(Hines Chapter 2)

# Diffusion Coefficients for Liquids

Molecular Diffusion Model:

Stokes-Einstein Eq:

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

$D$ self-diffusion coeff.

$r$ radius of diffusing particle

$\mu$ viscosity

Empirical Correction by Sutherland: ("slip condition")

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

$\beta$ sliding friction coefficient between solute and medium (solvent)

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

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

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

$$\Rightarrow D = \frac{kT}{4\pi r \mu}$$

works for some liquid metal diffusion

Because of a lack of success of the previous models more empirical eq. are used.

assuming spherical molecules with molar volume $V_A$, Einstein's eq $D = \frac{kT}{6\pi r\mu}$ $\Rightarrow D = K' \frac{T}{\mu V_A^{1/3}}$

## Modified Stokes-Einstein Eqs (empirical models)

**Wilke-Chang:**

$$D_{AB}^{\circ} = \frac{1.17 \times 10^{-13} (\}_B M_B)^{1/2} T}{V_A^{0.6} \mu}$$

from Stokes-Einstein as starting point $D \propto \frac{T}{\mu V_A^{1/3}}$ → introduced as an empirical model

Used to predict diffusivities in dilute solutions of nonelectrolytes.

$D_{AB}^{\circ}$ infinite dilution diffusivity or "interdiffusion coeff. in dilute solutions"

$V_A$ molar volume of solute at normal boiling point

$\}_B$ 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

$T$ temperature in K; $\mu$ viscosity of solution in cP (mPa·s)

## Experimentally found Diffusion Coefficients

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

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TABLE 2-6. EXPERIMENTAL DIFFUSION COEFFICIENTS AT INFINITE DILUTION (SHERWOOD ET AL., 1975)

| *Solute A* | *Solvent B* | $T(K)$ | $D^{\circ}_{AB} \times 10^9$ $(m^2/s)$ |
|---|---|---|---|
| Acetic acid | Acetone | 298 | 3.31 |
| Benzoic acid | Acetone | 298 | 2.62 |
| Carbon dioxide | Amyl alcohol | 298 | 1.91 |
| Water | Aniline | 293 | 0.70 |
| Acetic acid | Benzene | 298 | 2.09 |
| Carbon tetrachloride | Benzene | 298 | 1.92 |
| Cinnamic acid | Benzene | 298 | 1.12 |
| Ethanol | Benzene | 280.6 | 1.77 |
| Ethylene chloride | Benzene | 288 | 2.25 |
| Methanol | Benzene | 298 | 3.82 |
| Napthalene | Benzene | 280.6 | 1.19 |
| Carbon dioxide | *i*-Butanol | 298 | 2.20 |
| Acetone | Carbon tetrachloride | 293 | 1.86 |
| Benzene | Chlorobenzene | 293 | 1.25 |
| Acetone | Chloroform | 288 | 2.36 |
| Benzene | Chloroform | 288 | 2.51 |
| Ethanol | Chloroform | 288 | 2.20 |
| Carbon tetrachloride | Cyclohexane | 298 | 1.49 |
| Azobenzene | Ethanol | 293 | 0.74 |
| Camphor | Ethanol | 293 | 0.70 |
| Carbon dioxide | Ethanol | 290 | 3.20 |
| Carbon dioxide | Ethanol | 298 | 3.42 |
| Glycerol | Ethanol | 293 | 0.51 |
| Pyridine | Ethanol | 293 | 1.10 |
| Urea | Ethanol | 285 | 0.54 |
| Water | Ethanol | 298 | 1.132 |
| Water | Ethylene glycol | 293 | 0.18 |
| Water | Glycerol | 293 | 0.0083 |
| Carbon dioxide | Heptane | 298 | 6.03 |
| Carbon tetrachloride | *n*-Hexane | 298 | 3.70 |
| Toluene | *n*-Hexane | 298 | 4.21 |
| Carbon dioxide | Kerosene | 298 | 2.50 |
| Tin | Mercury | 303 | 1.60 |
| Water | *n*-Propanol | 288 | 0.87 |
| Water | 1,2-Propylene glycol | 293 | 0.0075 |
| Acetic acid | Toluene | 298 | 2.26 |
| Acetone | Toluene | 293 | 2.93 |
| Benzoic acid | Toluene | 293 | 1.74 |
| Chlorobenzene | Toluene | 293 | 2.06 |
| Ethanol | Toluene | 288 | 3.00 |
| Carbon dioxide | White spirit | 298 | 2.11 |