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DEFINITIONS OF TERMS FOR DIFFUSION IN THE SOLID STATE

(IUPAC Recommendations 1999)

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Abstract: This document provides definitions of terms and processes which are used in describing the migration of host and foreign species through solid materials. Both the phenomenological theory of diffusion and the detailed atomistic mechanisms by which atom transport occurs are treated. Also included are the various types of gradients such as electrical, chemical, thermal and mechanical, which provide the driving forces for diffusion.

INTRODUCTION

The definitions in this document relate specifically to the solid state and are intended for the professional scientist. But they will not necessarily meet all the needs of the specialist chemist, physicist or materials scientist. An attempt has been made to produce a set of concise definitions. In certain instances, definitions have been quoted directly from the literature, while in others, definitions have been modified or abridged to suit the document. Certain definitions have been expanded where clarification was considered necessary. A system of cross-referencing has been used in which italicised terms refer to other entries where relevant information is available and where terms are known by more than one name. The references cited in the bibliography are not unique but provide additional reading on specific definitions.

INDEX OF SYMBOLS

a_0 lattice constant [m]

b mobility [m/N/s]

c amount (of substance) concentration [mol/m^3]

D diffusion coefficient [m^2/s]

D_i self diffusion coefficient of species i [m^2/s]

$\tilde{D}$ chemical diffusion coefficient or interdiffusion coefficient [m^2/s]

D_i^* tracer diffusion coefficient of species i [m^2/s]

$\bar{D}_i$ intrinsic diffusion coefficient of species i [m^2/s]

D_R random walk diffusion coefficient [m^2/s]

e elementary charge [C]

$\boldsymbol{E}$ electrical field (vector) [V/m]

f correlation factor

$\boldsymbol{F}$ force [N]

G   Gibbs energy [J]

h Planck constant [J s]

H_R Haven ratio

$\boldsymbol{J}$ flux [m^{-2}/s]

k Boltzmann constant [J/K]

N_i mole fraction of species i

N_A Avogadro constant [mol^{-1}]

p probability

P pressure [Pa]

q electrical charge ($q = ze$) [C]

Q activation energy [J/mol]

R gas constant ($R = N_A k$) [J/K/mol]

T thermodynamic temperature [K]

t time [s]

u electrical mobility [m^2/V/s]

v drift velocity [m/s]

$\bar{V}_j$ partial molar volume of species j [m^3]

x cartesian coordinate [m]

X_i thermodynamic force on species i (generalised force in Onsager's relation)

z charge number

∂ partial derivative operator

Δ finite difference

∇ gradient operator

Φ thermodynamic factor

γ_i thermodynamic activity coefficient of species i

Γ_i jump frequency of species i [s^{-1}]

η electrochemical potential [J/mol]

μ chemical potential [J/mol]

σ electrical conductivity [S/m]

Σ summation sign

ω_0 atom or vacancy jump frequency [s^{-1}]

ζ nearest-neighbour co-ordination number

DEFINITION OF TERMS

Activation energy

The parameter Q, which characterises the exponential temperature dependence of the diffusion coefficient D in the empirical equation $D = D_0 \exp(-Q/RT)$. D_0 is a temperature independent constant, R is the gas constant and T the thermodynamic temperature. Q is called the activation energy for diffusion. D_0 is often referred to as the pre-exponential factor.

Activation volume

The pressure dependence of a diffusion coefficient, D, is often represented by

$$(\partial \ln D / \partial P)_T = -(\Delta V / RT) + (\partial \ln \omega_0 / \partial P)_T$$

where ΔV is called the activation volume, R is the gas constant, T the thermodynamic temperature and ω_0 is the atom *jump frequency*. The second term on the right is a small correction, only a few per cent of the first term, so in good approximation:

$$\Delta V \approx -RT (\partial \ln D / \partial P)_T$$

Ambipolar diffusion

Diffusion in systems with two (or more) diffusing species with opposite electrical charge.

　　See: *effective diffusion coefficient*.

Ascending diffusion

A specific type of diffusion that can take place in alloys of metals under the influence of stress gradients. When the constituents are of different sizes the larger elements tend to move in the directions of the dilated regions. Thus ascending diffusion disturbs the uniform distribution of the constituents and sets up a concentration gradient which opposes the stress gradient.

Attempt frequency

See: *jump frequency*

Barycentric frame of reference

See: *mean-mass frame of reference*

Boltzmann–Matano analysis

A procedure to determine the *chemical diffusion coefficient* in binary or multiphase systems from experimentally measured concentration profiles.

Bulk diffusion

See: *lattice diffusion*.

Chemical diffusion

Diffusion under the influence of a gradient in chemical composition. In concentrated solid solutions, e.g. $A_{1-x}B_x$, or in diffusion couples, the motion of one constituent causes a counterflow of the other constituent(s) or vacancies. In this case one can define a diffusion coefficient for the intermixing, which is called the chemical diffusion coefficient or interdiffusion coefficient $\tilde{D}$. One can also define diffusion coefficients for each of the constituents i, called intrinsic diffusion coefficient $\bar{D}_i$.

See: *Darken equation.*

Chemical diffusion coefficient

In N-component diffusion the chemical diffusion coefficient or interdiffusion coefficient $\tilde{D}_{ij}$ is obtained from the flux $\tilde{J}_i$ of species i, with concentration c_i, measured with respect to the laboratory frame of reference by applying Fick's First law (expressed here in one dimension):

$$\tilde{J}_i = -\sum_{j=1}^{N-1} \tilde{D}_{ij}\,(\partial c_i/\partial x)$$

For the units in this equation, see the note under Fick's First law. From irreversible thermodynamics one can show that for isotropic, one-dimensional diffusion there are $(N-1)N/2$ independent coefficients $\tilde{D}_{ij}$. These coefficients are sometimes called partial diffusion coefficients.

See: *Darken equation, Fick's first law, reference frames.*

Collinear interstitialcy mechanism

An *interstitialcy mechanism* in which an interstitial atom and the lattice atom which it displaces move along the same straight line.

Composition vector

A vector representing the concentration gradient at a point in a multicomponent diffusion couple.

Concentration profile

The variation in the concentration of a diffusing species as a function of distance in a material.

Conductivity diffusion coefficient

The conductivity diffusion coefficient $D_i(\sigma_i)$ of a mobile, charged particle i is derived from the measured partial electrical conductivity of that species, σ_i, by the *Nernst–Einstein equation*:

$$D_i(\sigma_i) = \frac{kT}{c_i q_i^2} \sigma_i$$

where k is the Boltzmann constant, T the thermodynamic temperature, c_i the concentration of i expressed in number of particles per unit volume and q_i the electrical charge of the particle.

Correlation factor

When the motion of a diffusing species is dependent on the presence of a defect on a neighbouring site, e.g. a tracer diffusing by a vacancy mechanism, the jumps of the diffusing species will not be random, but are correlated. The correlation factor, f, is a measure of the deviation of the motion of the diffusing atoms from the random walk. For a tracer it is defined as the ratio of the *tracer diffusion coefficient D_i^** and the *self-diffusion coefficient*, D_i:

$$f = D_i^*/D_i$$

For the *random walk*, $f = 1$ by definition. In general f is less than unity, but it can be larger than unity and in such cases the motion is called channelling.

Crowdion mechanism

In this mechanism diffusion takes place by a co-operative movement of a group of atoms one of which is typically centred on an interstitial position with the others relaxed from their normal lattice sites to accommodate the additional 'crowdion'.

Curie principle

See: *Neumann's principle*

Darken equation

This equation relates the *chemical diffusion coefficient*, $\tilde{D}$, for interdiffusion in binary systems and the *intrinsic diffusion coefficients*, $\bar{D}_A$ and $\bar{D}_B$, of the constituents A and B:

$$\tilde{D} = N_A \bar{V}_A \bar{D}_B + N_B \bar{V}_B \bar{D}_A$$

where $\bar{V}_A$ and $\bar{V}_B$ are the partial molar volumes of A and B and N_A and N_B are their mole fractions.

The chemical diffusion coefficient in this case is often called the *interdiffusion coefficient.*

When the Darken–Dehlinger relation between intrinsic and self-diffusion coefficients is substituted in the above expression one gets:

$$\tilde{D} = (N_A \bar{V}_A D_B^* + N_B \bar{V}_B D_A^*)\Phi$$

where Φ is the thermodynamic factor.

See: *intrinsic diffusion coefficient* for Darken–Dehlinger relation.

Darken–Dehlinger relation

See: *intrinsic diffusion coefficient*.

Defect diffusion coefficient

In the case of diffusion via a vacancy mechanism movement of a particle is associated with a movement of a vacancy in the opposite direction. If the vacancy concentration c_V is small with respect to the particle concentration c_i, the individual *jump frequencies* Γ_V and Γ_i are related as follows:

$$\Gamma_i/\Gamma_V = c_V/c_i = N_V$$

where N_V is the mole fraction of vacancies. From this relation it follows that the *self-diffusion coefficient* D_i of the atoms i is related to the self-diffusion coefficient D_V of the vacancies via:

$$D_i = D_V N_V$$

This only holds when there are only particles of type i on the sublattice under consideration. If this is not the case the equation has to be modified by introduction of a *correlation factor*.

The relation can be generalised to

$$\sum_i D_i N_i = \sum_d D_d N_d$$

where i indicates the different mobile species and d the different types of defects (vacancies, interstitials, ...).

Diffusion bonding

A solid state bonding process to join two materials by a diffusion reaction.

Diffusion coefficient

See: *Fick's First law.*

Diffusion controlled reaction

A reaction is diffusion controlled when the rate of reaction is controlled by the rate of diffusion of one of the reactants through the solid product layer towards the interface where the reaction takes place.

Diffusion flux

The diffusion flux J_i gives the number of species i crossing a unit area, fixed relative to the local centre of mass, per unit of time. *Fick's First law* states that the flux of particles in the presence of a concentration gradient ∇c is proportional to this gradient: $J_i = -D_i \nabla c_i$. Under the influence of external forces the particles move with an *average drift velocity*, v_{Fi}, which gives rise to a flux $c_i v_{Fi}$. Here c_i is the concentration of diffusing species i (see note on concentration units under Fick's First law). In this case the total flux is given by the relation:

$$J_i = -D_i \nabla c_i + c_i v_{Fi}$$

In the literature the first term on the right hand side is sometimes called the Fickian flux or diffusion flux and the second term is called drift.

See: *Fick's First law.*

Diffusion path

The sequence of structural and compositional modifications developed during isothermal diffusion in multiphase, multicomponent diffusion systems is called a diffusion path. This path is generally plotted superposed upon an isothermal phase diagram.

Diffusion potential

During diffusion of charged particles in ionic or electronic conducting solids an electrical charge is built up due to the differences in mobilities of the diffusing particles. The corresponding electrostatic potential, ψ, is known as the diffusion potential.

Diffusion–induced grain boundary migration (DIGM)

If a polycrystalline material undergoes an interdiffusion process, the grain boundaries move in a direction perpendicular to the diffusion flux. As a result the concentrations in the regions swept by the boundaries change.

Diffusivity

Generally used as an alternative word for diffusion coefficient. However, some authors restrict the term diffusivity to the matrix of *partial diffusion coefficients* for a multicomponent system.

    See: *Chemical diffusion coefficient, Fick's first law, partial diffusion coefficient.*

Diffusivity tensor

In an anisotropic crystal lattice the diffusion coefficient is generally direction dependent and has to be represented by a three-dimensional tensor with components D_{ij}. Under these circumstances the diffusion coefficient is also called the *diffusion tensor* (a second-rank tensor).

Direct interstitial mechanism

Diffusion taking place by the direct migration of an interstitial species from one interstitial position to another.

Dissociative diffusion

The process by which foreign atoms predominantly present at normal lattice sites migrate via interstitial sites.

Example: The diffusion of Cu in elemental Ge: $Cu_{Ge}^{x} + V_{i}^{x} \leftrightarrow V_{Ge}$

    [for defect notation see *Nomenclature of Inorganic Chemistry, IUPAC Red Book*, Chapter 6 (G. J. Leigh, ed.), Blackwell Scientific Publications, Oxford, 1990].

Divacancy mechanism

The process by which a vacancy pair is used by any constituent species of the material to effect diffusion is called a divacancy mechanism.

Drift velocity

The application of a *driving force* gives atoms a greater than random probability of jumping in the direction of the gradient. Atoms are said to have an average drift velocity $\boldsymbol{v}_F$ in that direction and contribute a term $c\boldsymbol{v}_F$ to the diffusion flux.

    See: *diffusion flux.*

Driving force

The driving force is defined as any influence which causes the jump frequency for a jump in one direction between two given sites to differ from that for a jump in the opposite direction between exactly analogous sites. Driving forces include gradients of stress, electrical potential, temperature or chemical potential.

Dumbbell interstitialcy mechanism

In some systems the equilibrium configuration during an interstitialcy jump consists of a dumbbell-like defect with each of the moving ions being displaced by an equal amount from the normal lattice position. Diffusion taking place via such species is said to proceed by a dumbbell *interstitialcy mechanism.*

Effective diffusion coefficient

In alloys or compounds transport of material can occur under the influence of a driving force, at constant composition in the whole sample. Examples are found in viscous creep and sintering processes. In this case the fluxes of the diffusing species must be coupled. In an ionic crystal a similar condition holds due to the necessity of preserving electroneutrality. For a compound A_rB_s with tracer diffusion coefficients

D_A^* and D_B^* the effective diffusion coefficient D_{eff} is given by:

$$D_{eff} = \frac{D_A^* D_B^*}{\mathbf{r} D_B^* + \mathbf{s} D_A^*}$$

which is often known as Herring's formula.

Note that if $D_A^* >> D_B^*$, then $D_{eff} \approx D_B^*/s$, i.e. the flux is determined by the slower diffusing species.

In interdiffusion the two species diffuse in opposite directions, while in the case of material transport migration occurs in the same direction. In the case of ionic crystals one uses the term *ambipolar diffusion*.

Einstein equation

In its most general form the Einstein equation relates the atomic *mobility* b_i of a species i to the diffusion coefficient D_i:

$$D_i = kTb_i$$

See: *Nernst–Einstein equation*, *mobility*

Einstein–Smoluchowski equation

An equation from *random walk theory* relating the diffusion flux to the path covered by the particle. For one dimension the flux J_x of a particle in the *x*-direction is given by

$$J_x = c\frac{\langle X \rangle}{t} - \frac{\partial c}{\partial x}\left(\frac{\langle X^2 \rangle}{2t}\right) - c\frac{\partial}{\partial x}\left(\frac{\langle X^2 \rangle}{2t}\right)$$

in which

$$\langle X^m \rangle = \int X^m p(X, t; x) dX$$

where $c(x)$ is the concentration, and $p(X, t; x)$ the probability that an atom which was on plane x at time zero is on plane $x + X$ at a time t later.

For dilute solutions of for instance B in a host A, which are homogeneous apart from the dilute concentration of B atoms, $\langle X \rangle = 0$ and $\langle X^2 \rangle$ is independent of position. In that case the equation reduces to the second term only, which gives the Einstein relation for Brownian motion: $D = \langle X^2 \rangle/2t$.

See: *tracer diffusion coefficient*

Electrical or electrochemical mobility

See: *mobility*

Electromigration

Transport of particles under the influence of an electric field.

Electron wind effect

When electrons flowing in response to the application of an electric field to a metal transfer some of their momentum to diffusing atoms and hence bias the directions of individual jumps, this additional driving force is called an electron wind effect.

Exchange mechanism

The atomic mechanism whereby diffusion takes place by the direct interchange of two neighbouring atoms.

Fast ionic conductors

A group of materials that exhibit unusually high ionic conductivities of the order of those found in molten

salts. The use of the term *superionic conductor*, which is found in older literature for fast ionic conductors is not encouraged.

Fick's First law

This law states the relationship between the flux vector $\boldsymbol{J}_i$ and the concentration gradient ∇c_i of the diffusing species i:

$\boldsymbol{J}_i = -D\,\nabla c_i$ where D is the *diffusion coefficient* or *diffusivity*. In three dimensions this is a second-rank tensor. The dimension of D is m^2/s. For the concentration the units can be chosen, the units for the flux depend on this choice, e.g. with c_i in mol/m^3, $\boldsymbol{J}_i$ is expressed in mol/m^2/s. The flux, and therefore also the diffusion coefficient, has to be chosen relative to a *frame of reference*.

For planar diffusion along the x direction the equation reduces to the scalar expression

$J_i = -D(\partial c_i/\partial x)$

Fick's reference frame

See: *mean-volume frame of reference.*

Fick's Second law

This law states the relationship between the concentration gradient ∇c_i of the species i and the rate of change of its concentration $\partial c_i/\partial t$ caused by its diffusion at a given point in the system:

$\partial c_i/\partial t = \nabla.(D\nabla c_i)$

where D is the *diffusion coefficient* or *diffusivity*.

For planar diffusion along the x direction this equation reduces to:

$\partial c_i/\partial t = \partial/\partial x[D(c_i)(\partial c_i/\partial x)]$

When D is independent of concentration it takes the form

$\partial c_i \partial t = D(\partial^2 c_i/\partial x^2)$

Solutions to this equation for given boundary conditions provide the basis for the experimental determination of *diffusion coefficients*.

Five-frequency model

A model describing impurity diffusion via monovacancies in face-centred-cubic (fcc) metals or on an fcc sublattice in ionic crystals. It is assumed that the only host atom jumps that differ from jumps in the pure lattice are those made by nearest neighbours of the impurity.

Flux

The flux of a species is the amount of substance crossing a plane of unit area in the medium in unit time.

Gorski effect

The migration of atoms in an elastically deformed material. The effect is particularly observed for solute atoms A with a strong size effect and high diffusivity in a matrix B, for instance hydrogen atoms in a metal.

Grain boundary diffusion

Diffusion taking place along a grain boundary.

See: *short circuit diffusion.*

Haven ratio

The Haven ratio H_R is defined by:

$$H_R = D_i^*/D_i(\sigma_\iota)$$

where D_i^* is the *tracer diffusion coefficient* and $D_i(\sigma_i)$ the *conductivity diffusion coefficient* of particle *i*. Note: H_R is not the same as the *correlation factor*.

Herring's formula

See: *effective diffusion coefficient.*

Heterodiffusion

The diffusion of foreign atoms in a material is called heterodiffusion (also called impurity diffusion or solute diffusion).

Impurity diffusion

See: *heterodiffusion*

Interchange diffusion

The process in which foreign atoms predominantly present at interstitial lattice sites migrate via normal sites.

Interdiffusion

See: *chemical diffusion, Darken equation.*

Interdiffusion coefficient

See: *Darken equation.*

Interstitial diffusion

Diffusion that takes place via interstitial sites.

   See: *direct interstitial mechanism*, *collinear interstitialcy mechanism*, *noncollinear interstitialcy mechanism* and *interstitialcy mechanism.*

Interstitialcy mechanism

A mechanism where the migration occurs by an interstitial atom moving onto a normal lattice site whilst simultaneously the original lattice atom moves into an interstitial position.

Intrinsic diffusion coefficient

The *diffusion coefficient* for each individual component of a multicomponent system. In the case of interdiffusion of two metals A and B and neglecting correlation effects, the intrinsic diffusion coefficient $\bar{D}_A$ is related to the self-diffusion coefficient D_A^* by the *Darken–Dehlinger relation*:

$$\bar{D}_A = D_A^*\left(1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A}\right) = D_A^* \Phi$$

where N_A denotes the mole fraction and γ_A the thermodynamic activity coefficient of A. An analogous expression holds for $\bar{D}_B$. The factor Φ is called the *thermodynamic factor*.

   The Darken–Dehlinger relation is an approximation. More complete derivations include *correlation* effects and the *vacancy wind*.

Jump frequency

The jump frequency of a particle i towards a given nearest-neighbour site is denoted by Γ_i. The total jump frequency, Γ, which denotes the average number of jumps of the particle per unit time, is given by $\Gamma = \zeta \Gamma_i$ where ζ is the nearest-neighbour co-ordination number.

In case an atom moves via a vacancy mechanism the total jump frequency, Γ, is given by the product of the mole fraction of vacancies, N_V, times the jump frequency of the vacancy in the nearest-neighbour site, ω_0:

$$\Gamma = N_v \omega_0$$

The frequency ω_0 can be written as

$$\omega_0 = n \exp(-\Delta G_m / RT)$$

The attempt frequency n can be related to the normal modes of vibration of the system and is of the order of a vibration frequency $\approx 10^{13}$ s^{-1}. ΔG_m is called the Gibbs energy of migration.

The mean time between two jumps of a particle in a given site is called the residence time τ, where $\tau = \Gamma^{-1}$.

The *self-diffusion coefficient D_i* of a particle i is related to the total jump frequency via:

$$D_i = g \Gamma a_i^2$$

Here a_i is the jump distance of the particle and g is a geometrical factor giving the jump probability of the particles in the particular direction under consideration. For instance for an isotropic cubic lattice $g = 1/6$.

Kirkendall effect

The Kirkendall effect occurs during interdiffusion between specimens in a diffusion couple when the intrinsic diffusion coefficients of the components are different. The greater flux of atoms in one direction over the other direction causes the original interface, called the Kirkendall plane, to be displaced by a distance called the Kirkendall shift. This shift can be observed by the movement of inert markers.

Kirkendall plane

See: *Kirkendall effect*, *laboratory frame*.

Kirkendall velocity

The velocity v_K of the diffusion zone in a multicomponent system, relative to the fixed ends of the specimen, results from the net nonzero flux of vacancies in the diffusion region. In a binary system with components A and B it can be expressed in terms of the intrinsic diffusion coefficients $\bar{D}_A$ and $\bar{D}_B$. For instance the relative velocity $v^{K/V} = v^K - v^V$ measured with respect to the *mean-volume frame* is

$$v_K = (\bar{D}_A - \bar{D}_B) \bar{V}_A (\partial N_A / \partial x)$$

where N_A is the mol fraction and $\bar{V}_A$ the partial molar volume of A.

Laboratory frame

In binary diffusion the fluxes J_A and J_B of species A and B generally will be different. The frame of reference defined by the condition $J_A + J_B = 0$ is called the laboratory frame. A convenient laboratory frame is the end of the specimen since at the ends $J_A = J_B = 0$, so that the condition $J_A + J_B = 0$ is always fulfilled. The *Matano plane* is an example of a laboratory frame.

See: *reference frames*.

Lattice diffusion

A diffusion process which takes place through the bulk lattice of the crystal and excludes such

mechanisms as short circuit diffusion along dislocations, grain boundary diffusion, and surface diffusion. Also called *bulk diffusion* or *volume diffusion.*

Lattice fixed frame

This *reference frame* is used when the diffusion flux gives rise to a net flux of material. The lattice fixed frame, also called inert-marker or Kirkendall frame, moves with the local flux of the material. The *Kirkendall plane* is an example of a lattice fixed frame. The frame is in the general case not connected to an average velocity of the constituents, but to the velocity of the markers v^K. Relations can be derived for v^K and for $\tilde{D}$ in different reference frames.

See: *reference frames*.

Linearized flux equation

See: *phenomenological coefficients*.

Ludwig–Soret effect

An alternative name for the Soret effect.

See: *thermomigration*.

Matano plane

The Matano plane is the interface through which equal amounts of substance have moved in the positive and negative directions during interdiffusion.

See: *laboratory frame*.

Mean-mass frame of reference

The mean-mass frame R^M moves in such a way that the net flux of mass, J_i^M, traversing a plane normal to the diffusion direction is zero everywhere and at all times. By definition the weighting factors, α^M, for the mean-mass frame are chosen such that $\alpha_i^M = w_i$, with $w_i = M_i c_i / \rho_i$ being the mass fraction, M_i the molar mass and ρ the density. So for a multicomponent system $\Sigma_i M_i J_i^M$. The velocity v^M of R^M with respect to the laboratory frame R^0 is $v^M = \Sigma_i M_i J_i^0$, where J_i^0 is the flux in R^0.

The mean-mass reference frame is also known as the barycentric frame of reference.

See: *reference frames*.

Mean-molar frame of reference

The mean-molar frame of reference R^N moves with respect to the laboratory frame so that the net flux expressed in number of moles of material traversing a plane normal to the diffusion direction is zero everywhere and at all times. By definition the weighting factors, α^N, for the mean-volume frame are chosen such that $\alpha_i^N = N_i$ with N_i the mole fraction of component i. So for a multicomponent system $\Sigma_i J_i^N = 0$. The velocity v^N of R^N with respect to the laboratory frame R^0 is $v^N = V_m \Sigma_i J_i^0$ where J_i^0 is the flux in R^0.

The frame is also called number-fixed frame.

See: *reference frames*.

Mean-volume frame of reference

The mean-volume frame R^V moves with respect to the laboratory frame R^0 so that the net flux expressed in volume of material traversing a plane normal to the diffusion direction is zero everywhere and at all times. By definition the weighting factors, α^V, for the mean-volume frame are chosen such that $\alpha_i^V = c_i \bar{V}_i$ with c_i the number of moles of component i per unit volume and $\bar{V}_i$ the partial molar volume. So for a multicomponent system $\Sigma_i \bar{V}_i J_i^V = 0$. The velocity v^V of R^V with respect to the laboratory frame R^0 is $v^V = \Sigma_i \bar{V}_i J_i^0$ where J_i^0 is the flux in R^0.

For the binary case $\bar{V}_A J_A^V + \bar{V}_B J_B^V = 0$. One can show that in this case the interdiffusion coefficient $\tilde{D}^V$ in the mean-volume frame is equal to the intrinsic diffusion coefficients of the components A and B: $\tilde{D}^V = \bar{D}_A^V = \bar{D}_B^V$.

The mean-volume frame is also known as Fick's reference frame.

See: *reference frames*.

Mobility

Mass transport is described by an atomic mobility b, defined by:

$$b_i = v_i/F_i$$

where v_i is the average *drift velocity* and F_i is the force on particle i.

For electrical conductivity an electrical mobility u_i (sometimes called electrochemical mobility) is defined as the velocity per unit of electrical field strength E:

$$u_i = v_i/E$$

so $u_i = b_i\, F_i/E$

Since the force on a particle with absolute electric charge $|q_i|$ is given by $F_i = |q_i|\, E$ one also has $u_i = b_i\, |q_i|$

Mobility coefficient

See: *phenomenological coefficients*.

Multiphase diffusion

A diffusion process leading to the formation of a new interface, such as occurs during formation of allotropic structures, new phases, solid solutions and/or chemical reactions. Sometimes this process is called reaction diffusion.

Nernst–Einstein equation

In ionic crystals the *Einstein equation* relates the ion *mobility*, u_i, of a particle i to the *conductivity diffusion coefficient*, $D_i(\sigma)$:

$$D_i(\sigma) = (kT/|q_i|)u_i$$

where $|q_i|$ is the absolute charge of the moving ion, k the Boltzmann constant and T the thermodynamic temperature

Since the partial electrical conductivity of species i can be written as $\sigma_i = c_i u_i |q_i|$ it follows that

$$D_i(\sigma) = (kT/c_i q_i^2)\sigma_i$$

where c_i is the concentration. These expressions are known as the Nernst–Einstein equations.

Nernst–Planck equation

For interdiffusion of two ionic crystals AX/BX the relationship between *the intrinsic diffusion coefficients* $\bar{D}_A$ and $\bar{D}_B$ and the *tracer diffusion coefficients* D_A^* and D_B^* is given by the Nernst–Planck equation as:

$$\bar{D}_A = \bar{D}_B = \frac{D_A^* D_B^*}{N_A D_A^* + N_B D_B^*}$$

where N_A and N_B are the mole fractions of constituents A and B. This relation holds under the assumption that only A and B are mobile, and that they diffuse on a common sublattice, the X sublattice being fixed and independent.

This should not be confused with the expression for the *interdiffusion coefficient* nor with the *effective diffusion coefficient*.

For nonideal solutions the above expressions for the intrinsic diffusion coefficients should be multiplied by the *thermodynamic factor*.

Neumann's principle

Neumann's principle (also known as Curie principle or Curie–Neumann's principle) states that if a coordinate transformation follows the symmetry operations of the crystalline lattice in question, then that transformation leaves the *diffusivity tensor* invariant. This principle can be written in a mathematical form. A general tensor coordinate transformation for the diffusivity from the coordinate system x_i into a new coordinate system $\overline{x}_i$ is accomplished in the following manner.

Let D'_{ij} represent the diffusivity tensor in the new coordinate system, then:

$$D'_{ij} = \sum_{k=1}^{3} \sum_{l=1}^{3} \frac{\partial \overline{x}_i}{\partial \overline{x}_k} \frac{\partial \overline{x}_j}{\partial \overline{x}_l} D_{kl} = \sum_{k=1}^{3} \sum_{l=1}^{3} a_{ik} a_{jl} D_{kl}$$

Where $a_{ik} = \partial \overline{x}_i / \partial x_k$ is the direction cosine for the transformation. Neumann's principle asserts that if a_{ik} follows a crystalline symmetry operation, then

$$D'_{ij} = D_{ij}$$

Non-collinear interstitialcy mechanism

An *interstitialcy mechanism* in which the interstitial atom and the lattice atom which it displaces do not move along the same straight line.

Number-fixed frame of reference

See: *mean-molar frame of reference.*

Onsager relation

Condition on the phenomenological coefficients in the Onsager expression for the diffusion flux: $L_{ik} = L_{ki}$ (also called Onsager's reciprocity theorem). The theorem holds in the absence of magnetic fields and rotations.

See: *phenomenological coefficients.*

Parabolic growth law

Growth of a reaction layer by diffusion such that the square of the layer thickness d increases proportional with time t: $d^2 \propto t$.

Partial diffusion coefficient

In an N-component system the flux $\boldsymbol{J}_i$ of species i may depend on the concentration gradients ∇c_k of $N-1$ species in the material. In that case a partial diffusion coefficient D_{ik} is defined by *Fick's First law* in the form:

$$\boldsymbol{J}_i = \sum_{k=1}^{N-1} D_{ik} \nabla c_k$$

In general, partial diffusion coefficients can be either intrinsic or interdiffusion coefficients, depending on the reference frame used to describe the flux.

Phenomenological coefficients

(Also called *transport coefficients* or *mobility coefficients*.)

The coefficients L in Onsager's generalised diffusion equation for component i in an N-component system, relate the fluxes of these species, J_i to the driving forces X_k:

$$J_i = \sum_{k=1}^{N-1} L_{ik} X_k \qquad i = 1, 2, \ldots, N-1$$

The driving forces can be expressed as gradients of a generalised potential. When only mechanical forces are acting, the X_k are identical with these mechanical forces; in an isothermal, isobaric system with a composition gradient, the driving force X_k can be written as a gradient in the chemical potential μ_k: $X_k = -\nabla(\mu_k - \mu_N)$; and for the case of diffusion in an electric field the driving force is the gradient in the electrochemical potential η, where $\eta_k = \mu_k + z_k F \psi$.

z_k is the valence, F the Faraday constant and ψ the *electrical potential* (*diffusion potential*).

Physical correlation factor

In cases where interaction occurs between diffusing particles, the paths of these particles are no longer independent but are correlated. In these cases one introduces a physical correlation coefficient to account for the departure from the laws of random motion.

See: *correlation factor*

Pipe diffusion

Diffusion which takes place along a dislocation line.

See: *short circuit diffusion.*

Pre-exponential factor

See: *activation energy*

Random walk

If successive jumps are random with no preferred direction, the path followed by that atom during diffusion is described as a random walk.

Random walk theory

The mathematical theory describing the motion of a particle moving in a series of discrete random jumps from one site to another.

See: *correlation factor*, *Einstein–Smoluchowski equation.*

Reaction diffusion

See: *multiphase diffusion*

Reference frames

In the case of diffusion in binary or multicomponent systems the expressions for fluxes and forces, and therefore the values of the diffusion coefficients, depend on the frame of reference in space with respect to which these quantities are measured.

Examples of often used frames are the *laboratory frame*, *mean-volume frame* (also called *Fick's frame*), *mean-molar frame* (also called *number fixed frame or particle reference frame*), *mean-mass frame*, *lattice fixed frame* (also called *Kirkendall frame*).

To define a frame of reference R independent of the chosen laboratory fixed frame R^0 an average velocity of the constituents is chosen such that

$$v^R = \sum_{i=1}^{n} \alpha_i^R v_1^{R0}$$

where v_i^{R0} is the velocity of constituent i in R^0 and the α_i^R are weighting factors normalised such that $\Sigma_i \alpha_i^R = 1$.

The flux J_i^R in a frame of reference R is related to the flux J_i^Q in frame Q by

$$J_i^R = J_i^Q + c_i v^{QR}$$

with $v^{QR} = v^Q - v^R$

v^R denotes the average velocity of the n constituents in the frame R.

Relaxation mechanism

If the atoms close to a vacancy relax to such an extent that the regular lattice structure out to several atom distances disappears, diffusion may occur by an irregular jostling motion similar to that for atoms in a liquid. Such diffusion is said to occur by a relaxation mechanism.

Residence time

See: *Jump frequency*

Ring mechanism

A variation of the exchange mechanism in which a group of atoms moves around in a circular fashion, each atom in the group taking the place of its neighbour in the direction of motion.

Self-diffusion

Diffusion which takes place in the absence of a chemical potential gradient, describing the uncorrelated movement of a particle.

Self-diffusion coefficient

See: *tracer diffusion coefficient.*

Short circuit diffusion

Any diffusion process occurring via grain boundaries, surfaces or dislocations.

Short circuit diffusion mechanisms often cause diffusion in polycrystalline materials to proceed more quickly than in single crystals.

Sintering

The process through which a solid body is formed from powders upon heat treatment by virtue of atomic transport processes. The driving force is the reduction of surface energy.

Solute diffusion

See: *heterodiffusion*

Soret effect

The establishment of a concentration gradient in a closed multicomponent system under the influence of a temperature gradient. Also called Ludwig–Soret effect.

See: *thermomigration.*

Superionic conductor

See: *fast ionic conductors*

Surface diffusion

Diffusion that takes place on a surface.

See: *short circuit diffusion.*

Thermal diffusion

See: *thermomigration.*

Thermodynamic factor

In the description of diffusion in nonideal solid solutions the term:

$$\Phi = 1 + \partial \ln \gamma_i / \partial \ln N_i$$

where γ_i is the thermodynamic activity coefficient and N_i the mole fraction of species i, is defined as the thermodynamic factor. Note that for a binary system A-B: $\Phi = \Phi_A = \Phi_B$ due to the Gibbs–Duhem relation.

See: *intrinsic diffusion coefficient.*

Thermomigration

The diffusion resulting from a temperature gradient is called thermomigration or thermal diffusion. For this case Fick's first law can be written as $J_i = -S_i \nabla T$. Here J_i denotes the flux of species i, and T the thermodynamic temperature. The coefficient S_i may be of either sign.

If an initially homogeneous two-component phase is placed in a temperature gradient thermomigration can lead to an unmixing of the components. That is, one component diffuses preferentially to the hot end, and the hot region becomes enriched in that component. This effect is called the *Soret effect* (also called *Ludwig–Soret effect*).

Tracer diffusion

Tracer diffusion refers to the migration of a tagged atom through a material of which it is a component.

Tracer diffusion coefficient

The diffusion coefficient D_i^* as defined by *Fick's First law* for an isotopically labeled atom. The term is usually restricted to the particular simple situation in which a tracer isotope in very dilute concentration is diffused into an otherwise homogeneous material with no *driving forces* other than the concentration gradient of the tracer itself.

In a homogeneous material the mean square displacement $\langle x_i^2 \rangle$ of the tracer i in the x-direction, as derived from the tracer concentration profile, is related to the tracer diffusion coefficient D_i^* by the *Einstein* formula for Brownian motion

$$\langle x_i^2 \rangle = 2D_i^* t$$

where t is the diffusion time. Often the tracer diffusion coefficient is not distinguished from the self-diffusion coefficient. This is only justified if diffusion takes place by uncorrelated atom jumps. For interstitial diffusion of particles A in an elemental crystal A this is the case, but for diffusion via a vacancy mechanism this does not hold. The tracer diffusion coefficient and self-diffusion coefficient are generally related by the *correlation factor*.

See: *random walk theory, Einstein–Smoluchowski equation.*

Transport coefficient

See: *phenomenological coefficients.*

Uphill diffusion

A diffusion process in which a diffusing species migrates against its concentration gradient. It occurs in ternary and higher order systems either because of thermodynamic effects or because of differences in mobilities of the species.

Vacancy diffusion coefficient

See: *defect diffusion coefficient*

Vacancy mechanism

A mechanism where diffusion is made possible by the exchange of positions between the diffusing species and a vacancy.

Vacancy wind effect

If diffusion gives rise to a flux of vacancies in one direction, the availability of vacancies for a given substitutional atom is biased. The atoms will be able to jump more frequently to the 'windward' side since the vacancy concentration at that side is higher than at the 'leeward' side. Therefore there is a preferential diffusion against the vacancy wind.

Volume diffusion

See: *lattice diffusion*.

Zero flux plane

In multicomponent diffusion-couple experiments the fluxes of individual components may go to zero at specific locations along the axis of the couple. These locations are called zero flux planes.

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