

Lecture Notes on the Estimation of Binary Diffusivities

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Information from Section 24.2 of the textbook by Welty et al.

Binary diffusivity in gases

Temperature and Pressure dependence

Gas phase diffusivities are approximately proportional to $T^{1.75} / P$, where T is the absolute temperature, and P is the absolute pressure. The inverse dependence on pressure holds up to about 25 atmospheres. If an experimental value of the diffusivity is available at a given temperature and pressure, the diffusivity at some other temperature and pressure can be estimated from the above dependence. Binary diffusivities in the gas phase are relatively insensitive to composition. This is not the case in liquids.

Hirschfelder, Bird, Spotz equation

Equation (24-33) on page 443 for pairs A-B of non-polar molecules:

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

D_{AB} : Binary gas phase diffusivity of A in B in cm^2 / s .

T : Absolute temperature in Kelvin

P : Absolute pressure in atmospheres

M_A, M_B : Molecular weights of A and B, respectively

σ_{AB} : Lennard-Jones collision diameter in Angstroms

Ω_D : Collision integral for molecular diffusion.

If σ_{AB} is not known for a given binary system composed of a non-polar molecular pair, construct it using

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B) \quad \text{Equation (24-39), page 444}$$

Individual values of σ_A are given in Table K-2 in Appendix K of the textbook.

Values of the collision integral for molecular diffusion are given in Table K-1 in Appendix K as a function of a dimensionless temperature kT / ε_{AB} . Table K-2 in the same Appendix lists values of ε / k for several molecules. For a binary system composed of a non-polar molecular pair, construct ε_{AB} / k using

$$\frac{\varepsilon_{AB}}{k} = \sqrt{\left(\frac{\varepsilon_A}{k}\right)\left(\frac{\varepsilon_B}{k}\right)}$$

which is the same result as Equation (24-40): $\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$

Fuller-Schettler-Giddings Equation

The Fuller-Schettler-Giddings Equation (Equation (24-42) on page 445) can be used for estimating binary diffusivities when the Lennard-Jones parameters are not available for one or both species in a nonpolar binary gas mixture.

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

D_{AB} : Binary gas phase diffusivity of A in B in cm^2 / s .

T : Absolute temperature in Kelvin

P : Absolute pressure in atmospheres

M_A, M_B : Molecular weights of A and B, respectively

$(\sum v)_A, (\sum v)_B$: molecular volumes in $cm^3 / g - mol$

Obtain the molecular volumes from Table 24.3 on page 445.

Predictions can be made for polar-non-polar pairs or for polar-polar pairs, but we won't be able to discuss them here. See pages 446-447 in the book for information about one approach called Brokaw's method.

Diffusion coefficient of species 1 in a mixture of n species

If we know binary diffusivities $D_{1-2}, D_{1-3}, \dots, D_{1-n}$, for species 1 in a mixture of n species, the diffusivity of species 1 in the mixture can be approximated using Equation (24-49) on page 448.

$$\frac{1}{D_{1\text{-mixture}}} = \frac{y'_2}{D_{1-2}} + \frac{y'_3}{D_{1-3}} + \dots + \frac{y'_n}{D_{1-n}}$$

y'_n is the mole fraction of component n in the gas mixture evaluated on a component-1-free basis, that is

$$\boxed{y'_2 = \frac{y_2}{y_2 + y_3 + \dots + y_n} = \frac{y_2}{1 - y_1}}$$

Binary diffusivity in liquids

In liquids, it is possible to estimate the diffusivity of a non-electrolyte solute in dilute solution (in principle, at infinite dilution) using the Wilke-Chang correlation, given as Equation (24-52) on page 449 of the textbook.

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

D_{AB} : Binary diffusivity of A at infinite dilution in B cm^2 / s .

T : Absolute temperature in Kelvin

μ_B : Viscosity of solvent B in cp (this means centipoise)

M_B : Molecular weight of solvent B

Φ_B : Association parameter of solvent B

V_A : Molal volume of solute A at normal boiling point in $cm^3 / g - mol$

Use Tables 24.4 and 24.5 on pages 449-450 to estimate atomic and molal volumes at the normal boiling point. The association parameter for common solvents can be found in a table that appears below Table 24.5 on page 450.

A simpler result that gives nearly the same prediction is the correlation of Hayduk and Laudie, which is to be used for evaluating the diffusion coefficients of non-electrolytes in water in dilute solution (in principle, at infinite dilution). It is given as Equation (24-53) on page 450 in the book.

$$D_{AB} = 13.26 \times 10^{-5} (\mu_B)^{-1.14} (V_A)^{-0.589}$$

The notation is the same as that used in the Wilke-Chang correlation, and the diffusivity of A at infinite dilution in B is obtained in cm^2 / s .

Note that the above estimates for a solute at infinite dilution. In practice, they can be used as adequate approximations so long as the solution is reasonably dilute; however, unlike binary gas phase diffusivities, liquid phase diffusivities depend strongly on concentration. In pages 451-452 in Chapter 24 of the textbook, the authors briefly mention a common method used to obtain binary diffusivities in non-dilute solutions.

Remarks added in April 2020

In a recent review article on separation column efficiency, Taylor and Duss (2019) discuss a general approach for estimating the diffusion coefficient of a key species in a multicomponent mixture in both gas phase mixtures and liquid mixtures. For example, when using the equations proposed by Hirschfelder, Bird, and Spatz or Fuller,-Schechter-Giddings for gas phase diffusion coefficients, if A is the key species in the mixture, we lump all the other species into B, and obtain M_B from

$$M_B = \sum_{i=1 \neq A}^n x'_i M_i \quad \text{where} \quad x'_i = \frac{x_i}{1 - x_A}$$

In the summation, the case $i = A$ is omitted, and the result for x'_i is used only for $i \neq A$. A similar weighted result is used for the “molecular volume” of B, if needed in the correlation.

$$V_B = \sum_{i=1 \neq A}^n x'_i V_i$$

These ideas also can be extended to the liquid phase in the correlations of Wilke-Chang or Hayduk and Laudie. Wherever information for species B is needed, a weighted average on an A-free basis obtained in the above manner is substituted. The viscosity of the solvent B is estimated using any method applicable to mixtures, but on an A-free basis.

For more details, please consult the article by Taylor and Duss (2019).

References

R. Taylor and M. Duss, *Industrial and Engineering Chemistry Research*, **58**, 16877-16893 (2019).

J. Welty, C.E. Wicks, G.L. Rorrer, and R.E. Wilson, *Fundamentals of Momentum, Heat, and Mass Transfer*, 5th edition, Wiley, Hoboken, NJ (2007).