V. Diffusion

Introduction

*Spontaneous diffusion* - the process of particles moving in a heterogeneous multicomponent system. Diffusion is caused by the chemical potential gradient components. The result of the diffusion effect is a diffusion flux (flow) of component $j_i$. Flux component is equal to the number of moles of component flowing in unit time through unit area perpendicular to the direction of flow:

$$J_i = \frac{1}{S} \cdot \frac{dn_j}{dt}$$

Flux component is proportional to the gradient of chemical potential of the ingredient and the chemical potential gradient of component is proportional to the gradient of thermodynamic activity of the component. In dilute solutions, the thermodynamic activity coefficient is close to unity, the gradient of thermodynamic activity of the component can be replaced by the concentration gradient of the component. The relationship between stream $J_i$, and the concentration gradient describes Fick's law:

$$J_i = -D \cdot \text{grad}c$$

where $D$ is the diffusion coefficient, which characterizes the size of the stream for a unit concentration gradient. Diffusion coefficient is characterized by properties of the system and its value depends on both the properties of the solute and the properties of solvent. Diffusion coefficient strongly depends on temperature and may depend on the concentration of the solution.

In the simplest case, where the concentration gradient occurs in only one direction, a process is called one-dimensional diffusion, and Fick's law can be written in simplified form:

$$J_i = -D \cdot \frac{dc_i}{dx}$$

$J_i$ stream component causes the component to equalize the concentration in the system. Concentration change at any point in the system depend on the duration of the process and can be determined by solving Fick's Second Law for the respective conditions.

For one-dimensional diffusion Fick's Second Law takes the form:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c_i}{\partial x} \right)$$

If the diffusion coefficient $D$ does not depend on the concentration of component equation takes a simpler form:

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial x^2}$$
Diffusion coefficient $D$ can be determined experimentally by solving Fick's Second Law for the relevant boundary and initial conditions. In specific cases where the jet component is stationary, i.e., constant during the process, the diffusion coefficient $D$ can also be determined from the first Fick's law. Such a method of determining the values of $D$ are called phones and the methods to count them chamber method. Diffusion chamber consists of two parts with volumes $V_1$ and $V_2$, respectively. Both parts of the chambers are separated by a porous septum (diaphragms), preventing the mechanical mixing of solutions. The porous septum is characterized by two parameters: the effective area $A$ and the effective thickness $l$.

The solution for Fick's law and the chamber is the equation:

$$\ln \frac{C_0^I - C_0^II}{C_t^I - C_t^II} = \frac{A}{l} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \cdot D \cdot t$$

where $C_0^I - C_0^II$ is the difference between the concentrations of solutions in both chambers at the beginning of the experiment, while $C_t^I - C_t^II$ is the difference between the concentrations in both chambers after a diffusion time $t$. In the simplest case, the diffusion component of the solution to pure solvent, which means that $C_0^II - 0$ equation takes a simpler form:

$$\ln \frac{C_0^I}{C_t^I} = \frac{A}{l} \left( \frac{1}{V_1} + \frac{1}{V_2} \right) \cdot D \cdot t \equiv \beta \cdot D \cdot t$$

where $\beta$ is called a fixed chamber. This is a typical size for a particular chamber, which depends on the volume of both parts of the chamber, the effective surface of the porous barrier and effective thickness of the porous barrier. Chamber constant is determined experimentally from the last equation based on the concentration change in the system with a known diffusion coefficient. The last equation shows that the appointment requires the diffusion coefficient determination of the concentration of the solution of the diffusion time.

**Tracer and chemical diffusion**

**Tracer diffusion**, which is a spontaneous mixing of molecules taking place in the absence of concentration (or chemical potential) gradient. This type of diffusion can be followed using isotopic tracers, hence the name. The tracer diffusion is usually assumed to be identical to self-diffusion (assuming no significant isotopic effect). This diffusion can take place under equilibrium.

**Chemical diffusion** occurs in the presence of concentration (or chemical potential) gradient and results in net transport of mass. This is the process described by the diffusion equation. This diffusion is always a non-equilibrium process, increases the system entropy, and brings the system closer to equilibrium.

The diffusion coefficients for these two types of diffusion are generally different because the diffusion coefficient for chemical diffusion is binary and it includes the effects due to the correlation of the movement of the different diffusing species.
Non-equilibrium system

Because chemical diffusion is a net transport process, the system in which it takes place is not an equilibrium system (i.e. it is not at rest yet). Many results in classical thermodynamics are not easily applied to non-equilibrium systems. However, there sometimes occur so-called quasi-steady states, where the diffusion process does not change in time, where classical results may locally apply. As the name suggests, this process is a not a true equilibrium since the system is still evolving.

Non-equilibrium fluid systems can be successfully modeled with Landau-Lifshitz fluctuating hydrodynamics. In this theoretical framework, diffusion is due to fluctuations whose dimensions range from the molecular scale to the macroscopic scale.

Chemical diffusion increases the entropy of a system, i.e. diffusion is a spontaneous and irreversible process. Particles can spread out by diffusion, but will not spontaneously re-order themselves (absent changes to the system, assuming no creation of new chemical bonds, and absent external forces acting on the particles).

The thermodynamic view

At constant temperature and pressure, the maximum non-expansion work that can be done per mole when a substance moves from a location where its chemical potential is \( \mu \) to a location where its chemical potential is \( \mu + d\mu \) is \( dw = d\mu \). In a system in which the chemical potential depends on the position \( x \).

\[
dw = d\mu = \left( \frac{\partial \mu}{\partial x} \right)_{p,T} dx
\]

In general work can always be expressed in terms of an opposing force, and that

\[
dw = -\mathcal{F} dx
\]

By comparing these two expressions, we see that the slope of the chemical potential can be interpreted as an effective force per mole of molecules. We write this thermodynamic force as:

\[
\mathcal{F} = -\left( \frac{\partial \mu}{\partial x} \right)_{p,T}
\]

There is not necessarily a real force pushing the particles down the slope of the chemical potentials.
**DIFFUSION**

*The thermodynamic force of a concentration gradient*

In a solution in which the activity of the solute is $a$, the chemical potential is

$$\mu = \mu^\circ + RT \ln a$$

If the solution is not uniform the activity depends on the position and can be write

$$\mathcal{F} = -RT \left( \frac{\partial \ln a}{\partial x} \right)_{p,T}$$

If the solution is ideal, $a$ may be replaced by the molar concentration $c$, and then

$$\mathcal{F} = -RT \left( \frac{\partial c}{\partial x} \right)_{p,T}$$

because $\left( \frac{d \ln c}{dx} \right) = (1/c) \frac{dc}{dx}$.

**Experimental procedure:**

1. Rinse both parts of the chamber with distilled water.
2. Flush the part of the chamber in which electrodes are placed using a small amounts of electrolyte solution indicated by the assistant. Then fill this part of the chamber using the electrolyte solution. Fill up the second part of the chamber using distilled water.
3. Connect the chamber to the conductivity meter and continue measurements every 10 minutes during 3 hours.
4. At the end of the measurement rinse both parts of the chamber and fill it with distilled water. Attention! Both parts of the chamber must be filled with distilled water.
5. The results of conductivity $\Gamma$ compile in the table.

<table>
<thead>
<tr>
<th>No</th>
<th>time [s]</th>
<th>$\Gamma$ [S]</th>
<th>$\ln \Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Data analysis:**

1. Perform the graph $\ln(\Gamma)=f(t.)$
2. Calculate the slope $a$.
3. Calculate the diffusion coefficient using $\beta=1.94[\text{cm}^2]$; $D = \frac{|a|}{\beta}$