Diffusion Coefficient for gases

(binary diffusion)

Kinetic Theory:

$$\boxed{D_{AB} = K' \frac{T^{3/2}}{P\bar{A}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}} \quad \text{(Eq. 2-5)}$$

$\bar{A}$ average cross-sectional area of gas molecules A and B

K' proportionality constant

P total pressure, atm (101.3 kN/m²)

Semiempirical Equations:

Gilliland: used eq. 2-5

$$\boxed{\begin{aligned} &\text{set } K' = 4.3 \times 10^{-9} \\ &\bar{A} = \left(V_A^{1/3} + V_B^{1/3}\right)^2 \end{aligned}}$$

reasonably accurate

V molar volume at the normal boiling point [m³/kgmol] $\Longrightarrow$ Table 2-1

Fuller et al: used eq. 2-5

$$\boxed{\begin{aligned} &\text{replaced } T^{3/2} \text{ by } T^{7/4} \\ &\text{set } K' = 1.0 \times 10^{-9} \\ &\bar{A} = \left[(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3} \right]^2 \end{aligned}}$$

Σv sum of the atomic diffusion volumes of all elements for each molecule

$\Longrightarrow$ Table 2-2

This eq. is recommended over Gilliland's

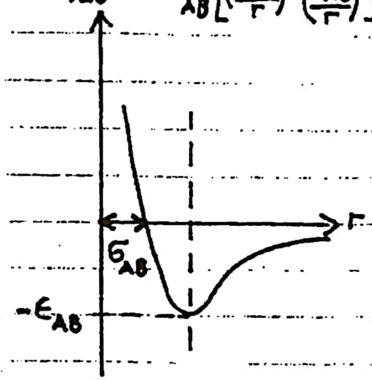
Semiempirical Equations cont.

Hirschfelder: used for non-polar gases

set in eq. 2-6

$$\boxed{\begin{aligned} K' &= 1.85 \times 10^{-27} \\ \bar{A} &= \sigma_{AB}^2 \, \Omega_D \end{aligned}}$$

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



σ_{AB} collision diameter, [m] (from LJ-Potential)

determined from component data, i.e.,

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \Longrightarrow \text{Table 2-3}$$

Ω_D collision integral

need ϵ_{AB}, max. energy of attraction

$$\frac{\epsilon_{AB}}{k} = \left(\frac{\epsilon_A}{k} \times \frac{\epsilon_B}{k} \right)^{1/2}$$

k Boltzmann constant $\Longrightarrow$ Table 2-3

determine Ω_D from $\left(\frac{\epsilon_{AB}}{k}\right)^{-1} T = \frac{kT}{\epsilon_{AB}}$

with Table 2-4

Diffusion Coefficients for Liquids

Molecular Diffusion Model:

Stokes - Einstein Eq :

$$\boxed{D = \frac{kT}{6\pi r\mu}}$$

D self-diffusion coeff.
r radius of diffusing particle
μ viscosity

Empirical Correction by Sutherland : ("slip condition")

$$\boxed{D = \frac{kT}{6\pi r\mu}\left(\frac{\beta r + 3\mu}{\beta r + 2\mu}\right)}$$

β sliding friction coefficient between solute and medium (solvent)

limiting cases : $\beta \to \infty$: no slip condition

$$\Rightarrow D \to \frac{kT}{6\pi r\mu} \quad \text{Stokes-Einstein eq.}$$

$\beta = 0$: void model (diffusing atoms move into voids)

$$\Rightarrow \boxed{D = \frac{kT}{4\pi r\mu}}$$ works for some liquid metal diffusion

Modified Stokes-Einstein Eqs (empirical models)

Wilke - Chang :

$$\boxed{D^{\circ}_{AB} = \frac{1.17 \times 10^{-13}(\xi_B M_B)^{1/2}\,T}{V_A^{0.6}\,\mu}}$$

Used to predict diffusivities in dilute solutions of nonelectrolytes.

D°_{AB} infinite dilution diffusivity or "interdiffusion coeff. in dilute solutions"

V_A molar volume of solute at normal boiling point

ξ_B association factor of solvent B

Recommended values:

1.0 nonpolar solvents (e.g., benzene, ether, aliphatic hydrocarbons)
1.5 ethanol
1.9 methanol
2.6 water

Experimentally found Diffusion Coefficients

for hydrocarbon liquid solutions at infinite dilution see Table 2-6