plane (which is fixed in an external reference frame). We will indicate this with the superscript M, i.e. J_i^M .

J_A^M consists of the flux J_A^K through the Kirkendall plane, plus the flux resulting from the displacement of the Kirkendall plane with respect to the Matano ($z=0$) plane, i.e. $c_z v_K$:

$$J_A^M = J_A^K + c_z v_K = -D_A \frac{\delta c_A}{\delta z} + c_A v_K$$

Substitution of v_K from Eq. (10) gives

$$J_A^M = -D_A \frac{\delta c_A}{\delta z} + \frac{c_A}{c_T} (D_A - D_B) \frac{\delta c_A}{\delta z}$$

Introducing molar fractions

$$N_A = c_A / c_T = 1 - N_B$$

we get

$$J_A^M = -(N_B D_A + N_A D_B) \frac{\delta c_A}{\delta z} \quad (11)$$

Experimentally we determine

$$\tilde{D} = -J_A^M / \left(\frac{\delta c_A}{\delta z} \right)$$

for instance with the Boltzmann-Matano procedure described in Section 2. Comparison with Eq. (11) shows that

$$\tilde{D} = N_A D_B + N_B D_A \quad (12a)$$

This equation is known as the Darken equation. It can be shown that, if we drop the limitation, introduced earlier, that the partial molar volume $\bar{V}_A = \bar{V}_B$, the equation becomes

$$\tilde{D} = N_A \bar{V}_A D_B + N_B \bar{V}_B D_A \quad (12b)$$

Equation (12) gives the relation between the chemical diffusion coefficient \tilde{D} and the intrinsic diffusion coefficients D_A and D_B in the Kirkendall plane. At this time it is good to consider once again the meaning of the Kirkendall plane. We have purposely inserted our markers at the interface between the two couple halves since this is a plane of constant concentration. This condition of constant concentration is only fulfilled at the Kirkendall interface. Since the concentration is constant $c(\lambda) = c(z/\sqrt{t})$ is constant. Therefore, the displacement of the Kirkendall plane is proportional to \sqrt{t} :

$$z_K = at^{1/2} \quad (13)$$

Consequently, the velocity of the displacement of this plane with respect to the Matano plane is:

$$v_K = \frac{\delta z_K}{\delta t} = \frac{\delta(at^{1/2})}{\delta t} = \frac{z_K}{2t} \quad (14)$$

This means that we can determine the velocity of the Kirkendall plane by measuring the marker displacement. Also, by combining Eqs. (10) and (14) we obtain

DIFFUSION IN BINARY SYSTEMS

$$D_A - D_B = \frac{c_T z_K}{2t} \left(\frac{\delta c_A}{\delta z} \right)^{-1}$$

Of course, we could have inserted markers at other places in our diffusion couple. However, at these markers the concentration varies continuously with time and Eq. (13) does not hold. Therefore, only for the Kirkendall plane relatively simple expressions are found for the intrinsic diffusion coefficients.

Relations (13) and (14) have been verified in many experiments. An example is shown in Fig. 4 for a couple of U against a U-Mo alloy.

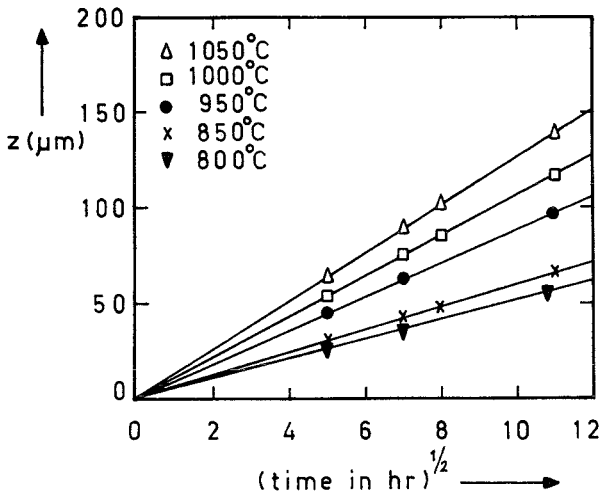


FIG. 4

The displacement of the marker plane in a diffusion couple of U vs. a U-Mo alloy, plotted as a function of the square root of time (from Y. Adda and J. Philibert, C.R. Acad. Sci. 246, 113 (1958)).

Exercise 2:

What is the velocity of the Kirkendall plane in the system U vs. U-Mo at 1000°C?

Answer:

From Fig. 4 at $t=100$ hr we find $z_K = 107 \mu\text{m}$ at 1000°C . Equation (14) then gives $v_K = 107 \times 10^{-6} / 200 \times 3600 = 1.5 \times 10^{-10} \text{ ms}^{-1}$.

Combination of Eqs. (4), (12) and (14) leads to an expression for D_A (or D_B) in the Kirkendall plane:

$$D_A(c_A^K) = \frac{1}{2t} \left(\frac{\delta z}{\delta c_A} \right)_{z_K} [c_A^K z_K - \int_{c_A^-}^{c_A^K} z dc_A]$$

In practice, one often prefers to carry out the integration with respect to the z -axis instead of the concentration axis. This is easily accomplished by partial integration of the above equation:

$$D_A(c_A^K) = \frac{1}{2t} \left(\frac{\delta z}{\delta c_Z} \right)_{z_K} [z_K c_A^- + \int_{-\infty}^{z_K} (c_A - c_A^-) dz] \quad (15a)$$

If at least one of the starting materials is a pure component, e.g. $c_A^- = 0$, Eq. (15a) reduces to

$$D_A(c_A^K) = \frac{1}{2t} \left(\frac{\delta z}{\delta c_Z} \right)_{z_K} \int_{-\infty}^{z_K} c_A dz \quad (15b)$$

Exercise 3:

Calculate the interdiffusion coefficients in the Kirkendall plane and the velocity of the markers for the system U vs. Zr at 1000°C , using the data in Fig. 5. Also calculate the chemical diffusion coefficient for the U/Zr ratio in the Kirkendall plane.

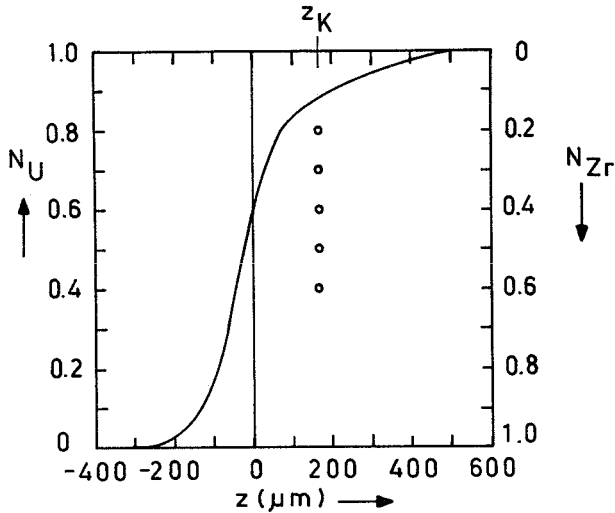


FIG. 5

Concentration profile as measured with an electron microprobe for a couple of U vs. Zr, after 24 hr at 1000°C. $z=0$ is chosen at the Matano plane, z_K indicates the marker plane. [From Y. Adda and J. Philibert, "La diffusion dans les solides," Presses Univ. de France (1966).]

Answer:

The Matano plane, $z=0$ is found according to the procedure shown in Fig. 1a. This has been done already in Fig. 5. (You can check this by measuring the areas left and right of the $z=0$ line.) The marker displacement $z_K=165 \mu\text{m}$. This is the displacement after 24 hr at 1000°C, so the velocity $v_K=165 \times 10^{-6} / 2.24 \times 3600 = 9.55 \times 10^{-10} \text{ m s}^{-1}$. The difference $(D_U - D_{Zr})$ is obtained from Eq. (10). To this end we measure the slope $(\delta N_U / \delta z)$ of the penetration curve in $z=z_K$. This yields a value of $(\delta N_U / \delta z)_z = 570 \text{ m}^{-1}$, so $D_U - D_{Zr} = 9.55 \cdot 10^{-10} / 570 = 1.67 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. Next we calculate D_{Zr} using Eq. (15b). From the figure we measure the area $\int_{\infty}^{z_K} N_{Zr} dz = 14 \cdot 10^{-6} \text{ m}$. This gives us

$$D_{Zr} = 14 \times 10^{-6} / 2.24 \times 3600 \times 570 = 1.42 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$$

so

$$D_U = (16.7 + 1.4) \times 10^{-13} = 18.1 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} .$$

The chemical diffusion coefficient is given by Eq. (12a). In the marker plane $N_U = 0.89$, $N_{Zr} = 0.11$, so $\bar{D} = (0.89 \times 1.4 + 0.11 \times 18.1) \times 10^{-13} = 3.2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. We can also calculate \bar{D} at $z = z_K$ directly from Eq. (5). From Fig. 5 we obtain

$$\begin{aligned} \int_0^{N_U=0.89} z \, dN_U &= \int_0^{0.6} z \, dN_U + \int_{0.6}^{0.89} z \, dN_U \\ &= -34 \cdot 10^{-6} \text{ m} \end{aligned}$$

Here the first integral is negative since $z < 0$. With this value we obtain $\bar{D} = 3.5 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The difference with the value calculated above is due to unavoidable errors in the reading of the graphs.

The diffusion coefficient can generally be written as

$$D(c) = D_0(c) \exp[-Q(c)/RT] \quad (16)$$

where D , D_0 and Q are concentration dependent. Further we notice that D , t and the penetration z are related to each other by the dimensionless quantity

$$k = z^2/Dt \quad (17)$$

If we combine Eqs. (16) and (17) and apply them to the Kirkendall plane, we find

$$z_K = (kD_{O,K}t)^{1/2} \exp(-Q_K/2RT) \quad (18)$$

Therefore, from the temperature dependence of the marker displacement we can directly calculate the activation energy Q_K .

THE RELATION BETWEEN CHEMICAL DIFFUSION AND SELF-DIFFUSION

We have defined the diffusion coefficient by means of Fick's first law [Eq. (1)]. In many cases, diffusion is not caused by a gradient in the concentration but by, e.g., a gradient in the electrical potential, or a temperature gradient, etc. Intuitively we therefore expect that a more general formulation should be possible. A sound base for this idea is given by the thermodynamics of irreversible processes (a general treatment of this theory is given, e.g., in ref. 2; a module on this topic is in preparation for JME by J.M. Chaix). In the thermodynamic theory it is assumed that the particle current J_i of component i can be expressed in terms of driving forces X , by

$$J_i = \sum_{j=1}^n L_{ij} X_j \quad i = 1, 2, \dots, n \quad (19)$$

For instance, the driving force could be a gradient in the chemical potential μ , i.e. $X_j = -\delta\mu_j/\delta z$. The coefficients L_{ij} , which are independent of the force X , are called phenomenological coefficients. It follows from Eq. (19) that the flux J_i depends not only on X_i , but also on X_j ($i \neq j$). Although the cross-terms $L_{ij}X_j$ can be quite significant, we here only consider the case that a particle diffuses without interaction with other components. Such is the case for a species migrating via the interstitial mechanism. Under this assumption, Eq. (19) simplifies to

$$J = -L \frac{\delta\mu}{\delta z} = -L \frac{\delta\mu}{\delta c} \frac{\delta c}{\delta z} \quad (20)$$

Comparison with Eq. (1) shows that

$$\bar{D} = L(\delta\mu/\delta c)$$

Next we apply this result to study a binary system, e.g. a diffusion couple of A/B. We assume that the cross-terms L_{ij} , which represent the interaction between A and B, are negligible. Equation (20) can now be used to obtain the

flux of atoms A and B. With the aid of $\mu_i = \mu_i^0 + RT \ln \gamma_i N_i$, where γ_i is the activity coefficient and N_i is the molar fraction of component i, Eq. (20) becomes

$$J_i = -L_{ii} RT \frac{\delta \ln a_i}{\delta z} = -L_{ii} RT \frac{\delta \ln \gamma_i N_i}{\delta z} \quad (21)$$

Let us now apply this equation to obtain the flux of A atoms in the marker plane. As an abbreviation we write $L_{11} = L_A$ and $L_{22} = L_B$. From Eq. (21) we find

$$\begin{aligned} J_A^K &= -L_A RT \frac{\delta \ln \gamma_A N_A}{\delta z} \\ &= -\frac{L_A RT}{c_T} \frac{\delta \ln \gamma_A N_A}{\delta N_A} \frac{\delta c_A}{\delta z} \\ &= -\frac{L_A RT}{c_A} \frac{\delta \ln \gamma_A N_A}{\delta \ln N_A} \frac{\delta c_A}{\delta z} \\ &= -\left[\frac{L_A RT}{c_A} \left(1 + \frac{\delta \ln \gamma_A}{\delta \ln N_A} \right) \right] \frac{\delta c_A}{\delta z} \quad (22) \end{aligned}$$

In Eq. (8), we have defined the intrinsic diffusion coefficient D_A , with

$$J_A^K = -D_A \frac{\delta c_A}{\delta z} \quad (8)$$

Comparison of Eqs. (8) and (22) shows

$$D_A = \frac{L_A RT}{c_A} \left(1 + \frac{\delta \ln \gamma_A}{\delta \ln N_A} \right) \quad (23)$$

DIFFUSION IN BINARY SYSTEMS

The expression in parentheses is often called the thermodynamic coefficient. In the case of tracer-diffusion of A^* in AB, the concentration gradient is negligible, so

$$\frac{\delta \ln \gamma_A}{\delta N_A} = 0 \quad \text{and} \quad D_A^* = \frac{L_A RT}{c_A}$$

This gives us a very useful relation between the intrinsic diffusion coefficient D_A and the directly measurable tracer-diffusion coefficient D_A^* (see Part I of this module):

$$D_A = D_A^* \left(1 + \frac{\delta \ln \gamma_A}{\delta \ln N_A} \right) \quad (14)$$

Another important relation is obtained if Eqs. (24) and (12a) are combined:

$$\tilde{D} = (N_A D_B^* N_B D_A^*) \left(1 + \frac{\delta \ln \gamma_A}{\delta \ln N_A} \right) \quad (25)$$

where we have used $\delta \ln \gamma_A / \delta \ln N_A = \delta \ln \gamma_B / \delta \ln N_B$. This latter relation can easily be derived from the thermodynamic Gibbs-Duhem relation i.e. $N_A d\mu_A + N_B d\mu_B = 0$. Equations (24) and (25) have been derived by Darken [3]. They are, in fact, approximations because we have neglected the off-diagonal terms in the derivation. For a more rigorous treatment we refer to the literature [4].

AMBIPOLAR DIFFUSION

The discussion of the preceding sections is valid for neutral diffusing particles, e.g. atomic movements in metals or alloys. In many cases, however, charged particles are involved. For instance, when a metal is oxidized metal ions or oxygen ions have to be transported through the oxide layer. Such an ion movement is possible

only if at the same time a counterdiffusion occurs of a species with the same charge or if a parallel diffusion occurs of a species with opposite charge (Fig. 6).

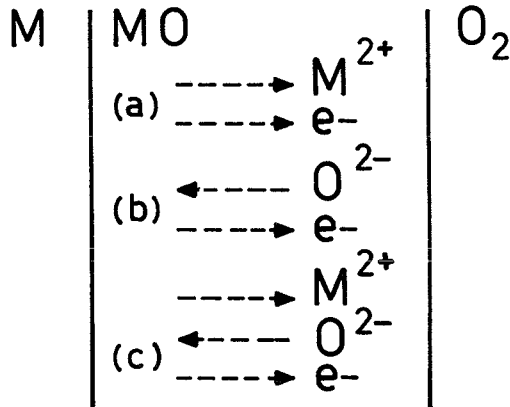


FIG. 6

Possible transport mechanisms involved in the oxidation reaction of a metal M into MO: (a) transport of metal ions and electrons, resulting in growth at the outside of the oxide layer; (b) transport of oxygen ions and counterdiffusion of electrons, resulting in growth at the M/MO interface; (c) transport of metal ions and electrons and counterdiffusion of oxygen ions, resulting in growth within the MO layer.

This is necessary because otherwise an electric field would be created which would counteract the ion movement.

Take, as an example, the situation of Fig. 6a. At the M/MO interface M atoms dissolve in MO forming M²⁺ ions and electrons. As a rule, the electrons move faster than the ions and an electric field $d\phi/dx$ is built up. Due to this field, the M²⁺ ions will try to keep up with the electrons and a stationary state is reached when

$$J_{M^{2+}} - J_{e^-} = 0 \quad (26)$$

DIFFUSION IN BINARY SYSTEMS

For a detailed discussion of ambipolar diffusion and its influence on chemical diffusion coefficients we refer to the literature [5]. However, some general conclusions can be given.

Looking at the example of Fig. 6a one finds that the mobility of the slowest of the two particles (here the metal ion) limits the diffusion rate. On the other hand, the chemical diffusion coefficient exceeds the intrinsic diffusion coefficient of the slowest particle by a factor of 2 or 3, depending on the charges involved. This effect is due to the drag exerted by the faster partner (the electron). This conclusion is always valid for the case that we are dealing with: two mobile species.

In the situation shown in Fig. 6c, there are three charged particles involved. In this case, the particle with the lowest mobility can be left out of our discussion.

INTERDIFFUSION IN MULTIPHASE, BINARY SYSTEM

In the preceding sections, the discussion has been restricted to single phase, binary systems. In practice, however, situations occur where several phases are present at the same time. For instance, in metallic diffusion couples this is frequently the case. Figure 7 shows an example of a diffusion couple A/B for a system with three solid solutions, called α , β and γ .

Figure 7a shows the composition temperature diagram. Figure 7b shows the concentration at temperature T_0 of component B as a function of distance going from pure A to pure B. The concentration of B gradually increases from zero in the α phase. Above a certain concentration, however, a mixture of α and γ is formed. From the phase rule it follows that there are only two degrees of freedom in a two-phase region of a binary system. Therefore, at a fixed pressure and temperature the concentrations of the components are constant. As a result, two-phase regions do not occur in diffusion couples of a binary system. The penetration curves of A and B have discontinuities at the boundaries between the different phases (Fig. 7b).

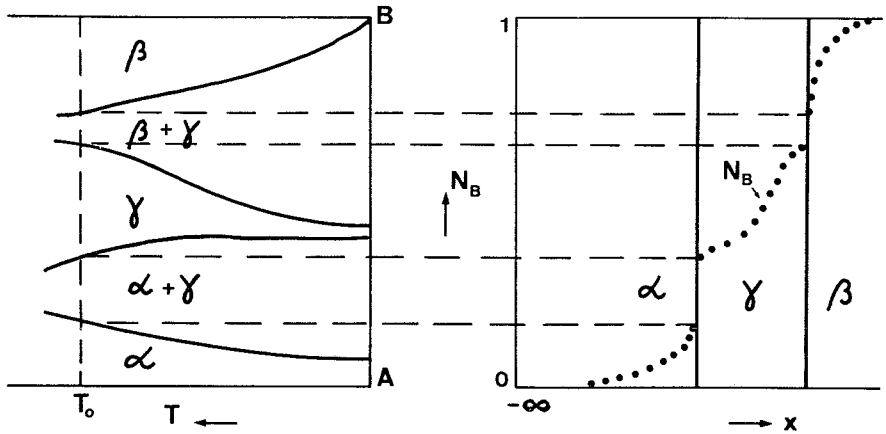


FIG. 7

(a) A fictitious phase diagram of the metals A and B, rotated 90 degrees. (b) The diffusion couple A-B with layers of α and β and the penetration curve of component B after t seconds at temperature T_0 .

However, the diffusion coefficients can still be determined with the aid of Eq. (15), since the only condition for its applicability is that the penetration curve can be integrated. In passing, we remark that multiphase diffusion experiments, as described above, are an important tool in investigating phase diagrams since, in principle, all equilibrium phases occur in such a diffusion couple.

Figure 8 gives an example of a penetration curve for the system Au-Pt after 200 hrs at 1020°C . We see from this curve that at 1020°C the maximum solubility of Au in Pt is reached at 14 at% Au, while the maximum solubility of Pt in Au is 34 at%.

This is only one of many examples. In many systems of practical importance, two-phase regions may occur. For instance, the Fe-C system or the Al-Cu system are well known in metallurgy.

DIFFUSION IN BINARY SYSTEMS

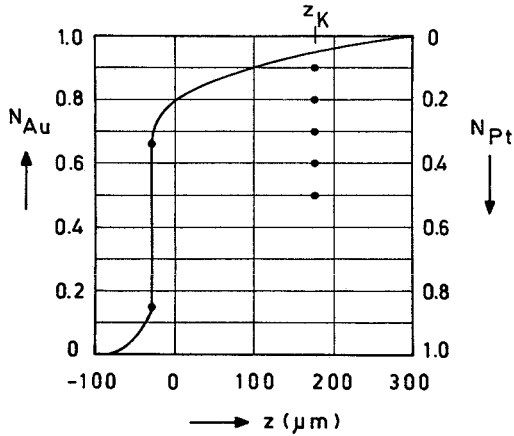


FIG. 8

Penetration curve of the couple Au-Pt
after 100 hrs at 1020°C.

In this module, we have only treated the basic phenomena of binary diffusion. Many points of great practical importance have not been discussed. For example, grain boundary diffusion may strongly influence the thickness of a diffusion layer; the formation of cracks can completely spoil the protective action of an oxide layer, etc. Another point to keep in mind is that systems are not always in thermodynamic equilibrium. For instance, the precipitation of a new phase may be hindered or completely suppressed when nucleation kinetics is slow. For more details and examples, the student is referred to the literature.

SELF-TEST

1. Figure 9 shows a concentration profile for a couple of metals, A and B, after 20-hr diffusion.
 - a. Verify that the Matano plane is situated at $z = -78 \mu\text{m}$.
 - b. Determine \bar{D} for $N_A = 0.2, 0.4, 0.6, 0.8$ and 0.88 (i.e. in the Kirkendall plane).
 - c. Calculate D_A and D_B in the Kirkendall plane.

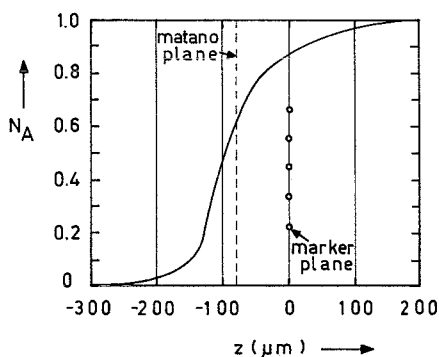


FIG. 9

Concentration profile of a couple A-B after 20-hr diffusion.

2. After a diffusion experiment with a couple of Al vs. Ni_2Al_3 , a layer of NiAl_3 is formed. The Kirkendall plane is found at the interface of Al and NiAl_3 .

What is your conclusion about the relative values of the diffusion coefficients D_{Ni} and D_{Al} in this system?

3. Calculate the activation energy (in kJ/mole) for the displacement of the Kirkendall plane for the couple U vs. U-Mo, using the data in Fig. 3.

ANSWERS TO SELF-TEST

- 1a. By integration, we verify

$$0 \int^{0.6} z dN_A = 0 \int^{0.4} z dN_B = 25.8 \cdot 10^{-6} \text{ m} .$$

- 1b. \tilde{D} values are calculated from Eq. (5b), with $2t = 1.44 \cdot 10^5 \text{ s}$.

N_A	$-\int z dN_A$ (μm)	$\delta z / \delta N_A$ (μm)	\tilde{D} ($\text{m}^2 \text{s}^{-1}$)
0.2	16.3	120	$1.35 \cdot 10^{-14}$
0.4	24.6	113	$1.93 \cdot 10^{-14}$
0.6	26.3	164	$2.99 \cdot 10^{-14}$
0.8	22.3	347	$5.38 \cdot 10^{-14}$
0.88	18.1	858	$1.08 \cdot 10^{-13}$

- 1c. The marker velocity is $v_K = 78 \times 10^{-6} / 1.44 \times 10^5 = 5.41 \times 10^{-10} \text{ ms}^{-1}$. With Eq. (10) we obtain $D_A - D_B = 5.41 \times 10^{-10} \times 858 \times 10^{-6} = 4.65 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. Combination with Eq. (12a) then gives $D_A = 5.1 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, $D_B = 5.2 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$. Another way to obtain D_A and D_B is to use Eq. (15b).

2. Only Al atoms take part in the diffusion process.
3. By plotting $\ln z_K$ for a fixed time as a function of reciprocal temperature T^{-1} we get a straight line with slope $-0.57 \cdot 10^4 \text{ K}$. From Eq. (18) we see $Q = 0.57 \cdot 10^4 \cdot 2R = 94.5 \text{ kJ/mole}$.

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