

# **BAE 820 Physical Principles of Environmental Systems**

## **Estimation of diffusion Coefficient**

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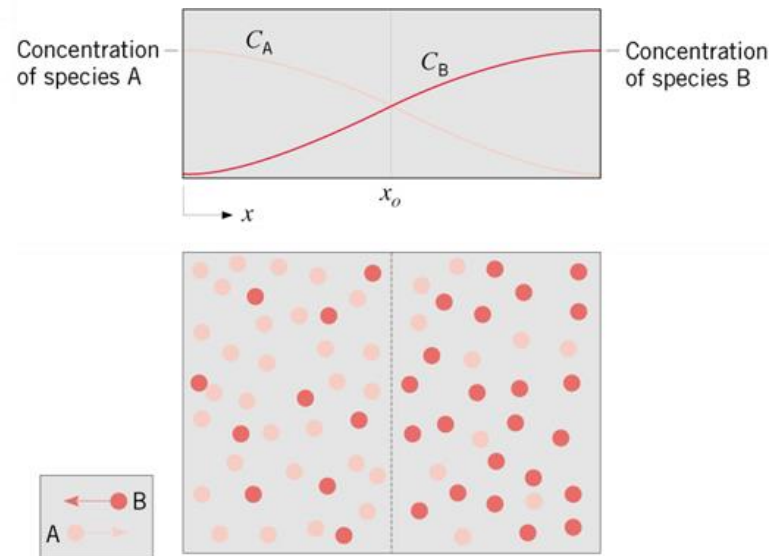
# Diffusion mass transfer

Diffusion mass transfer refers to mass in transit due to a species concentration gradient in a mixture

- It is a spontaneous mixing process aiming at homogenization of the mixture.
- Must have a mixture of two or more species for diffusion to occur.
- The driving force for diffusion is the concentration gradient of the species.
- Physical origins of diffusion is due to random molecular motion. The existence of thermal motion provides the driving force for molecular diffusion.
- Mass transfer by diffusion is analogous to heat transfer by conduction.
- There are two main mechanisms of mass transfer: diffusion and convection.

# Diffusion mass transfer

- Consider two species A and B at the same T and p, but initially separated by a partition.
- Diffusion in the direction of decreasing concentration dictates net transport of A molecules to the right and B molecules to the left. The diffusion tends to result in uniform concentrations of A and B.



# Steady-state equimolar counter diffusion

$$N = N_A + N_B = 0$$

The molar flux is

$$N_A = -CD_{AB} \frac{dx_A}{dz} + x_A(N_A + N_B) = -CD_{AB} \frac{dx_A}{dz}$$

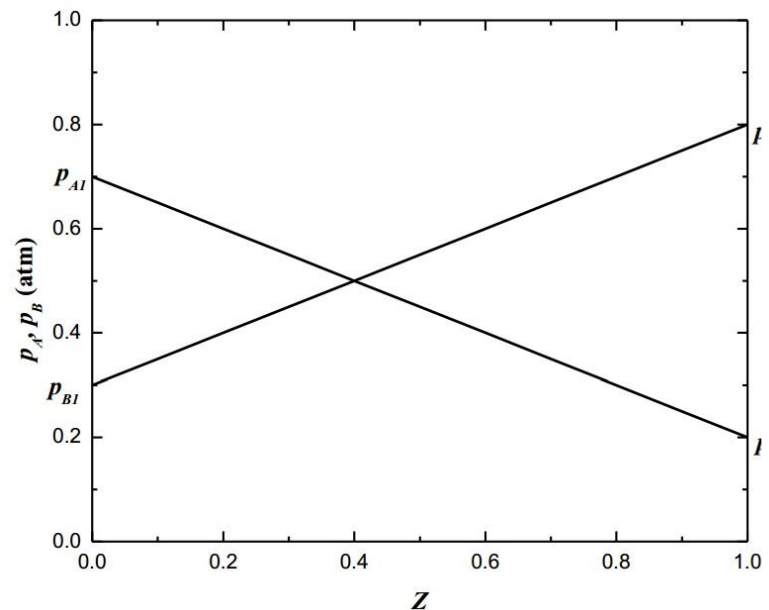
$$N_B = -CD_{BA} \frac{dx_B}{dz} + x_B(N_A + N_B) = -CD_{BA} \frac{dx_B}{dz}$$

$$D_{AB} = D_{BA}$$

The concentration profile is described by

$$\frac{dN_A}{dz} = \frac{d^2C_A}{dz^2} = C \frac{d^2x_A}{dz^2} = 0$$

$$\frac{C_A - C_{A1}}{C_{A1} - C_{A2}} = \frac{z - z_1}{z_1 - z_2}$$



# Steady-state diffusion of A through nondiffusing B

$$N_B \approx 0$$

- The molar flux is

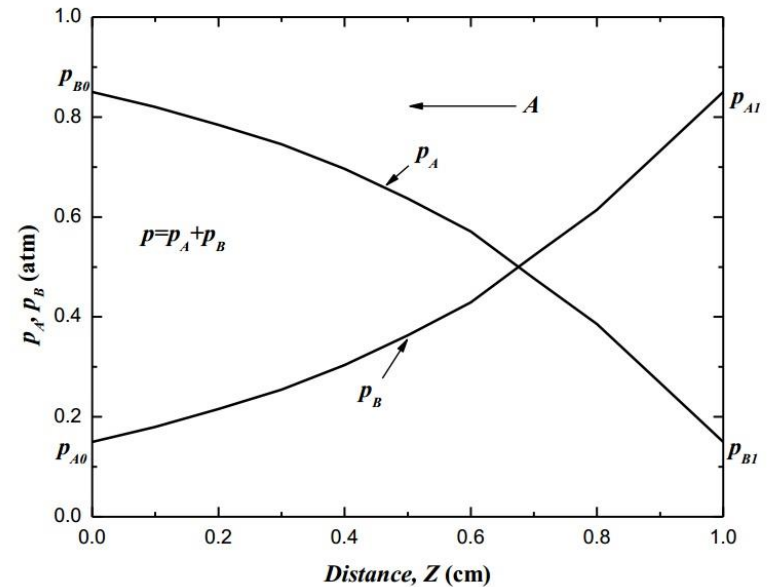
$$N_A = -CD_{AB} \frac{dx_A}{dz} + x_A(N_A + N_B) = -CD_{AB} \frac{dx_A}{dz} + x_A N_A$$

$$N_A = -\frac{CD_{AB}}{(1-x_A)} \frac{dx_A}{dz}$$

- The concentration profile is described by

$$N_A = -\frac{CD_{AB}}{(Z-Z_1)} \ln\left(\frac{1-x_A}{1-x_{A1}}\right)$$

$$x_A = 1 - (1-x_{A1}) \exp\left(\frac{N_A(Z-Z_1)}{CD_{AB}}\right)$$



# Diffusion coefficient for gas

- In gases the diffusion coefficient is proportional to the average molecular velocity times the mean free path.

$$D = \frac{\lambda v_{ave}}{3}$$

Where

- $v_{ave}$  is the average molecular velocity,  $v_{ave} = (8RT/\pi M)^{1/2}$
- $\lambda$  is mean free path,  $\lambda = \frac{K_B T}{\sqrt{2} \pi d^2 P}$
- $\tau$  is the average time between collisions.

Therefore,

- Diffusivity for gases are inversely proportional to pressure, and varies with the absolute temperature to around the 1.5 power.

# Average molecular velocity

- In kinetic theory, the average kinetic energy of the molecules can be expressed in terms of the kinetic temperature. The total three dimensional kinetic energy of a particle is given by

$$\frac{1}{2}mv_{\text{rms}}^2 = \frac{3}{2}k_B T$$

- Therefore, the root mean square molecular velocity

$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Where  $m$  is mass of a single molecular,  $M$  is molecular weight.

The speed distribution for the molecules of an ideal gas is given by the Maxwell distribution, which result in

$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}}$$

# Diffusion coefficient in binary gas mixtures

The mean free path of molecules of A,  $\lambda_A$ , in a binary gas mixture of A and B can be related to the binary diffusivity  $D_{AB}$  by

$$\frac{D_{AB}}{\lambda_A v_A} = \frac{3\pi}{32} \left(1 + \frac{M_A}{M_B}\right)$$

Where

- $v_A$  is the mean molecular speed of species A,  $v_A = (8RT/\pi M_A)^{1/2}$ ;
- $M_A$  and  $M_B$  are molecule weight of the two species respectively.



# Diffusion coefficient in binary gas mixtures

- Kinetic theory provides an explicit relation for diffusion coefficient in binary gas mixtures

$$D_{AB} = CT^{3/2} \frac{\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}}{P\sigma_{AB}^2\Omega}$$

Where

- $D_{AB}$  is the diffusion coefficient of gas mixture of species A and B,  $\text{cm}^2/\text{s}$ ;
- $C = 0.01883$ ;
- $T$  is temperature, K;
- $M_A$  and  $M_B$  is molecule weight of the species, g/mol;
- $P$  is pressure, Pa;
- $\sigma_{AB}$  is characteristic length of molecular separation at collision, Å;
- $\Omega$  is the diffusion collision integral, and is a function of  $k_B T/\varepsilon$ , where  $k_B$  is the Boltzmann constant,  $\varepsilon$  is a molecular energy parameter.

Values of  $\sigma_{AB}$  and  $\varepsilon$  can be found in literature for some species.

# Diffusion coefficient for liquid

- The theory of diffusion for liquid system is not nearly as advanced as for gas system.
- $D$  for liquid is around  $10^4$  -  $10^5$  times smaller than that for gas.
  - Mean free path much smaller (typically less than a molecule diameter).
- For large molecule in very dilute solution, The Stokes-Einstein equation can be used to estimate  $D$ .

# Einstein's law of diffusion

- Thermal energy imparts to each molecule a kinetic energy proportional to  $T$ . The kinetic energy may also be considered as the product of the force acting on the particle (proportional to friction factor  $\xi$ ) times the distance travelled (proportional to diffusion coefficient  $D$ ). In 1905, Einstein derived an equation that relate the diffusion coefficient to thermal energy.

$$D\xi = k_B T$$

Where  $k_B$ , the Boltzmann constant, is the ratio of the molar gas constant  $R$  to Avogadro's number, and is the gas constant per molecule,  $k_B = 1.38 \times 10^{-23} \text{JK}^{-1}$ .

- The equation connects the macroscopic diffusion coefficient to the microscopic friction factor of the particle (molecule).

$$D = k_B T / \xi = \frac{v}{F} k_B T = \mu k_B T$$

Where  $\mu = \frac{v}{F}$ , is the ratio of the particle's terminal drift velocity to an applied force, it is also called mobility.

# The Stokes-Einstein equation

- When Stokes law is obeyed, the friction factor

$$\xi = 6\pi r\eta$$

Therefore,

$$D = k_B T / (6\pi r\eta)$$

Where  $r$  can be estimated from the mass of particle.

$$r = \left( \frac{3m}{4\pi\rho_s} \right)^{1/3}$$

- If sedimentation rate measurements are available,

$$k_B T / D = \xi = \frac{\frac{4}{3}\pi r^3 (\rho_s - \rho_l) g}{v_t} = \frac{m (1 - \rho_l / \rho_s) g}{v_t}$$

# Magnitude of the diffusion coefficient

- For particles in water at 20°C,

$$D = k_B T / (6\pi r \eta) = \frac{1.38 \times 10^{-23} \text{ JK}^{-1} \times 293 \text{ K}}{6\pi \times 1.005 \times 10^{-3} \text{ kg}/(\text{m}\cdot\text{s}) \cdot r} = \frac{2.15 \times 10^{-19}}{r}$$

Calculated values using the above equation			Measured D for some particles in water at 20°C	
r (μm)	r (Å)	D (cm <sup>2</sup> /s)		
1	10000	2.15 × 10 <sup>-9</sup>	Serum Albumin	6.1 × 10 <sup>-7</sup>
0.1	1000	2.15 × 10 <sup>-8</sup>	Sucrose	4.7 × 10 <sup>-6</sup>
0.01	100	2.15 × 10 <sup>-7</sup>	Li <sup>+</sup>	9.4 × 10 <sup>-5</sup>
0.001	10	2.15 × 10 <sup>-6</sup>	Na <sup>+</sup>	1.2 × 10 <sup>-5</sup>
0.0001	1	2.15 × 10 <sup>-5</sup>		

# Limitation of the Stokes-Einstein equation

- The Stokes-Einstein equation is valid only if the molecules of the diffusing species are very large compared to the solvent molecules. It provide a start point for a number of semi-empirical correlations of diffusivities.
- The Stokes-Einstein equation underestimate real diffusivities because the actual drag on the molecules is less than postulated by the equation.
  - In the Stokes-Einstein equation ,  $D$  varies as  $V^{-1/3}$  (i.e.  $r^{-1}$ );
  - In reality,  $D$  varies as  $V^{-0.6}$ .

# Diffusion coefficient in dilute liquid mixtures

- The Wilke and Chang equation (1955)

$$D_{AB}^{\circ} = 7.4 \times 10^{-8} \frac{(\Phi_B M_B)^{1/2} T}{\eta_B V_A^{0.6}}$$

Where

- $D_{AB}^{\circ}$  is the diffusion coefficient of species A infinitely diluted in species B,  $\text{cm}^2/\text{s}$ ;
- $\Phi_B$  is association factor for the solvent (2.26 for water, 1.5 for ethanol);
- $M_B$  is molecule weight of the solvent,  $\text{g/mol}$ ;
- $T$  is temperature,  $\text{K}$ ;
- $\eta_B$  is solution viscosity,  $\text{mPa s}=\text{cP}$ ;
- $V_A$  is molar volume of solute A at its normal boiling point,  $\text{cm}^3/\text{mol}$ .

# Diffusion coefficient in concentrated liquid mixtures

- Diffusion coefficients in binary liquid mixture can be strong function of composition.
- The Vignes equation (1966)

$$D_{MS} = (D_{AB}^{\circ})^{x_B} (D_{BA}^{\circ})^{x_A}$$

Where

- $D_{MS}$  is Maxwell–Stefan multicomponent diffusion coefficient.
- $D_{AB}^{\circ}$  is the diffusion coefficient of species A infinitely diluted in species B;
- $D_{BA}^{\circ}$  is the diffusion coefficient of species B infinitely diluted in species A;
- $x_A$  and  $x_B$  are mole fraction of species A and B respectively.

The Fick diffusivity can be obtained from  $D_{MS}$  by multiply a thermodynamic factor  $\Gamma$ , which can be estimated from activity coefficient models in literature.

$$D = D_{MS} \Gamma$$



# Example values of diffusion coefficient

Phase	Species pair (solute-solvent)	Temperature (°C)	D (cm <sup>2</sup> /s)
Gas	Water-Air	25	0.282
	O <sub>2</sub> -Air	25	0.176
	NH <sub>3</sub> -Air	25	0.259
Liquid	O <sub>2</sub> -Water	25	2.1×10 <sup>-5</sup>
	NH <sub>3</sub> -Water	25	1.64×10 <sup>-5</sup>
	H <sub>2</sub> S-Water	25	1.41×10 <sup>-5</sup>
Solid	H <sub>2</sub> -Iron	10	1.66×10 <sup>-9</sup>
	H <sub>2</sub> -Iron	100	124×10 <sup>-9</sup>

# Diffusion in small pores

- When diffusion occurs in small pores, and pore diameter is less than mean free path, physical constraints of the pores will influence the rate of diffusion. This is known as Knudsen diffusion.
- For a cylindrical pore

$$D_k = \frac{D_{pore} v_{ave}}{3} = \frac{D_{pore}}{3} \sqrt{\frac{8RT}{\pi M}} \approx 9700r\sqrt{T/M}$$

- Where T is temperature in K, M is molecule weight, r is the radius in cm,  $D_k$  is Knudsen diffusivity in  $\text{cm}^2/\text{s}$ .

$$\frac{1}{D_{pore}} = \frac{1}{D_{AB}} + \frac{1}{D_k}$$

# Problem solving #4

1. Calculate the root mean square velocity and average velocity of an  $N_2$  molecule at room temperature ( $25^\circ\text{C}$ ).
2. Estimate the diffusivity of a  $1\mu\text{m}$  diameter particle in air at  $20^\circ\text{C}$  and 1 atm.

# Problem Solution #4-1

- $T = (25+273)\text{K} = 298\text{K}$
- $M = 28 \text{ g/mol} = 0.028\text{kg/mol}$
- $R = 8.314 \text{ J/mol K}$
- $v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 298}{0.028}} = 515\text{m/s}$
- $v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{3.14 \times 0.028}} = 475\text{m/s}$

## Problem Solution #4-2

- For a 1 $\mu$ m diameter particle in air at 20°C and 1 atm, the Cunningham correction factor can be estimated to be 1.17.

$$\begin{aligned} \bullet D &= k_B T C_c / (6\pi r \eta) = \frac{1.38 \times 10^{-23} \text{JK}^{-1} \times 293 \text{K} \times 1.17}{6\pi \times 1.8 \times 10^{-5} \text{kg}/(\text{m}\cdot\text{s}) \times 0.5 \times 10^{-6} \text{m}} \\ &= 2.8 \times 10^{-11} \text{m}^2/\text{s} \end{aligned}$$