CHEMICAL POTENTIAL, DIFFUSION AND STRESS – COMMON CONFUSIONS IN NOMENCLATURE AND UNITS

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ABSTRACT

Some confusion exists in the literature between different nomenclatures and units related to the equations of chemical potential, Einstein's relation, mobility, Fick's laws, and stress-assisted diffusion. Moreover, sometimes these concepts are simplified and important parameters are overlooked in textbooks, thus providing students with insufficient knowledge. This paper is aimed at gathering the most important equations, nomenclature and units in a systematic way. A critical discussion is made on the issues that tend to introduce confusion.

Keywords: Potential parameters, Kinetic parameters, Diffusion, Effects of stress.

1. INTRODUCTION

During the preparation of another paper on the influence of diffusion on bone modeling, the authors noticed that there is some confusion in the literature regarding nomenclature and units when applying the diffusion

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equations in the absence or in the presence of applied stress. This confusion appears even in articles by well known scientists. In addition, textbooks often simplify the theory of diffusion and thus provide only several, very basic equations (see, for example, Refs. /1/ and /2/). These books usually do not present any equations that contain the chemical potential and/or stress. The purpose of this paper is to gather and discuss, step by step, the equations that ultimately allow for describing Fick's laws of diffusion in the absence, and then in the presence of stress. A short literature survey will expose the reader to several papers where the confusion mentioned before exists.

In Section 2, the chemical potential is presented. Einstein's relation between diffusivity and mechanical mobility is described in Section 3. Fick's first and second laws are derived in Section 4. In Section 5, the effect of stress on diffusion is added. In all sections, units used for the variables are clearly delineated. The International System of Units (SI) is used throughout this paper.

2. THE CHEMICAL POTENTIAL

The fundamental thermodynamic function termed chemical potential μ ($J\cdot mol^{-1}$) was defined for mixtures of different constituents /3-5/. The energy of the system was differentiated with respect to the macroscopic mass of the substance, at constant entropy S and volume V. One meaning of the chemical potential is the change in a characteristic thermodynamic state function per change in the number of molecules. Depending on the experimental conditions, the characteristic thermodynamic state function is either internal energy U, Helmholtz free energy F, Gibbs free energy G, or enthalpy H. In his main paper, Gibbs actually used the term "intrinsic potential", and not "chemical potential". By this, he referred to a derivative that is "entirely determined at any point in a mass by the nature and state of the mass about that point" /4/. For a multi-component system with N components ($m = 1,...,N$), the chemical potential μ_k of substance k may be expressed in terms of partial derivatives as

$$\mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{V,S,n_{m\neq k}} = \left(\frac{\partial F}{\partial n_k}\right)_{T,V,n_{m\neq k}} = \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_{m\neq k}} \equiv \overline{G}_k \qquad (1)$$

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where n is the number of moles (mol), P is pressure (Pa), T is the thermodynamic (absolute) temperature (K), $n_{m \neq k}$ denotes that all n's except n_k are kept constant, and $\bar{G}_k$ is the partial Gibbs molar free energy of component k.

The measures fugacity f and activity a were introduced to define the chemical potential /6, 7/. The activity of substance k can be related to its concentration c_k via a factor, known as the activity coefficient γ_k, as

$$a_k = \gamma_k \, c_k \, . \tag{2}$$

The activity coefficient is dimensionless. For dilute solutions, the solvent usually follows Raoult's law, but the solute follows Henry's law. For infinitely dilute solid solutions or aqueous solutions, $\lim_{c_k \to 0} (\gamma_k) = 1$; thus, the activity and concentration can be treated as being equal. The extent to which the activity differs from the concentration can be calculated in the case of electrolytes, for example. As a rough rule of thumb, electrolytes with ion concentrations of 1 mM or less can often be treated as "infinitely dilute solutions". The use of activity coefficients is similar to that of virial coefficients in the equation of state of real gases, where the fugacity describes the deviation of pressure from the ideal state.

The dependency of the chemical potential on the dimensionless absolute activity λ_k may be expressed as

$$\mu_k = RT \ln \left(\lambda_k \right) \tag{3}$$

where R is the ideal gas constant (8.3145 J·K^{-1}·mol^{-1}). The activity, like the chemical potential, requires a designation of a reference value. It can be understood precisely if either a "reference state" for which $\gamma_k = 1$ (hence, $a_k = c_k$), or a "standard state" for which $a_k = 1$ (hence, $\mu_k = \mu_k^0$) is defined. If λ_k in Eq. (3) is defined in terms of the (relative) activity $\lambda_k \equiv a_k / a_k^0$, Eq. (3) becomes

$$\mu_k = RT \ln \left(\frac{a_k}{a_k^0} \right), \tag{4}$$

and if $\mu_k^0 \equiv -RT \ln \left(a_k^0 \right)$ is defined, then

$$\mu_k = \mu_k^0 + RT \ln \left(a_k \right) \tag{5}$$

is derived /7, 8/. The activity a_k may be expressed in units of molarity M (moles of solute per liter of solution, that is, units of $mol \cdot m^{-3}$), molality m (moles of solute per kg of solvent), or mole fraction X (moles of solute per total moles of species). However, a_k^0 and μ_k^0 must be substituted into Eqs. (4) and (5) in the corresponding values and units. In infinitely dilute solutions, c_k may replace a_k in these two equations. Molality is often preferred over molarity, because the mass does not depend on temperature and pressure, while the volume does. For dissolved substances, the standard chemical potential is both pressure and temperature dependent, and the standard state is defined at $T = 298.15$ K and $a_k^0 = 1$ $mol \cdot kg^{-1}$. The standard chemical potentials of $H_{(aq)}^+$ and $H_{2(g)}$, for example, are both defined as zero in electrochemical equilibria calculations, so that the hydrogen evolution reaction has a standard potential $E^0 = 0$ V, and the standard hydrogen electrode (SHE) is established. For gaseous substances, the standard state is defined at $f^0 = 1$ atm (101,325 Pa). Finally, for all pure metals in their neutral state, $\mu^0 = 0$.

3. THE EINSTEIN RELATION AND MECHANICAL MOBILITY

The relation between the average drag force F_k ($kg \cdot m \cdot s^{-2}$, or N) and the equilibrium drift velocity v_k ($m \cdot s^{-1}$) of substance k subjected to this force is

$$v_k = B_k \, F_k \tag{6}$$

where B_k is the mechanical mobility of substance k ($m^2 \cdot J^{-1} \cdot s^{-1}$, $m \cdot N^{-1} \cdot s^{-1}$, or simply $s \cdot kg^{-1}$). In the equations throughout this paper, boldface characters represent vectors. Other types of mobility, such as electrical mobility, are also described in the literature. If the drag force is caused by a gradient in the concentration of substance k at temperature T, the diffusional mobility (or diffusion coefficient) may be defined in terms of the Einstein relation /9-11/

$$D_k = k_B T \, B_k \,, \tag{7}$$

where k_B is Boltzmann's constant (1.3807×10^{-23} J·K^{-1}), defined by

$$R = N_A \, k_B \tag{8}$$

and N_A is Avogadro's number (6.022×10^{23} mol^{-1}). For anisotropic diffusion, D_k and B_k become tensors of rank two. For simplicity, they are treated here as scalars.

In order to derive the Einstein relation in Eq. (7) /11/, it is assumed that (1) the total particle flux or current vanishes in thermal equilibrium, (2) the particle concentration is expressed in statistical mechanics in terms of the Maxwell-Boltzmann distribution, namely

$$c_k \sim \exp\left(-\frac{\Pi_k}{k_B T}\right) \tag{9}$$

where Π_k is the potential energy, and (3)

$$\boldsymbol{F}_k = -\boldsymbol{\nabla}\, \Pi_k \, . \tag{10}$$

Here,

$$\boldsymbol{\nabla} = \frac{\partial}{\partial x}\boldsymbol{i} + \frac{\partial}{\partial y}\boldsymbol{j} + \frac{\partial}{\partial z}\boldsymbol{k} \tag{11}$$

where $\boldsymbol{i}, \boldsymbol{j}, \boldsymbol{k}$ are unit vectors in a Cartesian coordinate system (x, y, z).

There seems to be confusion in some publications with respect to both the units of Avogadro's number /12, 13/ and Einstein's relation. First, a mole is specifically defined in SI units as being a base unit, describing the amount of a substance. Therefore, it is not dimensionless as some believe. The official definition, adopted as part of the SI system in 1971 /14/, is that one mole of a substance contains just as many elementary entities (atoms, molecules, ions, electrons, etc.) as there are atoms in 12 grams of ^{12}C. Second, since the units in the numerator of Avogadro's number depend upon the substance being studied, it was agreed to use unity instead. Thus, atoms are referred to as dimensionless. Third, in this paper, the diffusion coefficient D (m^2·s^{-1}) determines the rate at which mass is transported /15/. In order to obtain it with the correct units, the coefficient of TB_k in Eq. (7) must be k_B, not R, as

sometimes mistakenly used in the literature /16/.

4. FICK'S LAWS OF DIFFUSION

Fick's laws of diffusion are presented in this section /17/. The particle flux vector $\boldsymbol{J}_k$ caused by the average drag force is given by

$$\boldsymbol{J}_k = c_k v_k . \tag{12}$$

Substituting Eq. (6) into Eq. (12) leads to

$$\boldsymbol{J}_k = c_k B_k \boldsymbol{F}_k . \tag{13}$$

Recall that the units of concentration are mol·m^{-3}, m^{-3}, or kg·m^{-3}; then, units of flux are, respectively, mol·m^{-2}·s^{-1}, m^{-2}·s^{-1} or kg·m^{-2}·s^{-1}.

The driving force for diffusion is the negative value of the gradient of the potential normal to the cross-sectional area. The negative sign results from the fact that mass transport takes place from regions of higher potential to regions of lower potential. In this regard, the driving force may be defined as any influence that causes the jump frequency in one direction between two given sites to differ from that of a jump in the opposite direction between exactly analogous sites. Driving forces include gradients of chemical potential, but also gradients of stress (as will be discussed in Section 5), electrical potential, or temperature. Since the gradient of the chemical potential may be different from zero even at constant concentrations, special phenomena such as uphill diffusion are covered by this formulation /15/. It should be noted that there is sometimes an objection to use of the term "driving force" with respect to diffusion because of the meaning of "force" in mechanics /5/. Although the authors disagree with this claim, discussion of this topic is outside the scope of this paper.

In the case of an inhomogeneous distribution of solute atoms, or if there are several interacting particles, the driving force for mass transport is associated with the gradient of the chemical potential /10, 18/. In deriving Fick's first law, it is common to replace the potential energy Π_k in Eq. (10) with the chemical potential μ_k so that $\boldsymbol{F}_k = -\nabla \mu_k$. One may easily examine the units of the right side of the equation to discern them to be N·mol^{-1},

which does not agree with the left hand side of the equation. In order to account for proper units, one should use the average force per particle, namely

$$\boldsymbol{F}_k = -\frac{1}{N_A} \nabla \mu_k . \tag{14}$$

Substituting Eq. (14) into Eq. (13) leads to

$$\boldsymbol{J}_k = -\frac{B_k c_k}{N_A} \nabla \mu_k . \tag{15}$$

The form of Eqs. (14) and (15) without the factor N_A has been presented in numerous publications (see, for example, Refs. /19/ and /20/).

The chain rule may be applied in Eq. (15) to obtain

$$\boldsymbol{J}_k = -\frac{B_k c_k}{N_A} \frac{\partial \mu_k}{\partial c_k} \nabla c_k . \tag{16}$$

Substituting Eq. (2) into Eq. (5), differentiating the result with respect to c_k and substituting into Eq. (16) leads to

$$\boldsymbol{J}_k = -\frac{RT B_k}{N_A} \nabla c_k . \tag{17}$$

Use of Eqs. (7) and (8) leads to

$$\boldsymbol{J}_k = -D_k \nabla c_k \tag{18}$$

which is the well known three-dimensional form of Fick's first law. It is assumed here that the diffusivity is independent of concentration. Note that Eq. (18) applies to different types of diffusion processes and, accordingly, to different types of diffusion coefficients, as will be defined in the sequel.

It may be emphasized that if the force in Eq. (13) would be substituted in units of N·mol^{-1}, Eq. (18) would be derived in an uncommon form as $\boldsymbol{J}_k = -N_A D_k \nabla c_k$ with incorrect units for the flux of mol^{-1}·m^{-2}·s^{-1}. Surprisingly, in spite of the considerations discussed here, the equation

$J_k = -B_k c_k \nabla \mu_k$ is the one presented most often in the literature instead of Eq. (15). For example, in one of the best known books in electrochemistry, Bockris and Reddy /20/ apply this equation while totally ignoring the aspect of units and referring to $\Delta \mu_k$ once as the "work done to transport a mole of species" *k* between two positions, and once simply as a "pseudoforce".

In certain cases, Fick's first law has been found insufficient to describe mass transport by irreversible processes, because it does not recognize all driving forces acting on substance *k*. A phenomenological diffusion theory to describe the transport process in an *N*-component system by a set of N generalized Fick's equations was proposed in /21/. A linear relation between the thermodynamic driving forces and the resulting atomic fluxes based upon a continuum mechanical approach, neglecting the underlying atomic structure of matter, was formulated. The phenomenological coefficients in the linear relations are termed "Onsager's coefficients" (or "kinetic coefficients"), and the matrix of coefficients is frequently called "the L matrix". A more comprehensive discussion is outside the scope of this paper.

The next issue to be discussed is the definition of the diffusion coefficients (diffusivity). In classical diffusion theory, the diffusion process is often described in terms of jumps over energy barriers (hopping), ignoring zero-phonon, few-phonon, thermally activated tunneling, or fluid motion processes. The change in the equilibrium constant to the change in temperature, assuming that the enthalpy change was constant over the temperature range, was first related in /22/. However, the effect of temperature on measured reaction rates is better known as the Arrhenius equation /23/, although this relation was actually adopted from the original presented by van't Hoff. The Arrhenius-type equation for diffusion may be written as

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \tag{19}$$

where D_0 is independent of temperature and E_a is the activation energy of diffusion. The factor D_0 depends on the solute-solvent couple and is sometimes called the "frequency factor" in the case of first-order reactions. In Eq. (19), RT and E_a are given in units of J·mol^{-1}. When k_B is used instead of R, E_a has units of J (J per atom).

Non-Arrhenius behavior (e.g. when the activation energy is temperature

dependent) has also been observed with respect to diffusion. Indeed, nonlinear plots of log D vs $1/T$ have been reported for hydrogen diffusion in metallic glasses /24-26/, ion hopping /27/, diffusion of molecules in low-temperature liquids /28/, and quantum dynamics/quantum statistics processes /29/. Inverse Arrhenius behavior (i.e. when the activation energy increases as the temperature increases) has also been observed, e.g. for self-diffusion in quenched aluminum and gold /30/ and diffusion of light interstitials, such as positive muons in metals /31, 32/.

A distinction should be made between several types of diffusion coefficients. The self-diffusion coefficient D_k of substance k describes the uncorrelated movement of a particle in the absence of a chemical potential gradient (e.g. an atom in a pure element). Therefore, there is no direct method to measure it. The tracer diffusion coefficient D_k^* refers to the migration of a specific isotope of the host (solvent) element k in an otherwise chemically homogeneous medium. The tracer diffusion coefficient and the self-diffusion coefficient are generally related by a correlation factor. This factor is equal to unity if both isotopes have the same diffusivity, thus representing a random walk (Brownian motion) /11/. When two or more substances diffuse simultaneously in a given medium, the fluxes of the substances become coupled, as first identified by the Kirkendall effect for interdiffusion of Cu and Zn. In concentrated solid solutions or in diffusion couples, the motion of one constituent causes a counter flow of the other constituent(s) or vacancies /17/. The chemical diffusion (or interdiffusion) coefficient $\tilde{D}_{kj}$ describes the flow of constituent k under the influence of a gradient in chemical composition in a multi-component system that contains j other types of constituents (i.e. intermixing under non-equilibrium conditions).

In binary or multi-component systems, the expressions for fluxes and forces, and consequently, the values of the diffusion coefficient, depend on the selection of a frame of reference in space. It is common practice to define an intrinsic diffusion coefficient D_k^i for each substance, so that no net mass flows across the frame of reference. The Darken equation relates the chemical diffusion coefficient for interdiffusion in binary systems and the intrinsic diffusion coefficients of its constituents A and B, resulting in

$$\tilde{D} = X_A D_A^i + X_B D_B^i \tag{20}$$

where X_k is the mole fraction of substance k as compared to the total number of moles in the material. For non-ideal solutions, and considering the effect of chemical potential gradients on diffusion, the intrinsic and self-diffusion coefficients are related via the following relation /33/

$$D_k = D_k^i \left[1 + \frac{\partial \left(\ln \gamma_k \right)}{\partial \left(\ln X_k \right)} \right]\Bigg|_{T,\sigma} \tag{21}$$

where σ is stress. This equation is only an approximation and is nowadays known as the Darken-Dehlinger relation. The term in square brackets in Eq. (21) is called the thermodynamic factor. Note that X_k in this equation should be dimensionless, and not molar volume as sometimes mistakenly used.

When concentration within the diffusion volume changes with time, Fick's second law may be derived. From mass conservation it follows that /18/

$$\frac{\partial c_k}{\partial t} = -\nabla \cdot \boldsymbol{J}_k \tag{22}$$

where t is time (s). Substituting Fick's first law in Eq. (18) into Eq. (22) leads to

$$\frac{\partial c_k}{\partial t} = \nabla \cdot \left(D_k \, \nabla c_k \right) \tag{23}$$

which is valid as long as there are no sources and sinks within the test volume. If the diffusivity is independent of position and concentration, Eq. (23) reduces to

$$\frac{\partial c_k}{\partial t} = D_k \nabla^2 c_k \; . \tag{24}$$

Note that Eqs. (23) and (24) apply to different types of diffusion processes and accordingly, to different types of diffusion coefficients, as mentioned previously. It may be noted that Eq. (24) is identical to the heat conduction equation when the concentration is identified with temperature and the diffusivity with thermal diffusivity /34/.

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5. STRESS-ASSISTED DIFFUSION (STRESS-INDUCED DIFFUSION)

Stress-assisted diffusion (SAD) may occur in the presence of stress fields resulting either from structural imperfections such as internal high pressure gas bubbles /35/, cracks, dislocations and inclusions, and/or from externally applied mechanical forces. In either case, the chemical potential of an interstitial solute in the stressed body μ_k^σ is related to the chemical potential of the solute at the same concentration in the relaxed (zero stress) body /16, 36/.

Stressed elastic solids that absorb fluids were treated in /4/. This formulation was later extended by Darken, Li and Oriani /16, 36, 37/ to include constrained chemical equilibria among components whose chemical potential may not be individually definable. In the framework of the extended formulation, a strain volume Ω_{ij} was introduced as a new tensorial extensive variable. Its increment is defined as /37/

$$\mathrm{d}\Omega_{ij} = V\,\mathrm{d}\varepsilon_{ij} \tag{25}$$

where ε_{ij} is the infinitesimal strain tensor *(i, j = 1,2,3)*. Equation (25) may be integrated, since the volume V is only a function of strain. No matter how the chemical potential is defined, its variation with stress must follow a Maxwell-type relation, derivable from the expression of Helmholtz free energy as /37/

$$\frac{\partial \mu_k}{\partial \sigma_{ij}} = -\frac{\partial \Omega_{ij}}{\partial n_k} \equiv -\Omega_{ij}^{\,k} \tag{26}$$

where σ_{ij} is the stress tensor and $\Omega_{ij}^{\,k}$ is the strain volume tensor for substance k. The independent variables (T, σ_{ij} and n_k) are kept constant in the partial differentiation where appropriate. The second term in Eq. (26) is the partial molar strain volume, a second-rank tensor, which does not require a reference state for its definition, since only a change of Ω_{ij} is involved. For some solutes and their chemical reactions, for randomly distributed solutes, and for some chemical reactions, the strain volume is isotropic, namely /37/

$$\Omega_{ij}^{\,k} = \frac{1}{3}\Omega^k \delta_{ij} \tag{27}$$

where δ_{ij} is the Kronecker delta. The scalar $\Omega^k = \Omega^k_{ii} \equiv \bar{V}_k$ is the partial molar volume (synonym: partial molal volume) of substance k. The volume expansion (partial atomic volume) for hydrogen, for example, is typically around $V_H = 3$ Å^3 per H-atom /10/, equivalent to a partial molar volume $\bar{V}_H = 1.807 \times 10^{-6}$ m$^3 \cdot$H-mol^{-1}.

For an isotropic solute, Eq. (26) may be integrated as /37/

$$\mu_k^\sigma - \mu_k = -\int_0^{\sigma_{rs}} \Omega^k_{ij} \mathrm{d}\sigma_{ij} \ . \tag{28}$$

The chemical potential μ_k is the same as that in Eq. (4), i.e. in the absence of stresses; whereas μ_k^σ is that at a stress σ_{rs} (r, s =1, 2, 3). It should be noted that both μ_k^σ and μ_k correspond to an equal concentration c_k of solute atoms. Substituting Eq. (27) into Eq. (28) yields

$$\mu_k^\sigma - \mu_k = -\int_0^{\sigma_h} \bar{V}_k \mathrm{d}\sigma \tag{29}$$

where $\sigma_h \equiv \left(\sigma_1 + \sigma_2 + \sigma_3 \right)/3$ is the hydrostatic stress and σ_i, i =1, 2, 3 are the principal stresses. If $\bar{V}_k$ is not a function of stress, then Eq. (29) reduces to /36, 37/

$$\mu_k^\sigma - \mu_k = -\bar{V}_k \ \sigma_h \ . \tag{30}$$

This equation describes the change in the chemical potential of an interstitial solute atom in an ideal solid solution as a result of applied or residual stresses. The equation may be modified to show the variation of concentration with stress for the same chemical potential of an interstitial atom in the stressed, as well as the unstressed body /16/. Usually, the partial molar volume is assumed constant, namely independent of the concentration. It should be noted that when measuring stress in Pa and the chemical potential in J·mol^{-1}, $\bar{V}_k$ in Eq. (30) is the partial molar volume, and not the partial atomic volume V_k. This has sometimes been ignored in publications (see, for example, the definition of units for symbols in Eq. (1) in Ref. /38/).

The interstitial atom flux J_k^σ, which flows in the direction of hydrostatic tensile stress, may be defined on the basis of Eq. (15) as

$$J_k^\sigma = -\frac{B_k c_k}{N_A} \nabla \mu_k^\sigma \tag{31}$$

where k refers to a substance. It may be noted that frequently in the literature reference is made only to "tensile stress" rather than hydrostatic stress /39, 40/. Clearly, at any point in a body, the normal stress may vary from tensile to compressive depending on the reference direction. Substituting Eq. (5) into Eq. (30) and then into Eq. (31), making use of Eqs. (7) and (8) leads to

$$J_k^\sigma = -\frac{D_k c_k}{a_k} \nabla a_k + \frac{D_k c_k \bar{V}_k}{R T} \nabla \sigma_h . \tag{32}$$

Since for infinitely dilute solid solutions, $a_k = c_k$ (see comment below Eq. (2)), Eq. (32) may be re-written as

$$J_k^\sigma = -D_k \nabla c_k + \frac{D_k c_k \bar{V}_k}{R T} \nabla \sigma_h \tag{33}$$

or

$$J_k^\sigma = -D_k \nabla c_k + \frac{D_k c_k V_k}{k_B T} \nabla \sigma_h . \tag{34}$$

These equations are in the correct form, not the one provided in many publications. In Eq. (34), V_k is the atomic volume (in units of $m^3 \cdot atom^{-1}$, or simply m^3) and not the molar volume $\bar{V}_k$. Based upon Eqs. (33) and (34), the flux of an interstitial atom (say, hydrogen) will be generated in an iso-concentration field from lattice points where the hydrostatic stress $\sigma_h < 0$ to points where $\sigma_h > 0$.

Diffusion of atoms in materials can lead to the evolution of local stresses, a phenomenon known as diffusion-induced stresses (DIS) or chemical stresses. When internal stresses are only of this type, the stresses always enhance the rate of diffusion /37/. Using numerical simulation, Larché and Cahn showed that long-range elastic interactions resulting from compositional inhomogeneities give rise to significant non-local contributions to the flux /41/. In the analyses, assumptions included

dislocation-free single crystals, isothermal conditions, and the absence of applied stress. The authors considered dependence of local flux on distant inhomogeneities as a failure of Fick's first law. The diffusion potential *M* was defined for a multi-component solid subjected to stress, with the diffusion process dependent upon gradients of *M*. Upon equilibrium of the stressed solid, the diffusion potential was set equal to the chemical potential in the case of an interstitial solid solution. In substitutional solid solutions, on the other hand, the diffusion potential was taken equal to the difference in chemical potentials of two distinguishable substitutional species /42/. Since not all symbols are defined with their corresponding units, there may be some confusion when utilizing reference 41. For example, it is not clear whether the "composition" *c* should have the same units throughout the paper, or instead it was sometimes used as mole fraction (e.g. in Eq. (6) in Ref. /41/) and sometimes as molar concentration. Yet, there is no doubt that Larché and Cahn are among the pioneers in developing modern diffusion theories that describe the synergistic effects of mass transport and stresses.

6. CONCLUSIONS

In this paper, the fundamental diffusion equations were discussed with incorporation of the effect of stress. Potential confusions in nomenclature and units were noted. The paper can be useful in (1) increasing the awareness of scientists to possible problems in using diffusion formulae, and (2) providing students with a methodological overview of diffusion theories.

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