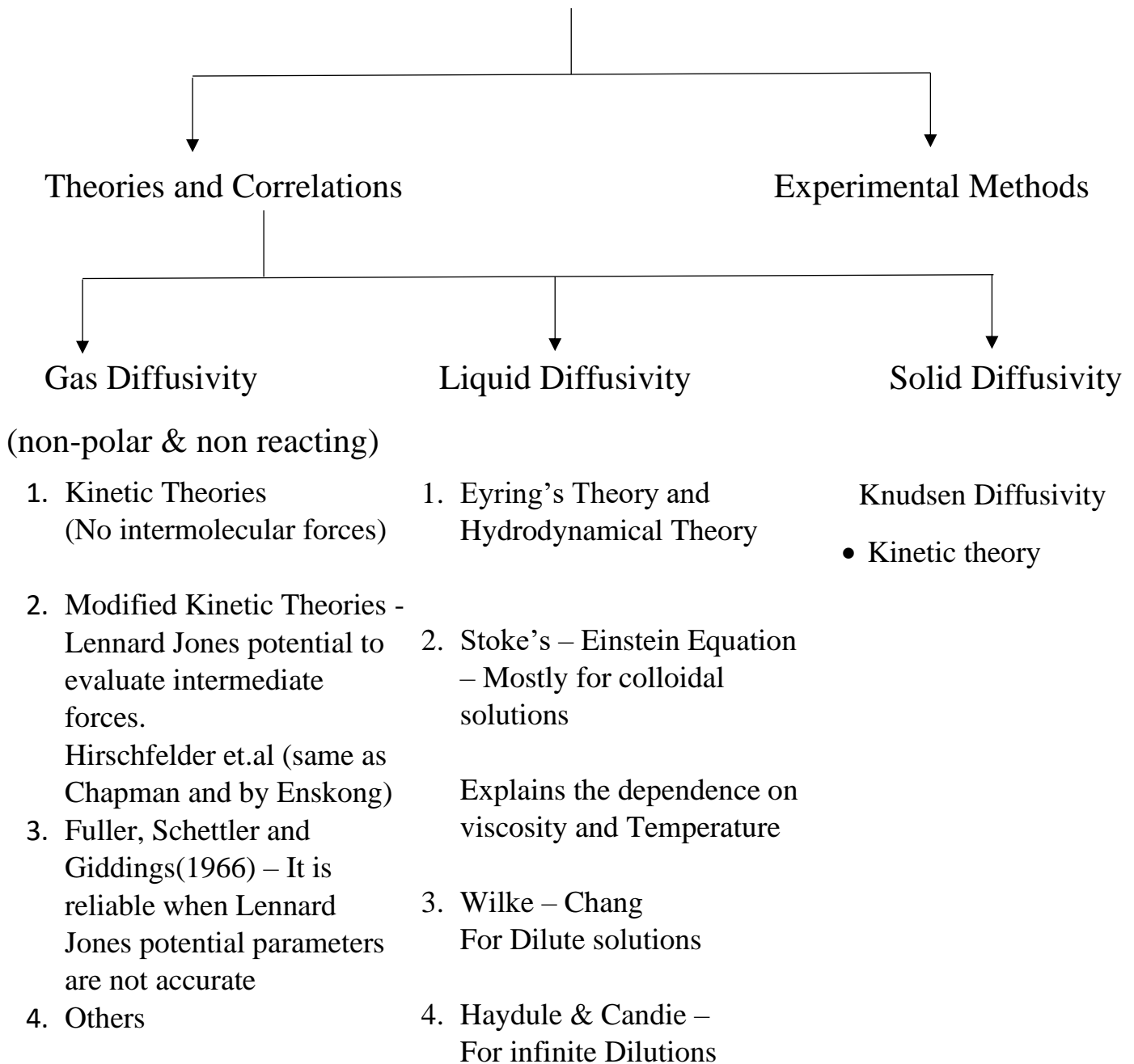


BINARY DIFFUSIVITY



Gas Diffusivity

Mostly governed by

- i. Kinetic Theory
- ii. Modified Kinetic Theory

According to Kinetic theory self-diffusion Coefficient of A, D_{AA}^* is given by

$$D_{AA^*} = \frac{1}{3} \lambda * \mu \dots\dots\dots (1)$$

$$\lambda = \frac{k T}{\sqrt{2} \pi \sigma_A^2 P} \dots\dots\dots (2)$$

$$\mu = \sqrt{\frac{8 k N T}{\pi M_A}} \dots\dots\dots (3)$$

Where,

λ = Mean free path

μ = Mean speed

k = Boltzmann's Constant

N = Avogadro's Number

σ_A = Lennard Jones diameter of spherical molecule.

M_A = Molecular weight of A

Combining (1), (2) and (3) we get

$$D_{AA^*} = \frac{2}{3} \cdot \left(\frac{k}{\pi}\right)^{\frac{2}{3}} \cdot N^{\frac{1}{2}} \cdot T^{\frac{3}{2}} \cdot \left(\frac{\left(\frac{1}{M_A}\right)^{\frac{1}{2}}}{P \sigma_A^2}\right) \dots\dots\dots (4)$$

Equation (4) can be modified to get diffusivity of A in B using proper average terms

$$D_{AB} = \frac{2}{3} \cdot \left(\frac{k}{\pi}\right)^{\frac{2}{3}} \cdot N^{\frac{1}{2}} \cdot T^{\frac{3}{2}} \cdot \left(\frac{\left(\frac{1}{2M_A} + \frac{1}{2M_B}\right)^{\frac{1}{2}}}{P \left(\frac{\sigma_A}{2} + \frac{\sigma_B}{2}\right)^2}\right) \dots\dots\dots (5)$$

Equation (5) is applicable for ideal gas where intermolecular forces are not accounted for.

Hirshfelder et. al. modified the equation derived from kinetic theory using Lennard Jones potential to evaluate the influence of molecular forces.

According to Hirshfelder, (same as Chapman Enskog)

$$D_{AB} = \frac{0.001858 T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}}}{P \sigma_{AB}^2 \Omega_D}$$

$$\Omega_D = f \left(\frac{kT}{\epsilon_{AB}} \right)$$

$$\epsilon_{AB} = (\epsilon_A \cdot \epsilon_B)^{\frac{1}{2}}$$

Note: 0.001858 is value for constants (when CGS unit system is used.

k = Boltzmann's Constant

ϵ_A, ϵ_B are Lennard Jones potential parameter.

Fuller correlation

When reliable Lennard Jones potential parameter σ , ϵ and Ω_D are not available,

$$D_{AB} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{P \left[\left((\Sigma v)_A^{\frac{1}{3}} \right) + \left((\Sigma v)_B^{\frac{1}{3}} \right) \right]^2}$$

Unit is cm²/s

Where v=atomic volume

P=atmospheric pressure

M_B M_A = Molecular weight of B and A

Hirshfelder, Chapman, Enskog and many other scientists introduced Lennard Jones parameters ϵ and Ω_D to account for the intermolecular force.

Introducing Lennard Jones parameters into the equation derived from kinetic theory. Hirshfelder, Chapman, Enskog derived following equation

$$D_{AB} = \frac{2}{3} \cdot \left(\frac{k}{\pi} \right)^{\frac{2}{3}} \cdot N^{\frac{1}{2}} \cdot T^{\frac{3}{2}} \cdot \left(\frac{\left(\frac{1}{2M_A} + \frac{1}{2M_B} \right)^{\frac{1}{2}}}{P \cdot \left(\frac{\sigma_A}{2} + \frac{\sigma_B}{2} \right)^2 \cdot \Omega_D} \right)$$

Where Ω_D = collision integral

ϵ_{AB} = energy of molecular interaction of A and B

CGS system, T in Kelvin

$$D_{AB} = \frac{0.001858 T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{P \sigma_{AB}^2 \Omega_D} \quad D_{AB} \text{ in cm}^2/\text{s}$$

SI unit

$$D_{AB} = \frac{1.858 \times 10^{-7} \times T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{P \sigma_{AB}^2 \Omega_D} \quad D_{AB} \text{ in m}^2/\text{s}$$

To get σ_A , σ_B , ϵ_A , ϵ_B and Ω_D Data table available

If data is not available then we it can be estimated from critical parameters like temperature, pressure and volume values or we can use Fuller equation

Steps for solving Hirschfelder equation to get D_{AB}

1. Get M_A and M_B which is molecular weight
2. Get T in kelvin
3. Get ϵ_A and ϵ_B from table if not calculate using correlation or use Fuller equation.

$$\frac{\epsilon_A}{k} = 0.77T_c \text{ or } \frac{\epsilon_A}{k} = 1.15T_b$$

Where T_C and T_B are critical and normal boiling temperatures

4. Get σ_A and σ_B from data table if not available it can be calculated from equations

$$\sigma = 1.18v_L^{\frac{1}{3}}$$

$$\sigma = 0.841v_c^{\frac{1}{3}}$$

$$\sigma = 2.44 \left(\frac{T_C}{P_C} \right)^{\frac{1}{3}}$$

$$\frac{\epsilon_A}{k} = 0.77T_C$$

Where,

v_L = molar volume at normal boiling point (cm^3)

T_B = Normal boiling point (K)

T_C = Critical Temperature (K)

P_C = Critical Pressure (atm)

v_C = Critical volume (cm^3)

Factors affecting Gas Phase Diffusivity

1. Temperature
2. Pressure
3. Molecular weight
4. Any other parameters which affect intermolecular force or non-ideality such as chemical nature.

$$\frac{D_{AB}|_{T1}}{D_{AB}|_{T2}} = \left(\frac{T_1}{T_2}\right)^{1.5} \cdot \left(\frac{P_2}{P_1}\right) \cdot \left(\frac{\Omega_{D2}}{\Omega_{D1}}\right)$$

Temperature Dependence

$$\frac{D_{AB}|_{T1}}{D_{AB}|_{T2}} = \left(\frac{T_1}{T_2}\right)^{1.5} \cdot \left(\frac{\Omega_{D2}}{\Omega_{D1}}\right) \quad \text{neglecting intermolecular forces}$$

Because Ω_D increases with temperature as $\Omega_D = f\left(\frac{kT}{\epsilon_{AB}}\right)$

Multicomponent Diffusion

$$D_{im} = \frac{N_i - y_i \sum_{j=1}^n N_j}{\sum_{j=1, j \neq i}^n \frac{1}{D_{ij}} (y_j N_i - y_i N_j)} \quad \text{where } D_{im} \text{ is the diffusivity of } i \text{ in mixture.}$$

Special Case

If only A is only diffusing and all other components are non-diffusing

$$\begin{aligned} D_{Am} &= \frac{1}{\sum_{i=2}^n \frac{y'_i}{D_{Ai}}} \\ &= \frac{1}{\frac{y_2}{D_{A2}} + \frac{y_3}{D_{A3}} \dots \dots \dots} \end{aligned}$$

Considering a gas mixture with components A, B, C, D

The diffusion of A in mixture is still governed by Fick's law by replacing the diffusivity by D_{AM} .

$$J_A = -D_{AM} \frac{dC_A}{dx}$$

$$\begin{aligned} \text{Where } D_{AM} &= \frac{1-y_A}{\frac{y_B}{D_{AB}} + \frac{y_C}{D_{AC}} + \frac{y_D}{D_{AD}}} \\ &= \frac{1}{\frac{y_B}{1-y_A} \frac{1}{D_{AB}} + \frac{y_C}{1-y_A} \frac{1}{D_{AC}} + \frac{y_D}{1-y_A} \frac{1}{D_{AD}}} \end{aligned}$$

Liquid Phase Diffusivity

- No reliable theory is available.
- Limited Correlation are available.
- Not as accurate as to gas phase diffusivity.
- Effect of different parameters such as T, viscosity, concentrations and non-ideality can be estimated.
- Eyring's Theory & Hydrodynamical Theory: Two meet commonly used theories.

Eyring concept: Ideal liquid is treated as quasi-crystalline lattice interspersed with holes. Diffusion occurs due to jumping of solute molecules into holes within the lattice. The rate of jumps are empirically related to Eyring's theory of reaction rate.

Hydrodynamical theory: Relations between force and velocity

Combining Eyring and Hydrodynamical theory it can be written as

$$\frac{D_{AB}\mu_B}{kT} = f(v_A)$$

Based on above Wilke Chang proposed following correlation

$$\frac{D_{AB}\mu_B}{T} = \frac{7.4 \times 10^{-8} (\Phi_B M_B)^{\frac{1}{2}}}{v_A^{0.6}}$$

where D_{AB} is in cm^2/s

M_B is mol. Wt.

Φ_B = Association factor (Data is available in book)

v_A = Data is available if not then use $v_A = 0.285 v_C^{1.048}$



Critical volume

As per book

$$\frac{D_{AB}\mu_B}{T} = \frac{1.173 \times 10^{-16} (\Phi_B M_B)^{\frac{1}{2}}}{v_A^{0.6}}$$

where all values are in SI unit

1. Stoke's and Einstein equation

- Based on Hydrodynamical theory
- Mostly applicable for colloidal particles or large round molecules.
- Establishes a relation between D_{AB} , T and viscosity

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

Even though S-E equation has limitations but establishes the fact that

$$\frac{D_{AB}\mu_B}{T} = \text{constant}$$

2. Hayduk & Laudie Correlation

- For infinitely dilute solutions
- Correction factor for concentrations

$$D_{AB}^0 = 13.26 \times 10^{-5} \mu_B^{-1.14} v_A^{-0.589}$$

D_{AB}^0 = Diffusivity of A in infinitely dilute solutions of A & B

Correction factor for concentration

$$D_{AB\mu} = (D_{AB}^0 \mu_B)^{x_B} (D_{BA}^0 \mu_A)^{x_A}$$

Factors affecting Liquid Phase Diffusivity

- Temperature
- Viscosity
- Concentration
- Molecular weight (Chemical nature)
- Solvent-solute interaction parameter