

Analysis of diffusion in metals based on non-equilibrium thermodynamics

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A general form of the first Fick law for diffusion in single-phase metallic alloys is obtained by the methods of non-equilibrium thermodynamics. Because the vacancies are treated as an independent component, the reactions for the creation of vacancies are considered. The electrons are also treated as a component, and therefore an internally generated electric field appears in the generalized equation, in addition to the usual externally applied electric field. Similarly, two types of temperature gradient are considered; consequently, even in nominally "isothermal" diffusion a gradient in temperature may exist. The power of an analysis based on non-equilibrium thermodynamics is shown by the fact that the resulting equations have produced solutions to three previously unresolved problems.

1. Introduction

Although diffusion in metals has been the subject of scientific research for about a century, many problems remain unsolved because an adequate basic analysis has not been available. For example, the accurate experimental data of Smith [1] on steady-state interstitial diffusion of carbon in face-centred cubic iron have not previously been explained theoretically because the internal electric field has not been included in the analysis. Similarly, thermo-migration in this system [2] could not be predicted quantitatively because the electric field associated with the Seebeck effect had not previously been taken into account. An anomalously large Kirkendall shift in the substitutional Cu-7 at % Sn alloy [3] was an unsolved problem for more than 30 years because the vacancies had not been adequately treated. Companion articles [4, 5] present detailed solutions to these longstanding problems.

The present application of non-equilibrium thermodynamics (NET) to diffusion in metals differs greatly from previous treatments, such as that of Adda and Philibert [6]. In particular: (i) the molecular reference frame plays a basic role; (ii) the vacancies are an independent component; (iii) the electrons enter explicitly into the analysis; and (iv) the effects of internal electric fields and temperature gradients are considered even in the case of normal, "isothermal" diffusion. As a consequence of these differences, the present analysis permits the deduction of results not previously obtainable.

From the viewpoint of materials science, NET makes three significant contributions to the analysis of diffusion in metals: the first is the basic concept of the Onsager relations; the other two are useful methodological procedures. The Onsager relations lead, for example, to a quantitative analysis of thermo-migration [5], but they have much broader significance for the general development of a basic treatment of diffusion. The two procedures that are conveniently adapted

from NET (but which are also available elsewhere) are: (i) a rigorously correct formulation of the quasi-linear phenomenological equations [7, 8] including the effect of an internally-generated electrical potential V_g , and (ii) methods for employing alternative reference frames for diffusion [9, 10]. Various reference planes must be employed in the solution of practical diffusion problems because the crystal lattice is the convenient choice for obtaining the basic diffusion coefficients (self-diffusion [11] and intrinsic-diffusion [4] coefficients), but the molecular (or number-fixed) reference frame greatly simplifies engineering-type calculations by permitting the use of a smaller number of mutual-coefficients.

The term "quasi-linear" signifies that the phenomenological coefficients may be functions of the thermodynamic state variables (concentration, temperature and pressure). Consequently, the present analysis is quite general and applies to any process of diffusion in metals within the wide range of applicability of quasi-linear NET. (Exceptions are diffusion along linear or planar defects, or in solid metals appreciably affected by additional components introduced, for example, by nuclear irradiation.) In view of the complication caused by a net rate of creation of vacancies (Equation 6 below), no attempt will be made at this time to treat the second Fick law although a relatively simple example has been published previously [4, 10]. Instead, the general form of the first Fick law for the one-dimensional case will be developed from the phenomenological equations of NET and the Onsager relations. Although the internally-generated quantities, V_g and $(dT/dx)_g$, are present in relatively simple cases of diffusion, the usual externally-applied electrical potential, V_a , and temperature gradient, $(dT/dx)_a$, will be considered explicitly only in a later article [5] concerned with the effect of external driving forces on diffusion.

Important quantities in the next section are the

fluxes, J , and the two types of driving forces, $d\bar{\mu}/dx$ and $\nabla T = dT/dx$; here $\bar{\mu}$ is the electrochemical potential, described below in connection with Equation 2. The fluxes are the flux of heat, J_q , the flux of electrons, J_e , and the fluxes of atomic particles, J_i , including the flux of vacancies, J_v ; therefore the index i takes on the values $v, 1, 2, \dots, n$ in an n -component alloy. The temperature gradient, ∇T , exists at a given point in the interior of a specimen, and is conveniently considered to be composed of two components,

$$\nabla T = \nabla_a T + \nabla_g T \quad (1)$$

$\nabla_a T$ is attributable to the usual *applied* means of producing a temperature gradient (for example, external heat sources, induction heating, or electrical resistance heating) and is zero in the absence of such an external source. $\nabla_g T$ is *generated* internally by redistribution of the particles of the system since each particle carries with it the enthalpy, h_i . The electrochemical potential, $\bar{\mu}$, of a particle having electrical charge q is composed of two parts,

$$\bar{\mu} = \mu + q(V_a + V_g) \quad (2)$$

where μ is the chemical potential, given by

$$\mu = \mu^0 + kT \ln(fX) \quad (3)$$

Here μ^0 is a reference value, k is Boltzmann's constant, T is absolute temperature, f is a thermodynamic activity coefficient and for the atomic particles X is the mole fraction:

$$X_i = \frac{c_i}{\sum_{i=v,1,\dots}^n c_i} \quad (4a)$$

where c_i is the number of particles per unit volume. For electrons X is conveniently chosen to be the particle ratio,

$$X_e = \frac{c_e}{\sum_{i=v,1,\dots}^n c_i} \quad (4b)$$

of electron to atomic particles. The division of the electrical potential into two components is analogous to the division of ∇T , (Equation 1). V_a is caused by an externally applied potential, V_A ; V_g is generated internally as a result of the redistribution of particles (electrons, atoms, and vacancies).

Experimental observations of several kinds indicate the existence of a relationship between the relative sizes of two interdiffusing atomic species and the behaviour of the vacancies [12]. A quantitative evaluation of this relationship has been given in a companion article (Section 5 of [4]), and for this purpose the present analysis must take account, not only of differences in atomic size, but of change in size with change in composition. This goal is achieved quite easily [10] by use of the variable partial molar volume, \bar{V}_i , of each atomic component. Not only substitutional atoms, but also interstitial atoms and vacancies have experimentally measurable values of \bar{V}_i . No necessity for a value of \bar{V}_e , the partial molar volume of the electrons, arises in the analyses being considered.

2. Formulation of diffusion and of creation reactions by use of non-equilibrium thermodynamics

The phenomena associated with the Kirkendall effect show that vacancies are being created and destroyed during the course of isothermal interdiffusion of two metals (Metals 1 and 2). Consequently, the formalism of non-equilibrium thermodynamics requires that the rate of entropy production, σ , be the following sum [7],

$$\sigma = -\frac{J_q}{T^2} \frac{dT}{dx} - \sum_{i=e,v,1,\dots}^n \frac{J_i}{T} \left(\frac{d\bar{\mu}_i}{dx} \right)_T - \frac{1}{T} \sum_{k=1}^r j_k A_k \quad (5)$$

of contributions from diffusion fluxes, J_i , and from rates of production, j_k , of the components (including the vacancies, component v) by the total of r chemical reactions that occur in the system. J_q is the heat flux and A_k is the chemical affinity of reaction k . The reader can find a full discussion of this equation in de Groot and Mazur [7].

For the purpose of this paper, Equation 5 is important for two reasons. First, because of the Curie principle [13] the fluxes J_i are functions of the forces dT/dx and $(d\bar{\mu}_i/dx)_T$ but *not* of the chemical affinities, A_k . Consequently the quasi-linear equations (Equations 10 to 12 below) have their usual form. Second, the change in concentration with time, $\partial c_i/\partial t$, is determined both by diffusion and by the chemical reactions. With a suitable choice of coordinate system, the quantitative relation can be represented as

$$\frac{\partial c_i}{\partial t} = \sum_{m=e,v,1,\dots}^n \frac{\partial}{\partial x} \left(\frac{D_{im}}{\bar{V}} \frac{\partial X_m}{\partial x} \right) + \sum_{k=1}^r r_{ik} \quad (6)$$

where D_{im} is an appropriate diffusion coefficient and r_{ik} is the rate of production of component i as a result of reaction k and \bar{V} is the total (average) molar volume. The significance of Equation 6 for the behaviour of vacancies depends on the character of the reactions that occur under given conditions of diffusion. We now briefly consider typical reactions.

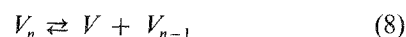
The creation of vacancies (or their destruction by the reverse reaction) can occur by many different reactions, but the following three types are of major importance for typical cases of interdiffusion:

1. Creation at a jog in a dislocation line by the reaction



in which the jog moves by one atom distance as a result of the formation of the vacancy. The crystalline matrix α , within which the vacancy is created, is essentially unchanged in this case and therefore cancels on the two sides of the equation. (See Equation 9 for a different case.)

2. Creation from porosity (a vacancy disk or tetrahedron) in the specimen by the reaction



where V_n represents a region of porosity containing n vacancies.

3. Creation during structural changes that occur in

the matrix as a result of the diffusion process

$$\alpha_m \rightleftharpoons V + \alpha' \quad (9)$$

where α_m represents the initial metastable matrix and α' represents the final matrix after the structural change that resulted in the production of the vacancy. For example, if an edge dislocation is in a region of tensile stress (condition α_m), this configuration of matrix can reduce its strain energy (to condition α') if the interleaved plane increases its area by producing a vacancy.

We will now consider some characteristics of each of these three reactions. The occurrence of the reaction of Equation 8 is indicated by the presence of porosity in the half of the diffusion specimen into which the vacancies flow. The velocity, ω , of a conventional reference system must then include a contribution dependent on the local rate of formation of vacancies. For simplicity, the reaction of Equation 8 is assumed to be negligible in the cases of diffusion covered by the present analysis.

The reaction of Equation 7 can be pictured as tending to maintain the vacancies at essentially their equilibrium concentration. It must occur in all cases of diffusion in which the atomic flux of Metal 1 is not equal and opposite to the flux of Metal 2. The driving force for this reaction is slight supersaturation of the vacancies. If the supersaturation of the vacancies is sufficiently great, then the mode of reaction changes to that of (the reverse of) Equation 8 or 9. In the case of the reaction of Equation 9, for example, the vacancy supersaturation supplies sufficient energy that the matrix changes from condition α' to a higher-energy state, α_m .

Although the reaction of Equation 9 (like that of Equations 7 or 8) can be driven by supersaturation of vacancies, a more interesting alternative for the present purpose is the case when it is driven by the extra energy of the metastable matrix, α_m . As an example of diffusion behaviour that can lead to a reaction of this type, consider an element of volume bounded by two imaginary Kirkendall interfaces perpendicular to the direction of diffusion. Let a certain net number n_1 of Metal 1 atoms be added to this volume element by diffusion and a net number n_2 of Metal 2 atoms be removed. The difference between n_1 and n_2 is the number of vacancies that must be destroyed (or created) by the reaction of Equation 7 as discussed in the previous paragraph. The resulting composition has changed, however, since Metal 1 was added and Metal 2 removed. Consequently the alloy in this volume element may be sufficiently unstable (α_m in Equation 9) that it undergoes a structural change to condition α' with the creation of a vacancy.

One of the many possible causes of an unstable condition is a difference in atomic volume between Metals 1 and 2. For example, if the volume of an atom of Metal 1 is 25% less than the average atomic volume of the solid solution, and the volume of an atom of Metal 2 is 25% greater, then the replacement of two atoms of Metal 2 by two atoms of Metal 1 leaves a "volume deficit" in this region of the matrix equal to the average atomic volume. The volume deficit causes two effects: (i) it increases the elastic energy of the

matrix and may lead to a structural change that includes the local production of one vacancy, and (ii) it creates a tensile stress which decreases the chemical potential of the vacancies. Consequently, vacancies tend to flow toward this region in the lattice. Thus, differences in atomic volume ($\bar{V}_1 \neq \bar{V}_2$) lead to an additional flux of vacancies, J_v^s , that is usefully distinguished from the usual flux, J_v^e , that results from the inequality of atomic fluxes ($J_1^e \neq J_2^e$) under equilibrium conditions. The precise meanings of the superscripts (s) and (e) are described in a companion paper [4].

The main topic of the present article is a generally valid formulation of the quasi-linear phenomenological equations for diffusion in metals. Equation 5 can serve as the starting place for such a formulation. This equation also explains the following paradox. If vacancies are to be considered as an independent component in the phenomenological equations, they must be capable of undergoing chemical reactions (Equations 7 to 9); yet these reactions need not be considered explicitly in the phenomenological equations.

3. Quasi-linear phenomenological equations

The basic kinetic coefficients (self-diffusion, tracer-diffusion and intrinsic diffusion) are measured relative to the lattice reference system (a system of coordinates fixed in the crystal lattice of the metal). For this reason the lattice reference system is also a convenient choice for the general phenomenological equations based on Equation 5. The standard procedure [14] then leads to the formulation

$$J_i = - \sum_{j=v,1,\dots}^n \left(\frac{M_{ij}}{T} \frac{d\bar{\mu}_j}{dx} \right)_T - \frac{M_{ie}}{T} \frac{d\bar{\mu}_e}{dx} - \frac{M_{iq}}{T^2} \frac{dT}{dx} \quad (10)$$

$$J_e = - \sum_{j=v,1,\dots}^n \left(\frac{M_{ej}}{T} \frac{d\bar{\mu}_j}{dx} \right)_T - \frac{M_{ee}}{T} \frac{d\bar{\mu}_e}{dx} - \frac{M_{eq}}{T^2} \frac{dT}{dx} \quad (11)$$

$$\begin{aligned} J_q &= J_q - \sum_{i=v,1,\dots}^n (J_i h_i) - J_e h_e \\ &= - \sum_{j=v,1,\dots}^n \left(\frac{M_{qj}}{T} \frac{d\bar{\mu}_j}{dx} \right)_T - \frac{M_{qe}}{T} \frac{d\bar{\mu}_e}{dx} - \frac{M_{qq}}{T^2} \frac{dT}{dx} \end{aligned} \quad (12)$$

Here J_i is the flux of an atomic component (or the vacancies), J_e is the flux of electrons, J_q is the actual flux of heat and J'_q (the reduced heat flux) is a useful quantity that is appropriate for use with $(d\mu/dx)_T$ (to be evaluated at constant temperature) [7]. The various M coefficients are concentration-dependent quantities closely related to the *theoretic coefficients*, which in turn are related to the experimentally determined coefficients (D values, electrical conductivity and thermal conductivity).

Without loss in generality, Equations 10 to 12 can be converted into a form more useful for application to diffusion in metallic systems. For simplicity the case of a binary solid solution ($n = 2$) will be considered here, and Equations 27 to 31 will be obtained. The

generalization to multicomponent solid solutions can be made in an analogous manner. (The case of diffusion in ternary solid solutions is particularly interesting because of the ambiguous character of the mutual coefficients, D_{ij}^0 , employed in practical calculations. The resolution of this problem is the subject of a subsequent article [15].)

The mole fraction, X_v , and the chemical potential, μ_v , of the vacancies have some unusual characteristics compared to the corresponding quantities for the atomic components. The sum

$$X_1 + X_2 + X_v = 1 \quad (13)$$

is so little affected by the vacancy concentration (about 10^{-4}) that within experimental error,

$$X_1 = (1 - X_2) \quad (14)$$

Also, because the diffusion coefficient for vacancies is larger by about 10^4 than D_1 or D_2 , the concentration gradient dX_v/dx is negligibly small [11] in the relation obtained from Equation 5, and therefore

$$\frac{dX_1}{dx} = -\frac{dX_2}{dx} \quad (15)$$

In view of the definition of chemical potential (Equation 3),

$$\frac{d\mu_i}{dx} = \phi_i \frac{kT}{X_i} \frac{dX_i}{dx} \quad (16)$$

where ϕ_i is the correction factor for thermodynamic nonideality of the solid solution;

$$\phi_i = 1 + \frac{d(\ln f_i)}{d(\ln X_i)} \quad (17)$$

From the Gibbs–Duhem equation,

$$\frac{d\mu_1}{dx} = -\frac{X_2}{X_1} \frac{d\mu_2}{dx} \quad (18)$$

In the case of vacancies, Equations 3 and 16 must be modified to take account of the change in the equilibrium concentration of vacancies, X_v^e , with change in composition of the alloy. This can be done by writing Equation 3 in terms of both X_v and X_v^e , to give

$$\mu_v = \mu_v^0 + kT \ln f_v X_v + g(X_2) \quad (19)$$

where $g(X_2)$ represents an appropriate function of X_2 . If X_2 changes, μ_v will remain constant provided X_v adjusts to maintain its equilibrium value, X_v^e . Consequently, Equation 19 gives the relation

$$\frac{d\mu_v}{dx} = 0 = 0 + \frac{d}{dx} (kT \ln f_v X_v) + \frac{d}{dx} [g(X_2)] \quad (20)$$

and therefore

$$g(X_2) = -kT \ln f_v X_v^e \quad (21)$$

$$J_1 = -M_{11} \left(\frac{\phi_1 k}{X_1} \frac{dX_1}{dx} - \frac{q_1 E}{T} \right) + 0 - M_{1v} \left(\frac{\phi_v k}{X_v} \frac{dX_v^s}{dx} - \frac{q_v E}{T} \right) - M_{1e} \left(\frac{\phi_e k}{X_e} \frac{dX_e}{dx} + \frac{eE}{T} \right) - \frac{M_{1q}}{T^2} \frac{dT}{dx} \quad (27)$$

$$J_2 = 0 - M_{22} \left(\frac{\phi_2 k}{X_2} \frac{dX_2}{dx} - \frac{q_2 E}{T} \right) - M_{2v} \left(\frac{\phi_v k}{X_v} \frac{dX_v^s}{dx} - \frac{q_v E}{T} \right) - M_{2e} \left(\frac{\phi_e k}{X_e} \frac{dX_e}{dx} + \frac{eE}{T} \right) - \frac{M_{2q}}{T^2} \frac{dT}{dx} \quad (28)$$

$$J_v = -M_{v1} \left(\frac{\phi_1 k}{X_1} \frac{dX_1}{dx} - \frac{q_1 E}{T} \right) - M_{v2} \left(\frac{\phi_2 k}{X_2} \frac{dX_2}{dx} - \frac{q_2 E}{T} \right) - M_{vv} \left(\frac{\phi_v k}{X_v} \frac{dX_v^s}{dx} - \frac{q_v E}{T} \right) - M_{ve} \left(\frac{\phi_e k}{X_e} \frac{dX_e}{dx} + \frac{eE}{T} \right) - \frac{M_{vq}}{T^2} \frac{dT}{dx} \quad (29)$$

Substitution of this expression in Equation 19 gives the following analogue of Equation 16;

$$\frac{d\mu_v}{dx} = \phi_v \frac{kT}{X_v} \frac{dX_v^s}{dx} \quad (22)$$

where

$$X_v^s = X_v - X_v^e \quad (23)$$

This represents the amount by which the vacancy concentration X_v is supersaturated above the equilibrium value, X_v^e . Negative values of X_v^s correspond to undersaturation of vacancies.

The following argument based on the vacancy mechanism can be used to show that

$$M_{12} = 0 \quad \text{and} \quad M_{21} = 0 \quad (24)$$

The existence of a flux of Metal 1, for example, depends on the presence of a vacancy next to an atom of Metal 1. But both X_2 and dX_2/dx are determined by the corresponding values for Metal 1. Consequently the distribution of Metal 2 can have no separate effect on the distribution of vacancies, and therefore M_{12} is zero. Although the relations in Equation 24 appear to be equivalent to an Onsager relation, $M_{12} = M_{21}$, no Onsager relation is expected in this case [16] because the driving forces in question are related by Equation 18. Similarly, even though $d\mu_v/dx$ is only *indirectly* related to $d\mu_1/dx$ and $d\mu_2/dx$, no corresponding Onsager relations exist and therefore

$$M_{v1} \neq M_{1v} \quad \text{and} \quad M_{v2} \neq M_{2v} \quad (25)$$

A linear relation exists among the three fluxes [17], so that

$$\frac{J_v}{F_v} = -\left(\frac{J_1}{F_1} + \frac{J_2}{F_2} \right) \quad (26)$$

where F_i is a correlation factor.

When the values given by Equations 16, 22 and 24 are substituted in Equations 10 to 12, the result for a binary solid solution is given by Equations 27 to 31. At first sight these equations may appear to be unnecessarily complex for adequate treatment of typical diffusion phenomena in metals, but in fact the entire array is needed for quantitative treatment of thermo-migration in a binary substitutional alloy. The equation for J_e , the flux of electrons, plays an important role even when no external field is applied since the internally-generated field (see Equation 2) has a major influence in the presence of a temperature gradient and cannot be neglected even in typical processes of isothermal diffusion.

In companion articles on a particular topic, the special (usually simpler) form of Equations 27 to 31 will be discussed. In the case of isothermal self-diffusion [11], for example, no electrical or thermal terms need to be considered.

$$J_c = -M_{e1} \left(\frac{\phi_1 k}{X_1} \frac{dX_1}{dx} - \frac{q_1 E}{T} \right) - M_{e2} \left(\frac{\phi_2 k}{X_2} \frac{dX_2}{dx} - \frac{q_2 E}{T} \right) - M_{ev} \left(\frac{\phi_v k}{X_v} \frac{dX_v^s}{dx} - \frac{q_v E}{T} \right) - M_{ec} \left(\frac{\phi_c k}{X_c} \frac{dX_c}{dx} + \frac{eE}{T} \right) - \frac{M_{eq}}{T^2} \frac{dT}{dx} \quad (30)$$

$$J_q = -M_{q1} \left(\frac{\phi_1 k}{X_1} \frac{dX_1}{dx} - \frac{q_1 E}{T} \right) - M_{q2} \left(\frac{\phi_2 k}{X_2} \frac{dX_2}{dx} - \frac{q_2 E}{T} \right) - M_{qv} \left(\frac{\phi_v k}{X_v} \frac{dX_v^s}{dx} - \frac{q_v E}{T} \right) - M_{cq} \left(\frac{\phi_c k}{X_c} \frac{dX_c}{dx} + \frac{eE}{T} \right) - \frac{M_{qq}}{T^2} \frac{dT}{dx} \quad (31)$$

4. Discussion

Because metals are only one of the materials of interest in materials science, an important question is the following: to what extent is the present analysis of diffusion applicable to other types of material? In view of the generality of thermodynamics, the basic approach employed here has wide applicability. The specific features of the analysis for a given material, however, begin to appear at the first step in the treatment; namely, the choice of the independent components. In the case of semiconductors, for example, holes may be important as well as electrons, and other point defects may operate in addition to vacancies. Another specific feature of practical importance is the adequate representation of the chemical potential of the electronic carriers. Their activity coefficient can often be considered to be constant in metals, but it varies greatly with carrier concentration in semiconductors. In summary, although a treatment valid for a different material can be developed along similar lines, the final equations will differ appreciably from those given here for metals.

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