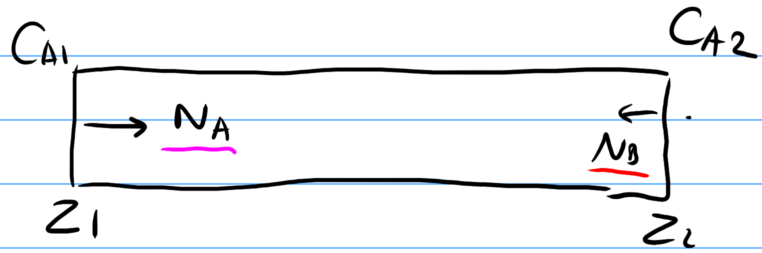
CHE 318 L04 Theories of D_{AB} (gas)

Jan-12 2026

1 Recap

General solution



$N_B = k N_A$

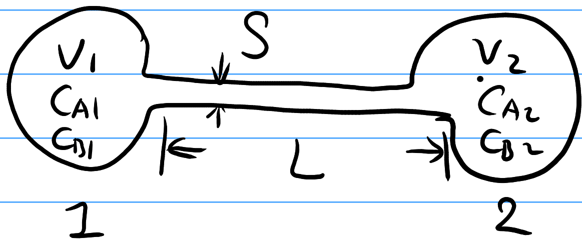
$s = N_A / (N_A + N_B)$

$$N_A = \frac{C_T D_{AB}}{z_2 - z_1} \, s \ln\left(\frac{s - x_{A2}}{s - x_{A1}}\right)$$

N_A : const

x_A : function of z

Measuring D_{AB}: two bulb EMCD

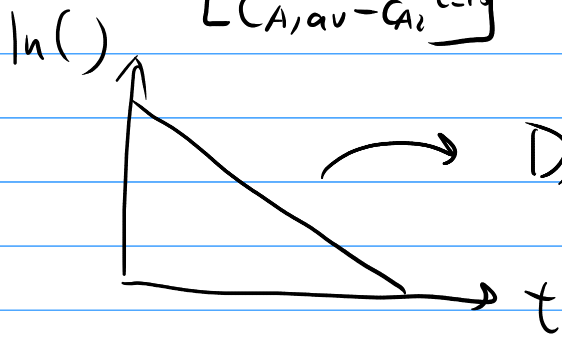


$t=0$ pure A in 1 Open

pure B in 2

$t=t$ mixed Close

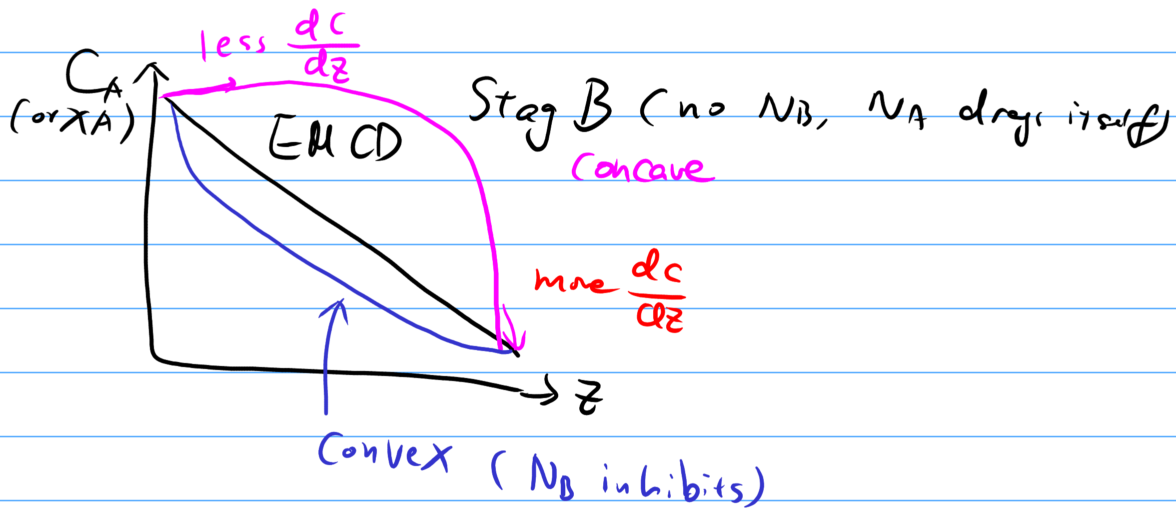
$$\ln\left[\frac{\left.C_{A,av} - C_{A2}\right|_{t=t_e}}{\left.C_{A,av} - C_{A2}\right|_{t=t_0}}\right] = -D_{AB} \cdot \frac{V_T S}{V_1 V_2 L} \cdot t$$



$\longrightarrow$ D_{AB} from slope

For gas $D_{AB} \simeq 10^{-5} \, m^2/s$

2. Demo ! See how flux change



All depends on S value

Stag B $S=1$ $\qquad N_{stag} = N_{EMCD} \frac{1}{x_{Bm}} (x_{A1} - x_{A2})$

$0 <$ log mean < 1

3. Today how do we get D_{AB}?

without experiment

① $D_{AB} = f(T, P)$

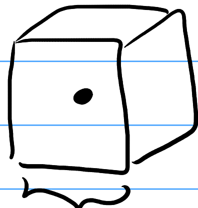
② $D_{AB}(z) = \text{const}$

③ $D_{AB} = D_{BA}$ (see assigment 1 Q1)

Kinetic theory of gas

Diluted gas

$$C = \frac{n}{V} = \frac{p}{RT}$$



at 1 atm $\qquad C \simeq 10^{25}\ m^{-3}$

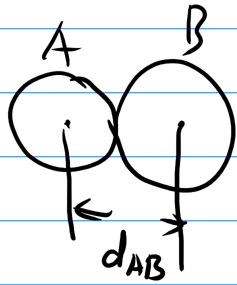
$\sim 10^{-8}$ m (10 nm)

Assumptions

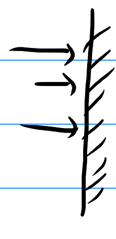
① A, B rigid sphere
② Far away only 2 can collide
③ Momentum conservation
④ Molecules travel very far (λ_{AB}) before colliding

$$u = \sqrt{\frac{8 k_B T}{\pi \overline{m}_{AB}}} \qquad \overline{m}_{AB} = \left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{-1}$$

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi d_{AB}^2 C_T}$$



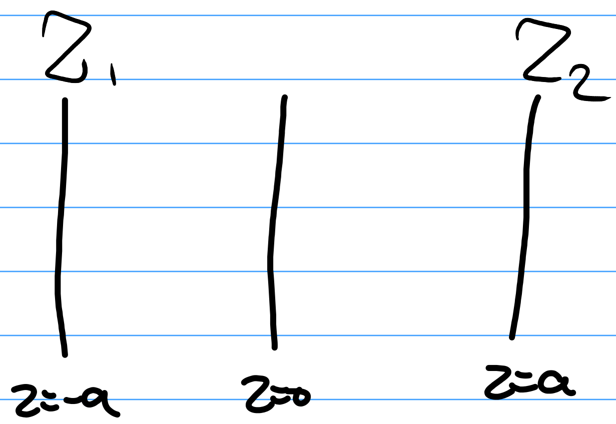
$$Z = \frac{1}{4} C_A \bar{u}$$



Z events per second

$a = \frac{2}{3}\lambda_{AB}$ avg. path

collision $\longleftrightarrow$ plane



In − Out

$x_{A2} - x_{A1}$

$= -2a \frac{dx_A}{dz}$

$\frac{1}{4} C_T x_{A1} \cdot \bar{u}$ $\qquad$ $\frac{1}{4} C_T x_{A2} \bar{u}$

Molecular: $\qquad a = \frac{2}{3}\lambda_{AB}$

$$J = -\frac{1}{4}\cancel{C_T} \cdot 2a \cdot \bar{u} \frac{dx_A}{dz}$$

Macro

$$J = -D_{AB}\cancel{C_T}\frac{dx_A}{dz}$$

$$\Rightarrow D_{AB} = \frac{1}{3}\bar{u}\lambda_{AB}$$

$$\propto \sqrt{\frac{T}{m_{AB}}} \qquad \frac{1}{d_{AB}^2 C_T} \qquad C_T \propto \frac{P_T}{T}$$

$$\propto \sqrt{T^3}\left(\frac{1}{m_{AB}}\right)^{\frac{1}{2}} \cdot \frac{1}{d_{AB}^2} \cdot \frac{1}{P_T}$$

$$\propto T^{1.5}\left(\frac{1}{m_{AB}}\right)^{\frac{1}{2}} \frac{1}{d_{AB}^{2}} \frac{1}{P_T}$$

Note the powers !

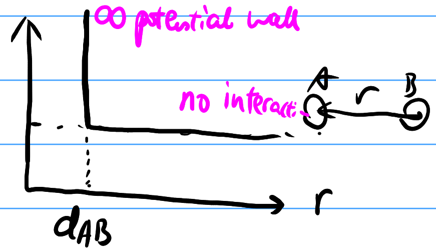
Chapman-Enskog Theory

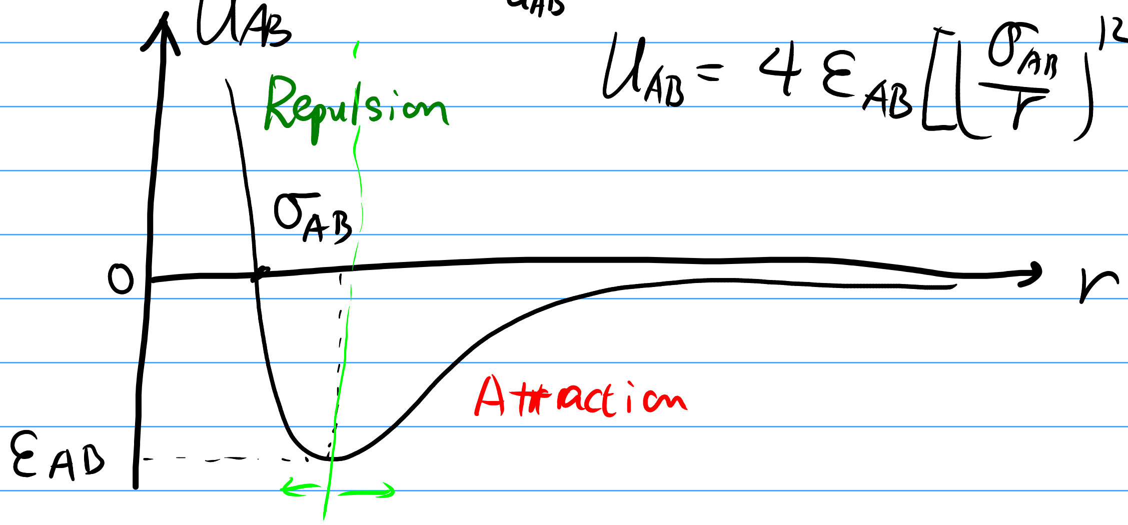
$$D_{AB} = \frac{1.8583\times10^{-7}\, T^{1.5}}{P_T\, \sigma_{AB}^{2}\, \Omega_{D,AB}}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}$$

D_{AB}: In m^2/s P_T: In atm σ_{AB}: In Å M_A, M_B: kg/(kg mol)

(Chapman-Enskog theory is just hard-sphere kinetic theory on steroid !!)

Hard sphere U_{AB}





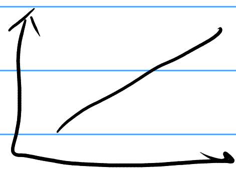
$$U_{AB} = 4\varepsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r}\right)^{12} - \left(\frac{\sigma_{AB}}{r}\right)^{6}\right]$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$$

$$T^{*} = \frac{k_B T}{\varepsilon_{AB}}$$

$\Omega_{D,AB}(T^{*})$



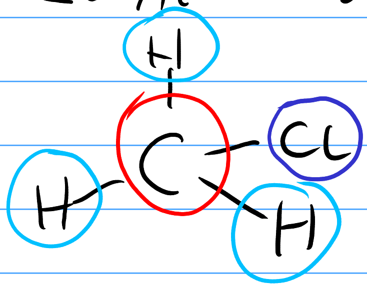
Fuller Method

$$D_{AB} = \frac{1.0 \times 10^{-7} \, T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}}}{P_T\left(\left(\Sigma v_{Ai}\right)^{\frac{1}{3}} + \left(\Sigma v_{Bi}\right)^{\frac{1}{3}}\right)^{2}}$$

Σv_{Ai} has meaning of volume $\Rightarrow [\text{Length}]^3$

$\left[\Sigma v_{Ai}^{\frac{1}{3}} + \Sigma v_{Bi}^{\frac{1}{3}}\right]^2 \Rightarrow$ has same meaning / unit as d_{AB}

Σv_{Ai} = sum of volum contrib



$$\Sigma v_{CH_3Cl} = v_C + 3 \cdot v_H + 1 \cdot v_{Cl}$$