3. Constitutive relations for diffusion flux

3.1. Fluxes

In most transport phenomena we use a flux concept as a measure of transport. For example if we are talking about heat transport, we will use the Fourier's law:

$$Q = -k\nabla T \tag{3.1}$$

where: Q – heat flux $\left[\frac{W}{m^2}\right]$

k – thermal conductivity $\left[\frac{W}{mK}\right]$

∇T – temperature gradient $\left[\frac{K}{m}\right]$

Similarly, for transport of electric charge, we can use Ohm's law:

$$j = -\sigma\nabla\phi \tag{3.2}$$

where: j – electric current $\left[\frac{A}{m^2}\right]$

σ – electrical conductivity $\left[\frac{1}{\Omega m}\right]$

$\nabla\varphi$ – electric potential gradient $\left[\frac{V}{m}\right]$

There are some obvious analogies, the most notable is that fluxes are proportional to the negative gradients of physical values. It is quite logical: heat will be transported from hot areas to cold ones, the bigger difference of electric potential, the bigger the current will be etc. This general rule will also be true for mass transport.

It is time to introduce a **diffusion** concept. Formally speaking, diffusion is a irreversible process, in which energy is dissipated and the entropy grows. However it is much easier to understand it, as a mass transport phenomena that results in mass mixing/transport without requiring bulk motion.

In the first paper we already mentioned **mass flux**. The most common mass flux is a **diffusion flux**, which is a result of presence of gradient of chemical potential. Chemical potential is a state function which can be described as a form of potential energy. It's numerical value is equal to the value of increase of functions *U*, *F*, *H*, *G* if one mol of the i-th component is added (when amounts of other components are constant):

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{i\neq j},} = \left(\frac{\partial H}{\partial N_i}\right)_{S,p,N_{i\neq j}} = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_{i\neq j}} = \left(\frac{\partial G}{\partial N_i}\right)_{p,T,N_{i\neq j}} \tag{3.3}$$

We should mention here, that flux equations are constitutive equations – it means that in most cases they are not derived from the most basic thermodynamic principals, but they do describe what is the response of the system to a given stimuli.

3.2. Constitutive equations for diffusion flux

Now we will write the most popular diffusion flux equation – **Fick's first law:**

$$J_i^{diff} = -D_i \nabla c_i \tag{3.4}$$

where: J_i^{diff} – diffusion flux of the i-th component $\left[\frac{mol}{m^2 s}\right]$

D_i – diffusion coefficient of the i-th component $\left[\frac{m^2}{s}\right]$

∇c_i – concentration gradient of the i-th component $\left[\frac{mol}{m^4}\right]$

We can see, that form of equation (3.4) is analogues to equation (3.1) and (3.2). We mentioned, that diffusion flux should be proportional to the chemical gradient potential, while in Fick's law we can see gradient of concentration – that is why for calculations we often use another, more accurate expression called **Nernst-Planck equation:**

$$J_i^{diff} = B_i c_i \vec{F_i} \tag{3.5}$$

where: B_i – atom mobility for i-th component

$\vec{F_i}$ – forces acting on atoms of i-th component

$$\vec{F_i} = -\nabla \mu_i \tag{3.6}$$

Mobility B_i and diffusion coefficient D_i are correlated by **Nernst-Einstein relation:**

$$B_i = \frac{D_i}{kT} \tag{3.7}$$

One may ask: "what if for example the ions are transported, and electrical field is present?", or:"does the pressure influence mass transport?". That is why we will introduce the **general form of Nernst-Planck equation**:

$$J_i^{diff} = B_i c_i \sum_{j=1} \vec{F_j} \tag{3.8}$$

where: $\sum_{j=1} \vec{F_j}$ –sum of all forces acting on the atoms:

$$\sum_{j=1} F_j = -\nabla(\mu_i^{chem} + \mu_i^{mech} + \mu_i^{elec} + \dots) = -\nabla \mu_i^{diff} \tag{3.9}$$

where: μ_i^{chem} – chemical potential of the i-th component

μ_i^{mech} – mechanical potential of the i-th component

μ_i^{elec} – electrical potential of the i-th component

μ_i^{diff} - diffusion potential of the i-th component

The last diffusion flux equation presented here, will be the one postulated by Lars **Onsager.** In 1931 he presented theory of **irreversible thermodynamics.** He used following assumptions:

- All transport fluxes (charge, mass, heat etc.) are linearly correlated with all thermodynamic forces present in the system. For "n" transport processes:

$$\vec{J_1} = L_{11}\vec{X_1} + L_{12}\vec{X_2} + L_{13}\vec{X_3} + \cdots + L_{1n}\vec{X_n}$$
$$\vec{J_2} = L_{21}\vec{X_1} + L_{22}\vec{X_2} + L_{23}\vec{X_3} + \cdots + L_{2n}\vec{X_n}$$
$$\vec{J_3} = L_{31}\vec{X_1} + L_{32}\vec{X_2} + L_{33}\vec{X_3} + \cdots + L_{3n}\vec{X_n} \qquad (3.10)$$
$$\vdots$$
$$\vec{J_n} = L_{n1}\vec{X_1} + L_{n2}\vec{X_2} + L_{n3}\vec{X_3} + \cdots + L_{nn}\vec{X_n}$$

$\vec{X_i}$ — thermodynamic force

L_{ij} – kinetic response coefficient/phenomenological coefficient/transport coefficient

In a more general way, we can write equation (3.10) as:

$$\vec{J_i} = \sum_{j=1}^{n} L_{ij}\vec{X_j} \qquad (3.11)$$

The general meaning of this assumption, is that every transport process affects all the others processes. We have to remember, that transport coefficients are not dependent on forces.

- Onsager matrix of transport coefficients consists of two types of elements: diagonal and off-diagonal. Diagonal terms L_{ii} connects each generalized force with its conjugate flux e.g. heat flux with thermal gradient, flux of electrons with electrical potential gradient etc. Off-diagonal terms determines the influence of each force on the non-conjugate fluxes, e.g. how transport of electrons influence heat flux (Peltier effect). For all off-diagonal coefficients following relation, known as **Onsager's reciprocity theorem,** is true (assuming that magnetic field is not present):

$$L_{ij} = L_{ji} \qquad (3.12)$$

- The last of Onsager's assumption, is that each of the thermodynamic forces acting with its conjugate flux response, dissipates free energy and produces entropy. Production of entropy is characteristic for irreversible processes, the rate of its production can be described as:

$$\dot{\sigma} = \sum_{i} \vec{J_i} \cdot \vec{X_i} \geq 0 \qquad (3.13)$$

Thermodynamic equilibrium is reached, when:

$$\dot{\sigma} = 0 \qquad (3.14)$$

Example 3.1.

Write an Onsager matrix for a one dimensional system, in which heat, mass and charge are transported.

Solution

Looking at equations (2.1), (2.2) and (2.4) we can write equations for fluxes of mass, charge and heat:

$$mass: \quad J = -D\frac{dc}{dx}$$

$$heat: \quad Q = -\lambda\frac{dT}{dx}$$

$$charge: \quad j = -\kappa\frac{d\phi}{dx}$$

Now, we can describe forces in our system:

$$chemical\ force: \quad -\frac{1}{T}\frac{d\mu}{dx}$$

$$thermal\ force: \quad \frac{d}{dx}\frac{1}{T}$$

$$electrical\ force: \quad -\frac{1}{T}\frac{d\phi}{dx}$$

Forces are defined in such way, that transport coefficients have the same units. This is necessary due to the Onsager's reciprocity theorem. In the first equation, instead of concentration, we can use chemical potential. Relation between those two is (for ideal solutions):

$$\mu_i = \mu_i^0 + kT \ln n_i$$

where: n_i - molar fraction of i-th component, and $c_i = n_i c$

Now we can write our fluxes in form similar to (2.12):

$$Q = L_{qq}\frac{d}{dx}\frac{1}{T} - L_{q\mu}\frac{1}{T}\frac{d\mu}{dx} - L_{q\phi}\frac{1}{T}\frac{d\phi}{dx}$$

$$J = L_{q\mu}\frac{d}{dx}\frac{1}{T} - L_{\mu\mu}\frac{1}{T}\frac{d\mu}{dx} - L_{\mu\phi}\frac{1}{T}\frac{d\phi}{dx}$$

$$j = L_{q\phi}\frac{d}{dx}\frac{1}{T} - L_{\mu\phi}\frac{1}{T}\frac{d\mu}{dx} - L_{\phi\phi}\frac{1}{T}\frac{d\phi}{dx}$$

Onsager matrix looks as follows:

$$\begin{pmatrix} Q \\ J \\ j \end{pmatrix} = \begin{pmatrix} L_{qq} & L_{q\mu} & L_{q\phi} \\ L_{q\mu} & L_{\mu\mu} & L_{\mu\phi} \\ L_{q\phi} & L_{\mu\phi} & L_{\phi\phi} \end{pmatrix} \cdot \begin{pmatrix} \dfrac{d}{dx}\dfrac{1}{T} \\ -\dfrac{1}{T}\dfrac{d\mu}{dx} \\ -\dfrac{1}{T}\dfrac{d\phi}{dx} \end{pmatrix}$$

Example 3.2.

Write an Onsager matrix for diffusion fluxes for a binary A-B alloy, where acting forces are gradients of molar fraction.

Solution

In this case, our forces are gradients of chemical potential of each component (notice analogy to Nernst-Planck flux). Our fluxes are:

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} L_{AA} & L_{AB} \\ L_{AB} & L_{BB} \end{pmatrix} \begin{pmatrix} -\nabla\mu_A \\ -\nabla\mu_B \end{pmatrix}$$

Chemical potentials of our components:

$$\mu_A = \mu_A^0 + kT \ln n_A$$
$$\mu_B = \mu_B^0 + kT \ln n_B$$

After inserting (1.23) to (1.22):

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} kTL_{AA} & kTL_{AB} \\ kTL_{AB} & kTL_{BB} \end{pmatrix} \begin{pmatrix} -\nabla \ln n_A \\ -\nabla \ln n_B \end{pmatrix}$$

What can be transformed into:

$$\begin{pmatrix} J_A \\ J_B \end{pmatrix} = \begin{pmatrix} \dfrac{kTL_{AA}}{n_A} & \dfrac{kTL_{AB}}{n_B} \\ \dfrac{kTL_{AB}}{n_A} & \dfrac{kTL_{BB}}{n_B} \end{pmatrix} \begin{pmatrix} -\nabla n_A \\ -\nabla n_B \end{pmatrix}$$