

Materials Engineering Science
MESC. 5025

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Chapter 7.
Diffusion

Transport Laws

- Conditions of **thermodynamic equilibrium** were discussed in chapter I and can be stated as follows: equilibrium occurs at constant Temperature and Pressure when the Gibbs Free Energy is minimum. This implies that the chemical potential of any species must be the same within each part of the system under consideration. Similarly, temperature and pressure must be uniform throughout the system (thermal and mechanical equilibrium). The latter assertion relies on the assumption that gravitational forces can be neglected.
- A system can depart from equilibrium for a number of reasons:
 - Heat transfer occurs as a result of temperature gradients
 - Fluid flow results from the lack of balance of forces
 - Mass transfer results from an inhomogeneity in concentration

Similarity in Transport Laws

- Newton's Law of Viscous Flow $\tau_{yx} = -\mu \frac{\partial v_x}{\partial y}$
 - Fourier's Law of Heat Transfer $\vec{q} = -k \vec{\nabla} T$
 - Ohm's Law of Electrical Conductivity $\vec{i} = \sigma \vec{E} = -\sigma \vec{\nabla} \phi$
 - Fick's First Law of Mass Diffusion $\vec{J} = -D \vec{\nabla} c$
- Transport Laws $\vec{J} = -P \vec{\nabla} \phi$

where J is the flux of the quantity, P is the material property and $\vec{\nabla} \phi$ is the gradient of the potential ϕ . The arbitrary choice of the negative sign insures that P is positive and reflects a transport takes place in the direction of decreasing potential.

- These transport laws are justifiable on the basis that: first they are simple (!?) (linear), second they suggest that transport occurs in the direction of greatest change in the corresponding potential. Finally, the rate of transport is proportional to the magnitude of the driving force, which is itself defined in terms of the extent of departure from equilibrium.
- However, note that the linear aspect of these equations also suggest that they might only be valid for small driving forces or for small departures from equilibrium. Processes in nature are highly non-linear and the use of linear transport laws may be a great oversimplification (chaos) for systems far from equilibrium...

Diffusion

- Diffusion refers to the spontaneous mixing that results from thermal agitation and from the existence of concentration gradients (i.e. chemical potential gradients) in a non-uniform system.
- Diffusion processes occur in all states of matter but the underlying molecular processes may differ significantly. The property P will be significantly different for gases, liquids and solids.
- We will be first considering a phenomenological approach to solving diffusion problems, which has the advantage of generality but does not consider the specific details of the transport process.
- We start by defining the mass flux \mathbf{J} of particles moving across a reference plane as the mass of particles crossing a unit area of the plane per unit time or $\mathbf{J} = -D \nabla c$ (c is the mass concentration or mass density (mass of particles per unit volume)).

- We will limit the discussion to the simplest case of a binary system (A,B). Simple extensions can be made for any multicomponent system having a larger number of chemical species.
- We define ρ_A and ρ_B as the mass concentrations of A and B respectively (g/cm^3). $\rho = \rho_A + \rho_B$ is the mass density of the mixture. The mass fluxes J_A and J_B are defined as $\rho_A v_A$ and $\rho_B v_B$. The mass fraction of A and B are defined as w_A and w_B and are equal to ρ_A / ρ and ρ_B / ρ respectively. The Fick's law of diffusion can then be written as:

$$\vec{J}_A = -\rho D_{AB} \vec{\nabla} w_A = -D_{AB} \vec{\nabla} \rho_A$$

$$\vec{J}_B = -\rho D_{BA} \vec{\nabla} w_B = -D_{BA} \vec{\nabla} \rho_B$$

The second equalities (RHS) are only valid if ρ is constant and $D_{AB} = D_{BA}$ are the intrinsic diffusivities of A in B or B in A.

- A similar set of equations can be obtained in terms of mole fractions x_A and x_B of the molar flux of species, \mathbf{j}_A and \mathbf{j}_B .

$$\vec{j}_A = -cD_{AB} \vec{\nabla} x_A = -D_{AB} \vec{\nabla} c_A$$

$$\vec{j}_B = -cD_{BA} \vec{\nabla} x_B = -D_{BA} \vec{\nabla} c_B$$

where c_i are the molar concentrations (c_i/M_i), $c = c_A + c_B$, and x_i are the mole fractions.

- We then use the continuity equation (conservation of mass) under conditions where there is no net flow of the material as a whole.

$$\frac{\partial \rho_A}{\partial t} = -\vec{\nabla} \cdot (\rho_A \vec{v}_A) = -\vec{\nabla} \cdot \mathbf{J}_A$$

$$\frac{\partial \rho_B}{\partial t} = -\vec{\nabla} \cdot (\rho_B \vec{v}_B) = -\vec{\nabla} \cdot \mathbf{J}_B$$

Combination of the continuity equation and Fick's 1st law leads to:

$$\frac{\partial \rho_i}{\partial t} = -\vec{\nabla} \cdot (\rho D_{AB} \vec{\nabla} w_i) \quad \text{and} \quad \frac{\partial c_i}{\partial t} = -\vec{\nabla} \cdot (c D_{AB} \vec{\nabla} x_i)$$

- The last equation can then be rewritten as follows if the diffusivity and the density are constant:

$$\frac{\partial c_i}{\partial t} = D_{AB} \nabla^2 c_i$$

This equation is known as **Fick's second law** or simply as the **diffusion equation**.

- Magnitude of the Mass Diffusivity varies with class of materials

CO ₂ -N ₂	273.2K		0.144 cm ² . sec ⁻¹
	288.2K		0.158 cm ² . sec ⁻¹
	298.2K		0.165 cm ² . sec ⁻¹ -
Cl- Br	283.2K	0.03	1.007 10 ⁻⁵ cm ² . sec ⁻¹
		0.5	1.146 10 ⁻⁵ cm ² . sec ⁻¹
		0.97	1.291 10 ⁻⁵ cm ² . sec ⁻¹
He-pyrex	293.2K		4.5 10 ⁻¹¹ cm ² . sec ⁻¹
	773.2K		2.0 10 ⁻⁸ cm ² . sec ⁻¹
Al-Cu	293.2K		1.3 10 ⁻³⁰ cm ² . sec ⁻¹

Temperature and Pressure Dependence of Diffusivities

- The mass diffusivity of a binary system is a function of temperature, pressure and composition, whereas k and m were only function of temperature and pressure.
- **Binary Gas Mixtures:**
 - At low pressure (using corresponding-states arguments)

$$\frac{PD_{AB}}{(P_{cA}P_{cB})^{1/3} (T_{cA}T_{cB})^{5/12} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}} = a \frac{T^b}{\sqrt{T_{cA}T_{cB}}}$$

for D_{AB} in $\text{cm}^2.\text{sec}^{-1}$, p in atm., T in K, and M in g.mol^{-1}

For non-polar gas-pairs $a = 2.745 \cdot 10^{-4}$ and $b = 1.823$

For H_2O with non-polar gases $a = 3.640 \cdot 10^{-4}$ and $b = 2.334$

This equation works well at atmospheric pressure (within 8%)

- **At high pressure**

The previous equation no longer works (D_{AB} not prop. to $1/P$).
Some useful approximation may be obtained from self diffusivities D_{AA} obtained from the principle of corresponding-states (see BSL).

- **Chapman-Enskog Theory:**

Was found useful for estimation of k and μ for non-polar gases.
Similarly, one can estimate D_{AB} within 5% for such gases

$$cD_{AB} = 2.2646 \cdot 10^{-5} \frac{\sqrt{T \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{\sigma_{AB}^2 D_{AB}}$$

where D_{AB} in $\text{cm}^2 \cdot \text{sec}^{-1}$, c in $\text{mol} \cdot \text{cm}^{-3}$, T in K , and M in $\text{g} \cdot \text{mol}^{-1}$ and σ_{AB} in Angstroms. Note that here again $D_{(AB)}$ is a dimensionless function of temperature and of the intermolecular potential field for one molecule of A and one molecule of B.

Liquid Diffusion Theory

- There is no rigorous and universal theory of liquid diffusion. Two rough theories are available: Hydrodynamic Theory and the Eyring Theory which can be used to make order of magnitude estimates of liquid diffusivities.

- Hydrodynamic Theory:

Starting from the Nernst-Einstein relation between the diffusivity of a single particle (solute) of A through a stationary medium B:

$$D_{AB} = kT \frac{u_A}{F_A}$$

where u_A is the steady state velocity of the particle reached under the action of a force F_A . The relation between force and velocity can be obtained for a rigid sphere from hydrodynamics accounting for slip and is given for the case of creeping flow ($Re \ll 1$) by:

$$F_A = 6\pi\mu_B u_A R_A \frac{2\mu_B + R_A\beta_{AB}}{3\mu_B + R_A\beta_{AB}}$$

μ_B : viscosity of pure B

R_A : radius of particle A

β_{AB} : coefficient of sliding friction

- Two limiting cases of the previous equation are of interest:
 - 1) If there is no slip of fluid at the interface with the particle, then μ_{AB} is infinity and we get Stokes law: $F_A = 6\pi\mu_B u_A R_A$ which leads to the Stokes-Einstein equation:

$$\frac{D_{AB}\mu_B}{kT} = \frac{1}{6\pi R_A}$$

This approach is of interest in the case of diffusion of large spherical particles or molecules in a liquid which can be treated as a continuum.

- 2) If there is no tendency for the fluid to stick at the interface with the particle then μ_{AB} is zero and we obtain: $F_A = 4\pi\mu_B u_A R_A$ which for identical molecules arranged on a cubic lattice with molecules in contact leads to:

$$\frac{D_{AA}\mu_A}{kT} = \frac{1}{2\pi} \frac{\tilde{N}^{1/3}}{\tilde{V}_A}$$

This equation predicts self-diffusion coefficients within +/- 12%

- Eyring Rate Theory:

This theory provided a simple model to explain the viscosity of liquids in terms of unimolecular rate processes (existence of a well defined activated state). This theory when applied to the calculation of diffusivity leads to:

$$\frac{D_{AA}\mu_A}{kT} = \frac{\tilde{N}^{1/3}}{\tilde{V}_A}$$

which does not fit the data as well as that based on the hydrodynamic theory. Other empirical equations and modifications of the above equation are available which provide slightly better fits without yielding further physical insights.

Solid State Diffusion

- We will restrict ourselves with diffusion processes in crystalline solids which are amenable to modeling at the molecular level.
- The diffusion process for impurity atoms or vacancies in a crystalline solid follow Fick's laws. The diffusivity is often found to vary with temperature in Arrhenius fashion.

$$D = D_0 \exp \frac{-E}{k_B T}$$

where E is the activation energy for the process. Typical values of D_0 and E are given next page:

- To diffuse, an atom must overcome the potential energy barrier resulting from the presence of its nearest neighbors. The diffusion of impurity atoms is dealt in the same fashion considering the impurity is residing at interstitial sites (C in Fe). The same argument applies for the diffusion of vacancies.

Diffusivities in Solids and Activation Energies

Host Cryst.	Atom	D_0 $\text{cm}^2.\text{s}^{-1}$	E eV	Host Cryst.	Atom	D_0 $\text{cm}^2.\text{s}^{-1}$	E eV
Cu	Cu	0.2	2.04	Si	Al	8.0	3.47
Cu	Zn	0.34	1.98	Si	Ga	3.6	3.51
Ag	Ag	0.40	1.91	Si	In	16.0	3.90
Ag	Cu	1.20	2.00	Si	As	0.32	3.56
Ag	Au	0.26	1.98	Si	Sb	5.60	3.94
Ag	Pb	0.22	1.65	Si	Li	0.002	0.66
Na	Na	0.24	0.45	Si	Au	0.001	1.13
U	U	0.002	1.20	Ge	Ge	10.0	3.1