Chemistry 24b ***Lecture 2 RWR***
Spring Quarter 2004
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Reading Assignment: *Ch 6: Tinoco; Ch 16: Levine; Ch 15: Eisenberg&Crothers*

Diffusion

Real processes, such as those that go on continually in biological systems are always attended by a free energy decrease for the system. One of the simplest ways to describe this approach of the system towards a state of lower free energy is by way of the concept of the thermodynamic force. We can illustrate the power of this approach first by deriving Fick's Law of Diffusion.

You might recall from elementary mechanics in physics that a particle in a mechanical or gravitational field always moves from a point of high potential energy to one of lower potential energy. Another way of stating this fact is that there is a force on the particle given by

$$\vec{F}_{(\vec{r})} = -\vec{\nabla} V(\vec{r})$$

or in one dimension

$$F_x = -\frac{dV}{dx} \quad \text{or} \quad -\frac{\partial V}{\partial x}$$

However, in contrast to motion in free space or a vacuum, motion of molecules in a gas or liquid involves resistance or frictional forces. A particle moving in such a medium must cause displacement and separation of these interacting molecules. Force is required and the net result is an expenditure of energy. When the path of a particle involves the separation of two or more molecules, work is done by the particle on these two or more molecules. This work or energy expenditure by the particle is not recovered by the particle when the two or more molecules again return to their average intermolecular distances. Instead, this work of separation is dissipated as heat characteristic of irreversible processes. In fact, the rate of energy dissipation by the moving particle is proportional to its velocity.

One frequently speaks of this rate of energy dissipation as a frictional force. This frictional force is not only a property of the particular medium through which the particle is moving, but is also dependent on the particle size and shape. The larger the size, the greater the resistance encountered. The inherent property of the medium which determines the friction force is called the viscosity h, and is related, in part, to the degree of molecular interaction and molecular size and shape. In 1850, Stokes showed that for a sphere

$$\vec{F}_f = -6prh\vec{v}$$

where $\vec{F}_f$ = frictional force

r = radius of sphere

h = viscosity

$\vec{v}$ = velocity of motion of sphere

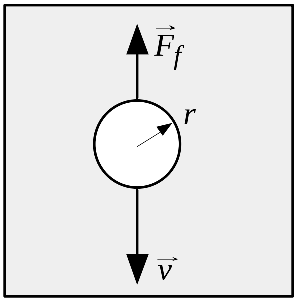

Figure 1-1

The quantity $6prh$ is often referred to as the frictional coefficient, i.e.,

$$f = 6prh$$

Since the frictional force encountered by a particle moving in a viscous medium is proportional to the velocity of the particle, it is evident that a driving force acting on the particle cannot lead to its continual acceleration. The particle will reach a velocity such that the frictional force opposing the motion becomes equal to the driving force. Given a constant driving force, the velocity of motion of a particle in a viscous medium will be a constant, and is obtained by equating

$$\vec{F}_f = -\vec{F}_d$$

where $\vec{F}_d \equiv$ driving force on particle

or $\vec{F}_d = 6prh\vec{v}$

$$\vec{v} = \frac{1}{f}\vec{F}_d = l\vec{F}_d$$

$l = f^{-1} \equiv$ mobility $\equiv$ velocity of particle assumed when unit driving force is acting on it

Concept of a Flux

Now consider a large number of molecules k moving with an average velocity $\vec{v}_k$ as a result of this driving force $\vec{F}_d$.

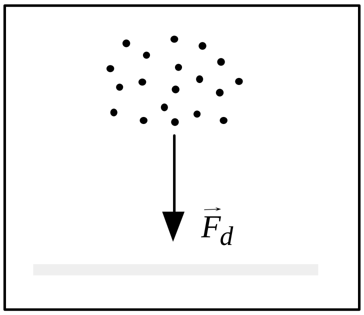

Figure 1-2

Let us calculate the number of such molecules crossing 1 cm^2 of this imaginary boundary $\perp$ flow per unit time or sec. This quantity is called the flux.

$$\vec{J}_k = C_k \vec{v}_k$$

where $C_k \equiv$ concentration of moles / cm^3

Substituting for $\vec{v}_k$,

$$\vec{J}_k = \lambda_k C_k \vec{F}_{d_k} \quad \text{flux moles / cm}^2\text{ / sec}$$

Derivation of Fick's Law of Diffusion (First Law)

The above discussion assumes that the particles are subjected to gravitational potential. However, $\vec{F}_d$ need not be mechanical in origin. $\vec{F}_d$ could be the thermodynamic force. For neutral solutes, we can define a thermodynamic force

$$\vec{F}_{d_k} = -\vec{\nabla}\mu_k(\vec{r}) \cdot \frac{1}{N_A}$$

or in 1-D,

$$\left(F_{d_k}\right)_x = -\frac{\partial \mu_k(x)}{\partial x} \cdot \frac{1}{N_A}$$

Now

$$\mu_k(x) = \mu_k^0 + RT \ln C_k(x)$$

Therefore,

$$\left(F_{d_k}\right)_x = -\frac{1}{N_A} RT \frac{d \ln C_k(x)}{dx} = -k_B T \frac{1}{C_k}\left(\frac{dC_k(x)}{dx}\right)$$

From this result, we see that a concentration gradient provides a thermodynamic force for the particles or molecule to diffuse. Also, particles diffuse from higher m_k to lower m_k, or from higher C_k to lower C_k.

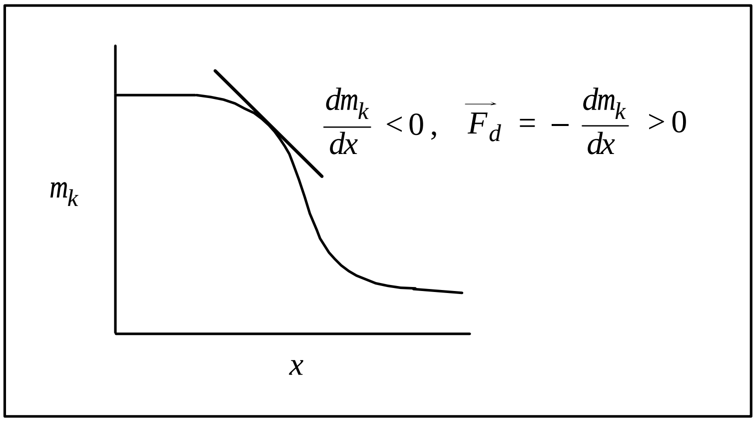

Figure 1-3

With this result, we can obtain the flux:

$$\vec{J}_k = l_k C_k \vec{F}_{d_k}$$

$$J_k = -l_k C_k k_B T \frac{1}{C_k} \frac{dC_k(x)}{dx}$$

$$J_k = -l_k k_B T \frac{dC_k(x)}{dx} = -D_k \frac{dC_k}{dx} \qquad \text{Fick's Law } (\textbf{First} \text{ Law})$$

where $D_k \equiv$ diffusion coefficient of species k

$$= \frac{k_B T}{f} = k_B T l_k \ (\text{cm}^2 / \text{sec})$$

Table 1-1. Typical Diffusion Coefficients at 20° C in H_2O (cm^2/sec)

Glycine	9.5×10^{-6}
Leu–Gly–Gly	4.6×10^{-6}
Ribonuclease	10.2×10^{-7}
Human Serum Albumin	6.1×10^{-7}
Human Hb	6.8×10^{-7}
Tobacco Mosaic Virus	3.0×10^{-8}
H_20	10^{-6}
Phospholipids in Bilayer Membrane	10^{-7} to 10^{-8}
Membrane Proteins	10^{-10} or lower

Diffusion of Electrolytes

For charged species k (as opposed to neutral solutes discussed above)

$$\vec{F}_{d_k} = -\vec{\nabla}\overline{m}_k(\vec{r}) \ , \quad \overline{m} = \text{ electrochemical potential}$$

where $\overline{m}_k(x) = m_k^0(T,P) + RT\ln C_k(x) + z_k F\ F(x)$

From this,

$$\begin{aligned} J_k &= -l_k C_k \left(\frac{1}{N_A}\right)\frac{d\overline{m}_k}{dx} \\ &= -l_k C_k \left(\frac{1}{N_A}\right)\left[\frac{RT}{C_k}\frac{dC_k}{dx} + z_k F\ \frac{dF(x)}{dx}\right] \\ &= -l_k k_B T\left[\frac{dC_k(x)}{dx} + \frac{z_k|e|C_k}{k_B T}\frac{dF(x)}{dx}\right] \end{aligned}$$

which shows that the flux is controlled by both the concentration and the electrical potential gradient. Now $\dfrac{dF}{dx}$ may exist purely as a result of diffusion of the electrolyte (or free diffusion of ions), or it may be imposed on the system from an external source, with the use of appropriate electrodes. For example:

(1) Free Diffusion

You cannot have macroscopic separation of charges in space. Accordingly, there is no net charge flow

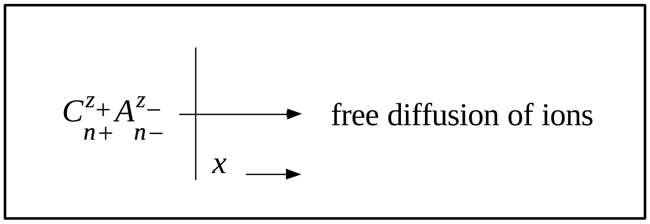

Figure 1-4

Therefore

$$\sum_k z_k J_k = 0 \qquad \text{for all values of } k$$

For simplicity, consider a binary electrolyte:

Conditions for Free Diffusion:

$$0 = z_+ l_+ \frac{dC_+(x)}{dx} + \frac{l_+ z_+^2 F}{RT} C_+ \frac{dF(x)}{dx} + z_- l_- \frac{dC_-(x)}{dx} + \frac{l_- z_-^2 F}{RT} C_- \frac{dF(x)}{dx}$$

Since for binary electrolytes

$$C_k = n_k C$$

where $n_k \equiv$ stoichiometric number of ions

We obtain

$$\frac{dF}{dx} = -\frac{RT}{F}\left[\frac{z_+ n_+ l_+ + z_- n_- l_-}{z_+^2 n_+ l_+ + z_-^2 n_- l_-}\right]\frac{d\ln C(x)}{dx}$$

This result shows that in general one expects some electrical potential gradient to be associated with the simple diffusion of an electrolyte. $\frac{dF}{dx}$ depends on:

(a) $z_+ n_+ l_+ + z_- n_- l_-$

(b) $\frac{d\ln C(x)}{dx}$

Only if $z_+ n_+ l_+ + z_- n_- l_- = 0$ would $\frac{dF}{dx} = 0$ in the presence of $\frac{d \ln C}{dx}$.

For a simple univalent-univalent electrolyte, where

$$z_+ = 1\,,\ \ z_- = -1\,,\ \ n_+ = 1\,,\ \ n_- = 1$$

$$\frac{dF}{dx} = -\frac{RT}{F}\frac{\left(l_+ - l_-\right)}{\left(l_+ + l_-\right)}\frac{d \ln C}{dx}$$

Thus, if the mobility of the cation l_+ is larger than that of the anion l_-, then the resulting electrical potential gradient has the opposite sign to the concentration gradient, or in other words, opposes the motion of cations.

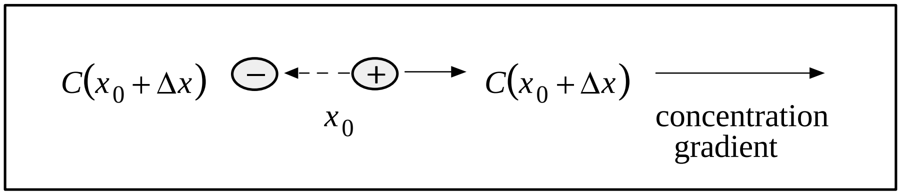

Figure 1-5

If l_- is greater than l_+, then $\frac{dF}{dx}$ has the same sign as $\frac{dC}{dx}$, and tends to oppose the motion of anions. In effect, what exists in a diffusion system is a slight displacement of charge; the more mobile charge leads the less mobile one by a slight amount, just enough to give rise to $\frac{dF}{dx}$ observed. The diffusion of cations and anions are coupled together in this fashion by their electrical attraction for each other.

(2) Electrophoresis

Discuss later.