Chapman-Enskog Theory for $\mathcal{D}_{AB}$ in a gas:

$$c\,\mathcal{D}_{AB} = \frac{3}{16}\sqrt{\frac{2RT}{\pi}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\;\frac{1}{\tilde{N}\,\sigma_{AB}^2\,\Omega_{\mathcal{D}_{AB}}}$$

"collision integral" for diffusion.

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

$$= 2.2646\times10^{-5}\sqrt{T\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\;\frac{1}{\sigma_{AB}^2\,\Omega_{\mathcal{D}_{AB}}}$$

if gas is ideal, $p = cRT$ or $c = p/RT$

$$\mathcal{D}_{AB} = \frac{3}{16}\sqrt{\frac{2(RT)^3}{\pi}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\;\frac{1}{\tilde{N}\,p\,\sigma_{AB}^2\,\Omega_{\mathcal{D}_{AB}}}$$

$$= 1.858\times10^{-3}\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\;\frac{1}{p\,\sigma_{AB}^2\,\Omega_{\mathcal{D}_{AB}}}$$

$\mathcal{D}_{AB}$ in $\frac{cm^2}{s}$ when σ_{AB} in Å

T in K

p in atm

$\Omega_{\mathscr{D}_{AB}} \Rightarrow$ collision integral for diffusion is a function of KT/ε_{AB} from Table E.2.

$\mathscr{D}_{AB}$ varies as T^2 at lower T

$T^{1.65}$ at high T

estimates of σ_{AB}. , $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$.

of ε_{AB} , $\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$

For isotopic pairs, A, A^*

$$\sigma_{AA^*} = \sigma_A = \sigma_A^*$$

$$\varepsilon_{AA^*} = \varepsilon_A = \varepsilon_A^*$$

$$c\mathscr{D}_{AA^*} = 3.2027 \times 10^{-5} \sqrt{\frac{T}{M_A}} \frac{1}{\sigma_A^2 \Omega_{\mathscr{D}_{AA^*}}}$$

Problem: 17A.1 Estimate $\mathscr{D}_{AB}$: A = methane, B = ethane
$T = 293\,K$, $p = 1\,atm$.

a). A: $M_A = 16.04 \frac{g}{mole}$ $T_{c,A} = 191.1\,K$ $p_{c,A} = 45.8\,atm$

B: $M_B = 30.07$ " $T_{c,B} = 305.4\,K$ $p_{c,B} = 48.2$ "

$\boxed{\text{Eqn } 17.2\text{-}1}$

$$\mathscr{D}_{AB} = a\left(\frac{T}{\sqrt{T_{cA}T_{cB}}}\right)^b (p_{c,A}p_{c,B})^{1/3}(T_{c,A}T_{c,B})^{5/12}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}\frac{1}{p}$$

$a = 2.745\times10^{-4}$ $b = 1.823$ – non-polar gas pairs.

$$\boxed{= 0.152\ cm^2/s}$$

b). Fig. 17.2-1, eqn. 17.2-3

$$c\mathscr{D}_{AB} = 2.96\times10^{-6}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}\frac{(p_{c,A}p_{c,B})^{1/3}}{(T_{c,A}T_{c,B})^{1/12}}$$

$$= 4.78\times10^{-6}\ \frac{g\text{-}mole}{cm\cdot s}$$

$$T_r = \frac{T}{\sqrt{T_{c,A}T_{c,B}}} = \frac{293}{\sqrt{(191.1)(305.4)}} = 1.21$$

$$P_r = \frac{P}{\sqrt{P_{c,A}\,P_{c,B}}} = \frac{1}{\sqrt{(45.8)(48.2)}} = 0.021$$

From Fig 17.2-1 $\quad (c\mathcal{D}_{AB})_r \sim 1.20$

$$\therefore\ c\mathcal{D}_{AB} = 1.20(c\mathcal{D}_{AB})_c = 5.74\times10^{-6}\ \frac{\text{g-mole}}{\text{cm}\cdot\text{s}}$$

$$\div \text{ by } c = \frac{P}{RT} = 4.16\times10^{-5}\ \frac{\text{g-mole}}{\text{cm}^3}$$

$$\boxed{\mathcal{D}_{AB} = 0.138\ \frac{\text{cm}^2}{\text{s}}}$$

c) Chapman-Enskog (Eq. 17.3-12)

Table E.1

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) = (3.78 + 4.388)\frac{1}{2} = 4.084\ \text{Å}$$

$$\varepsilon_{AB}/K = \sqrt{(\varepsilon_A/K)(\varepsilon_B/K)} = \sqrt{(154)(232)} = 189\,K$$

Thus, $KT/\varepsilon_{AB} = \dfrac{293}{189} = 1.550$

Table E.2 gives $\Omega_{\mathcal{D}_{AB}} = 1.183$

Eqn. 17.3-12

$$\mathcal{D}_{AB} = 1.8583\times10^{-3}\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\ \frac{1}{p\sigma_{AB}^2\,\Omega_{\mathcal{D}_{AB}}}$$

$$= 1.8583\times10^{-3}\sqrt{(293)^3\left(\frac{1}{16.04}+\frac{1}{30.07}\right)}\ \frac{1}{(1)(4.084)^2(1.183)}$$

$$\boxed{= 0.146\ \frac{cm^2}{s}}$$

17.4 Diffusion in Binary Liquids

Wilke-Chang Eqn. (17.4-8)

$$\mathcal{D}_{AB} = 7.4\times10^{-8}\ \frac{\sqrt{\psi_B M_B}\ T}{\mu\ \tilde{V}_A^{0.6}}$$

$\tilde{V}_A$ = molar volume of solute A at T_b. ($cm^3/g\cdot mole$)

μ = in centipoise

ψ_B = association parameter

, for B = water $\psi_B = 2.6$

B = hydrocarbons $\psi_B \sim 1.0$

B = methanol $\quad \psi_B = 1.9$

Prob. 17A.10 $\mathcal{D}_{AB}$ in Dilute Aqueous Solution

a) Acetic Acid (A), Water (B)

$\rho_A = 0.937 \ g/cm^3$ at T_b

$$\tilde{V}_A = \frac{M_A}{\rho_A} = \frac{60.052}{0.937} = 64.1 \ \frac{cm^3}{g \cdot mole}$$

$\mu = 1.22$ cp for dilute aqueous soln.

$\psi_B = 2.6$

$$\mathcal{D}_{AB} = 7.4 \times 10^{-8} \frac{\sqrt{\psi_B M_B}\ T}{\mu \tilde{V}_A^{0.6}}$$

$$= 7.4 \times 10^{-8} \frac{\sqrt{(2.6)(18.016)}\ (273.15 + 12.5)}{(1.22)(64.1)^{0.6}}$$

$$\boxed{= 9.8 \times 10^{-6} \ cm^2/s}$$

b) Effect of T on $\mathcal{D}_{AB}$ (liquid).

$\mathcal{D}_{AB} = 1.28 \times 10^{-5}\ cm^2/s$ @ $15°C$.

$$\mathcal{D}_{AB}(100°C) = \mathcal{D}_{AB}(15°C)\left(\frac{\mu(15°C)}{\mu(100°C)}\right)\left(\frac{373.15}{288.15}\right)$$

$$= 1.28 \times 10^{-5}\left(\frac{1.14\ cp}{0.282\ cp}\right)\left(\frac{373.15}{288.15}\right)$$

$$\boxed{= 6.7 \times 10^{-5}\ \frac{cm^2}{s}}$$

17.4 Diffusion of Small Particles in Liquids

"Brownian" Motion

erratic motion of v. small particles in a fluid due to random collisions by solvent molecules with particle.

$$\mathcal{D}_{AB} = \frac{KT}{6\pi \mu_B R_A}$$

for example

$\mu_B \sim 1\ cp$ for water $= 10^{-3}\ \frac{kg}{m \cdot s}$

$R_A \sim 10^{-6}\ m$

$K = 1.38066 \times 10^{-23}\ J/K$ $\quad 1J = 1\ \frac{kg \cdot m^2}{s^2}$

$T = 25°C\ (298.15K)$

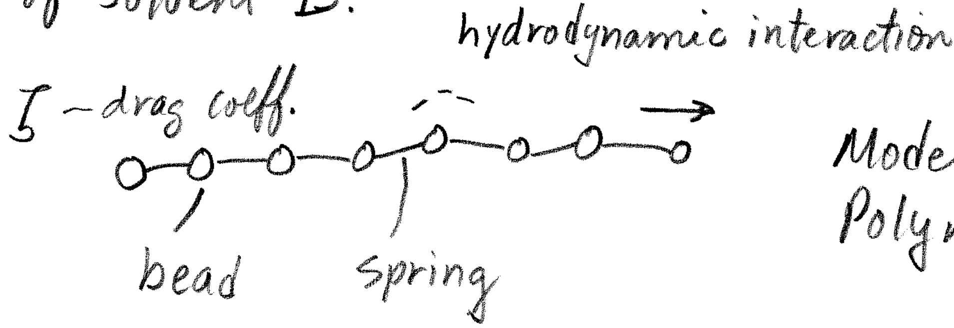
$$\mathcal{D}_{AB} = \frac{KT}{6\pi \mu_B R_A}$$

$$= \frac{\left(1.38066\times10^{-23}\ \frac{\cancel{kg}\cdot m^2}{s^{\cancel{2}}\cdot \cancel{°K}}\right)(298.15\ \cancel{°K})}{6\pi\left(10^{-3}\ \frac{\cancel{kg}}{\cancel{m}\cdot \cancel{s}}\right)(10^{-6}\ \cancel{m})}$$

$$= 2.18\times10^{-13}\ \frac{m^2}{s}$$

$$\boxed{= 2.18\times10^{-9}\ \frac{cm^2}{s}}$$

17.6 Diffusion of Polymers in Dilute Solution of Solvent B.



Model Polymer

$$\mathcal{D}_{AB} \sim \frac{1}{N^{1/2}}$$

N = no. of "beads" in polymer.

$$\sim \frac{1}{\sqrt{M}} \quad \text{for high } N.$$

Wed 3/29/06