Mass transfer

Lecture 11: *Diffusion*

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Learning objectives

- **Be able to apply Fick's first law in analyzing mass transfer during equimolar and one-way diffusion.**

- **Have both qualitative and quantitative knowledge of diffusion by gases and liquids, especially with respect to diffusivities.**

- **Have practical understanding of Schmidt number.**

Today's outline

- **Background**
  - ✓ Introduction
  - ✓ Four types of situations
  - ✓ Fick's first law, and molar flowrate
  - ✓ Equimolar diffusion
  - ✓ One-way diffusion

- **Diffusivities and Schmidt number**
  - ✓ Relations between diffusivities
  - ✓ Diffusion of gases, experimental values
  - ✓ Diffusion of liquids
  - ✓ Schmidt number

- Convection versus diffusion

https://www.youtube.com/watch?v=EG4ZoVTSA5I&t=9s

17.1 Introduction

- **Diffusion can be due to gradient in many conditions including concentration, temperature, pressure, activity, and external force.**
  - ✓ We will only consider diffusion due to concentration gradient in this chapter.

  - ✓ Why does molecules diffuse from higher concentration to a lower concentration?

17.1 Four types of situations

- **Mass transfer through diffusion results in one of the following 4 types of situations:**
  1) Only one component A of the mixture is transferred
  2) Diffusion of A is balanced by opposite molar flow of B, resulting in zero net molar flow.
  3) Diffusion of A and B occur in opposite directions with unequal amounts.
  4) Two or more components diffuse in the same direction but at different rates.

17.1 Fick's first law

- **For steady state, 1D diffusion in a direction perpendicular to the interface,**

$$J_A = -D_v \frac{\mathrm{d}c_A}{\mathrm{d}b}$$

where J_A is the molar flux [mol/m^2/hr],

D_v is the volumetric diffusivity [m^2/hr]

c_A is the concentration of A [mol/m^3]

b is the distance in the direction of diffusion [m]

✓ For 3D diffusion,

$$J_A = -D_v \nabla c_A = -\rho_M D_v \nabla x_A$$

where ρ_M is the molar density of the mixture [mol/m^3]

x_A is the mole fraction of A

17.1 Molar flow rate

- **For components A and B crossing a stationary plane, the molar fluxes are**

$$N_{\boldsymbol{i}} = c_i\, u_i$$

where u_i is the *volumetric average* velocity [m/hr] of component *i*

- **For a reference plane moving at the volume-average velocity *u_0*,**
  - ✓ There is no net volumetric flow across this plane.
  - ✓ The molar flux of A through this reference plane becomes

$$J_A = c_A\, u_A - c_A\, u_0 = c_A(u_A - u_0) = -D_{AB}\frac{\mathrm{d}c_A}{\mathrm{d}b}$$

$$N_A = c_A\, u_0 + -D_{AB}\frac{\mathrm{d}c_A}{\mathrm{d}b}$$

where D_{AB} is the diffusivity of *A* in its mixture with *B*.

  - ✓ The *diffusion velocity* is relative to volume-average velocity u_0.

17.1 Equimolal diffusion

- **For ideal gases consisting of A and B, this is the case when there is no net volumetric/molar flux:**

$$u_0 = 0 \quad \rightarrow \; N_A = -D_v \frac{\mathrm{d}c_A}{\mathrm{d}b} = -D_v \, \rho_M \frac{\mathrm{d}y_A}{\mathrm{d}b}$$

✓ Integrating this eqn for a film of thickness B_T gives

$$-D_v \, \rho_M \int_{y_{Ai}}^{y_{A0}} \mathrm{d}y_A = N_A \int_0^{B_T} \mathrm{d}b$$

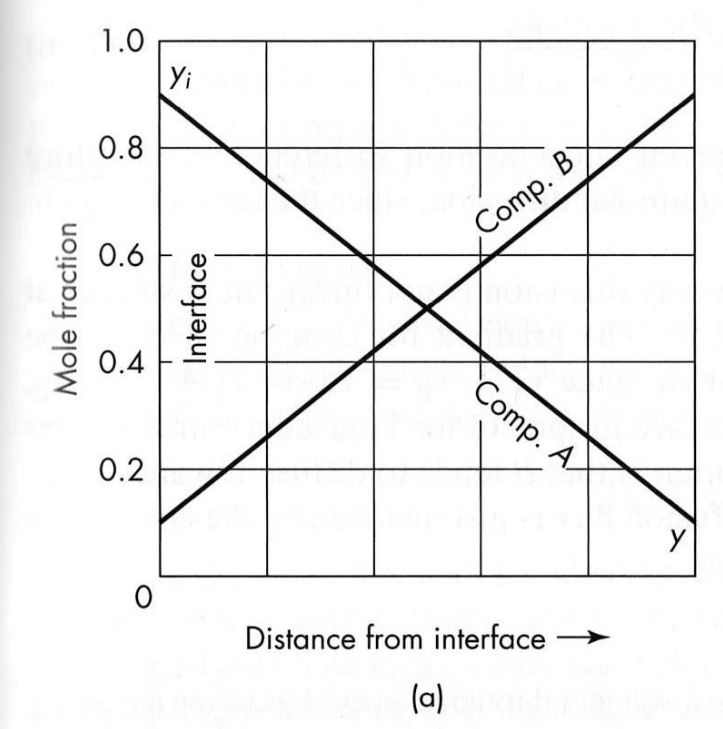
$$N_A = J_A = \frac{D_v \, \rho_M}{B_T}(y_{Ai} - y_{A0})$$

$$= \frac{D_v}{B_T}(C_{Ai} - C_{A0}) = -N_B$$

where y_{A0} = mole fraction at outer edge

y_{Ai} = mole fraction at interface

(or inner edge of the film)



17.1 One-way diffusion

- **For ideal gases consisting of A and B, this is the case when only component A is being transferred:**

$$N = N_A \quad \rightarrow \; N_A = y_A \, N_A - D_v \, \rho_M \, \frac{\mathrm{d}y_A}{\mathrm{d}b}$$

✓ Rearranging *and* integrating this eqn for a film of thickness B_T gives

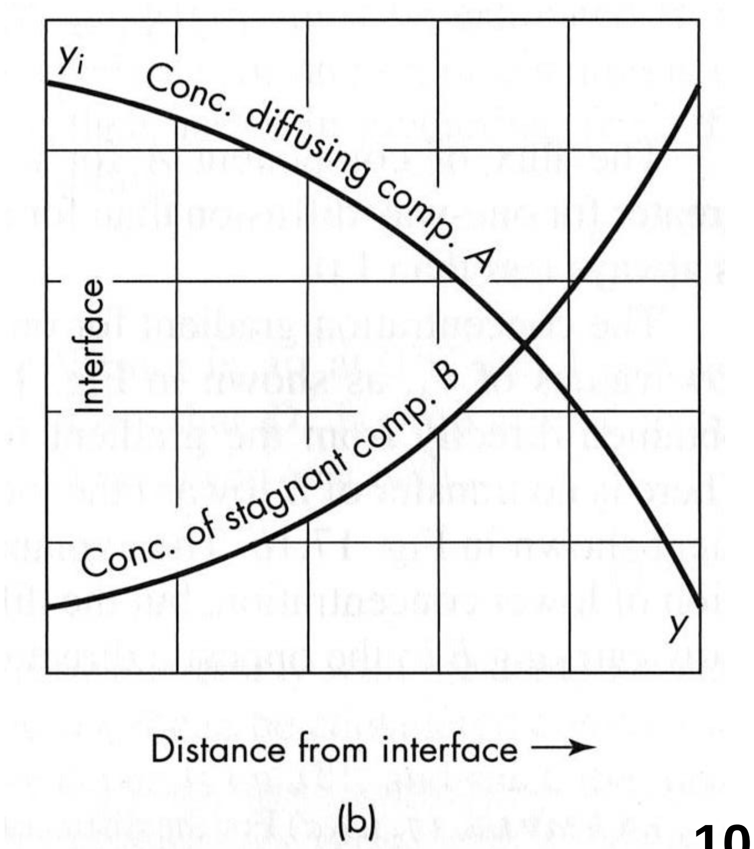
$$-D_v \, \rho_M \int_{y_{Ai}}^{y_{A0}} \frac{1}{1-y_A} \, \mathrm{d}y_A = N_A \int_0^{B_T} \mathrm{d}b$$

$$N_A = \frac{D_v \, \rho_M}{B_T} \ln \frac{1-y_{A0}}{1-y_{Ai}}$$

$$= \frac{D_v \, \rho_M}{B_T} \frac{y_{Ai}-y_{A0}}{\overline{(1-y_A)}_L}$$

where $\overline{(1 - y_A)}_L = \dfrac{y_{Ai}-y_{A0}}{\ln\left[\frac{1-y_{A0}}{1-y_{Ai}}\right]}$

✓ For a given $y_{Ai} - y_{A0}$, is one-way diffusion faster or slower than the equilmolar diffusion?



17.1 Relations between diffusivities

- **For ideal gases consisting of A and B,**

$$c_A + c_B = \rho_M = \frac{P}{R\,T} \quad [\text{mol/m}^3]$$

where R is the ideal gas constant; P and T are pressure and temp.

✓ At constant T & P, the mixture density remains constant, meaning

$$\mathrm{d}\rho_M = \mathrm{d}c_A + \mathrm{d}c_B = 0$$

$$-D_{AB}\frac{\mathrm{d}c_A}{\mathrm{d}b} - D_{BA}\frac{\mathrm{d}c_B}{\mathrm{d}b} = 0 \quad \rightarrow \quad D_{AB} = D_{BA}$$

- **For liquid mixture of A and B**,

$$c_A\,M_A + c_B\,M_B = \rho = constant \qquad [\text{kg/m}^3]$$

where M_i is the molecular weight of a component i.

✓ If all mixtures have the same ρ,

$$\mathrm{d}\rho = M_A\,\mathrm{d}c_A + M_B\,\mathrm{d}c_B = 0$$

$$-D_{AB}\frac{\mathrm{d}c_A}{\mathrm{d}b}\frac{M_A}{\rho} - D_{BA}\frac{\mathrm{d}c_B}{\mathrm{d}b}\frac{M_B}{\rho} = 0 \quad \rightarrow \quad D_{AB} = D_{BA}$$

17.1 Diffusion of gases

- **Simple theory states**

$$D_v \cong \frac{1}{3}\,\bar{u}\,\lambda$$

where $\bar{u}$ and λ are the average molecular velocity and mean free path.

- **Using the modern kinetic theory,**

$$D_{AB} = \frac{0.001858\,T^{3/2}\,[(M_A+M_B)/M_A\,M_B]^{1/2}}{P\,\sigma_{AB}^2\,\Omega_D}$$

where σ_{AB} and Ω_D are effective collision diameter and integral, respectively.

- **When diffusing through a cylindrical pore (D << λ),**

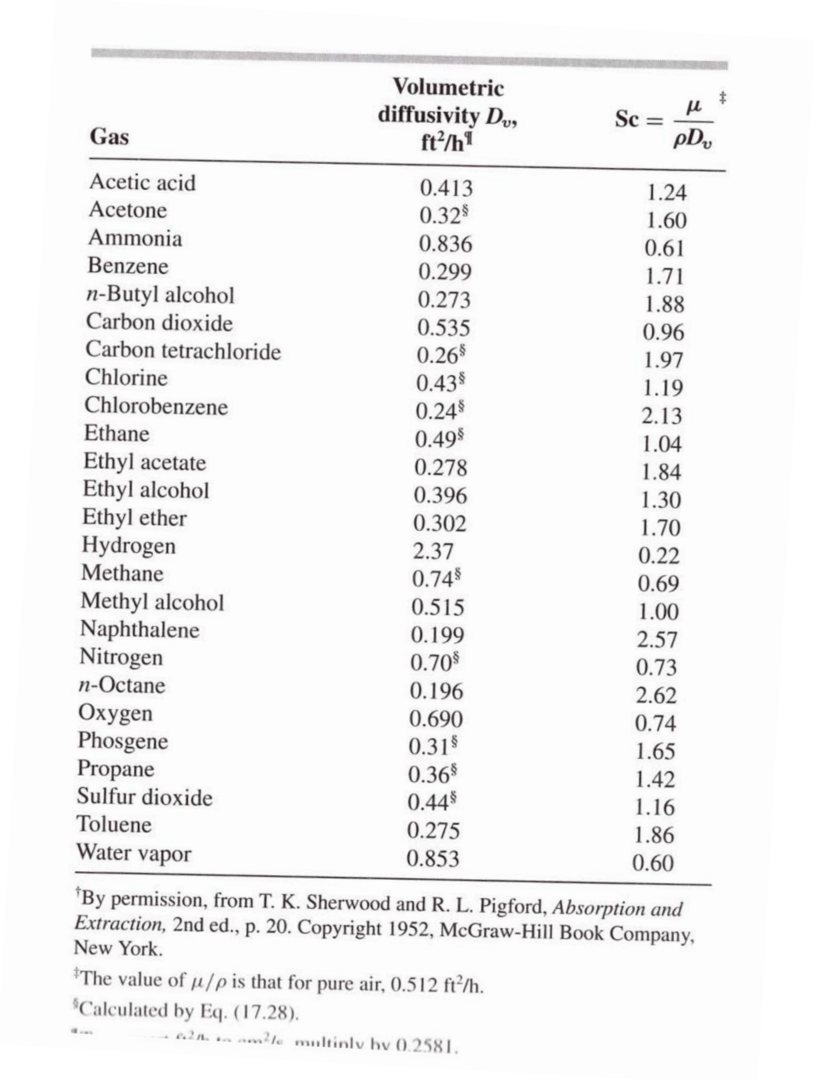
$$D_K = 9{,}700\,r\,\sqrt{T/M}$$

where D_K = Knudsen diffusivity [cm^2/s], *r* = pore radius [cm],

T = temp. [K], and *M* = molecular weight [g/mol]

17.1 Experimental values

- **Diffusivities are best obtained by experimental measurements but can be estimated using published correlations.**
  - ✓ Values of D_v for some common gases diffusing in air (0 °C, 1 atm)
  - ✓ Typical diffusivity ~ **?** cm^2/s



Gas	Volumetric diffusivity D_v, ft^2/h[¶]	$\mathrm{Sc} = \frac{\mu}{\rho D_v}$[‡]
Acetic acid	0.413	1.24
Acetone	0.32[§]	1.60
Ammonia	0.836	0.61
Benzene	0.299	1.71
n-Butyl alcohol	0.273	1.88
Carbon dioxide	0.535	0.96
Carbon tetrachloride	0.26[§]	1.97
Chlorine	0.43[§]	1.19
Chlorobenzene	0.24[§]	2.13
Ethane	0.49[§]	1.04
Ethyl acetate	0.278	1.84
Ethyl alcohol	0.396	1.30
Ethyl ether	0.302	1.70
Hydrogen	2.37	0.22
Methane	0.74[§]	0.69
Methyl alcohol	0.515	1.00
Naphthalene	0.199	2.57
Nitrogen	0.70[§]	0.73
n-Octane	0.196	2.62
Oxygen	0.690	0.74
Phosgene	0.31[§]	1.65
Propane	0.36[§]	1.42
Sulfur dioxide	0.44[§]	1.16
Toluene	0.275	1.86
Water vapor	0.853	0.60

[†] By permission, from T. K. Sherwood and R. L. Pigford, *Absorption and Extraction,* 2nd ed., p. 20. Copyright 1952, McGraw-Hill Book Company, New York.

[‡] The value of μ/ρ is that for pure air, 0.512 ft^2/h.

[§] Calculated by Eq. (17.28).

[¶] ft^2/h to cm^2/s, multiply by 0.2581.

17.1 Diffusion of liquids

- **Limited experimental data and models are available.**
  - ✓ Diffusivities are usually 10^4~10^5 lower than gases at 1 atm. Why?
  - ✓ Fluxes for a given mole fraction, however, is similar to gases. Why?

- **For large spherical molecules in dilute solution,**

$$D_v = \frac{k\,T}{6\pi\, r_0\, \mu} = \frac{7.32 \times 10^{-16}\, T}{r_0\, \mu} \qquad [\mathrm{cm^2/s}]$$

where r_0 is the molecular radius [cm], μ is viscosity [cP], and *k* is ???

- **For small to moderate molecules (MW < 400 g/mole),**

$$D_v = 7.4 \times 10^{-8} \frac{(\psi_B\, M_B)^{1/2}\, T}{\mu\, V_A^{0.6}} \qquad [\mathrm{cm^2/s}]$$

where ψ_B and V_A are association parameter for solvent, and molar volume of solute as liquid at its normal bp, respectively.

17.1 Diffusion of liquids

- **For dilute aqueous solutions of non-electrolytes,**

$$D_v = \frac{13.26 \times 10^{-5}}{\mu_B^{1.14}\, V_A^{0.589}} \qquad [\mathrm{cm^2/s}]$$

where μ_B is viscosity of water [cP].

- **For dilute solutions of completely ionized univalent electrolytes,**

$$D_v = \frac{2R\,T}{\left(\frac{1}{\lambda_+^0} + \frac{1}{\lambda_-^0}\right) F_a^2} \qquad [\mathrm{cm^2/s}]$$

where λ_+^0 and λ_-^0 are limiting (zero-concentration) ionic conductance [A cm^2 /V/g]; F_a is Faraday constant (96,500 C/g].

- **Is diffusivity the same for the same liquid? Why or why not?**

17.1 Schmidt number

- **It is the ratio of kinematic viscosity to the diffusivity:**

$$Sc = \frac{\upsilon}{D_\upsilon} = \frac{\mu}{\rho\, D_\upsilon}$$

✓ For gases in air (0 °C, 1 atm), it is about 0.2~3.0.

✓ For liquids, it ranges from 10^2 to 10^5 for typical mixtures: D_υ ~ 10^{-5} cm^2/s and *Sc* ~ 10^3 for small solutes in water (20 °C).

✓ What would happen, for liquids, if T increases?