MASS TRANSFER

Molecular Mass Transfer

- Molecular diffusion
- Mass transfer law components:
  - Molecular concentration:

$$c_A = \frac{r_A}{M_A} = \frac{n_A}{V} = \frac{p_A}{RT}$$

  - Mole fraction:

(gases) $$x_A = \frac{c_A}{c}$$ (liquids,solids) , $$y_A = \frac{c_A}{c}$$

For gases, $$y_A = \frac{p_A / RT}{P / RT} = \frac{p_A}{P}$$

– Velocity:

mass average velocity, $$\mathrm{v} = \frac{\sum_{i=1}^{n} \rho_i \mathrm{v}_i}{\sum_{i=1}^{n} \rho_i} = \frac{\sum_{i=1}^{n} \rho_i \mathrm{v}_i}{\rho}$$

molar average velocity, $$\mathbf{V} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{c}$$

velocity of a particular species relative to mass/molar average is

the diffusion velocity.

The composition of air is often given in terms of only the two principal species in the gas mixture

$$\begin{array}{lll} \text{oxygen,} & O_2, & y_{O_2} = 0.21 \\ \text{nitrogen,} & N_2, & y_{N_2} = 0.79 \end{array}$$

Determine the mass fraction of both oxygen and nitrogen and the mean molecular weight of the air when it is maintained at 25°C (298 K) and 1 atm (1.013×10^5 Pa). The molecular weight of oxygen is 0.032 kg/mol and of nitrogen is 0.028 kg/mol.

As a basis for our calculations, consider 1 mole of the gas mixture

$$\text{oxygen present} = (1\ \text{mol})(0.21) = 0.21\ \text{mol}$$

$$= (0.21\ \text{mol})\frac{(0.032\ \text{kg})}{\text{mol}} = 0.00672\ \text{kg}$$

$$\text{nitrogen present} = (1\ \text{mol})(0.79) = 0.79\ \text{mol}$$

$$= (0.79\ \text{mol})\frac{(0.028\ \text{kg})}{\text{ml}\,\text{mol}} = 0.0221\ \text{kg}$$

$$\text{total mass present} = 0.00672 + 0.0221 = 0.0288\ \text{kg}$$

$$\omega_{O_2} = \frac{0.00672\ \text{kg}}{0.0288\ \text{kg}} = 0.23$$

$$\omega_{N_2} = \frac{0.0221\ \text{kg}}{0.0288\ \text{kg}} = 0.77$$

Since 1 mole of the gas mixture has a mass of 0.0288 kg, the mean molecular weight of the air must be 0.0288. When one takes into account the other constituents that are present in air, the mean molecular weight of air is often rounded off to 0.029 kg/mol.

This problem could also be solved using the ideal gas law, $PV = nRT$. At ideal conditions, 0°C or 273 K and 1 atm of 1.013×10^5 Pa pressure, the gas constant is evaluated to be

$$R = \frac{PV}{nT} = \frac{(1.013 \times 10^5\ \text{Pa})(22.4\ \text{m}^3)}{(1\ \text{kg mol})(273\ \text{K})} = 8.314\,\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}} \tag{24-12}$$

The volume of the gas mixture, at 298 K, is

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})\left(8.314\,\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(298\ \text{K})}{1.013 \times 10^5\ \text{Pa}}$$
$$= 0.0245\ \text{m}^3$$

The concentrations are

$$c_{O_2} = \frac{0.21\ \text{mol}}{0.0245\ \text{m}^3} = 8.57\,\frac{\text{mol O}_2}{\text{m}^3}$$

$$c_{N_2} = \frac{0.79\ \text{mol}}{0.0245\ \text{m}^3} = 32.3\,\frac{\text{mol N}_2}{\text{m}^3}$$

$$c = \sum_{i=1}^{n} c_i = 8.57 + 32.3 = 40.9\ \text{mol/m}^3$$

The total density, ρ, is

$$\rho = \frac{0.0288 \text{ kg}}{0.0245 \text{ m}^3} = 1.180 \text{ kg/m}^3$$

and the mean molecular weight of the mixture is

$$M = \frac{\rho}{c} = \frac{1.180 \text{ kg/m}^3}{40.9 \text{ mol/m}^3} = 0.0288 \text{ kg/mol}$$

– Flux:

A vector quantity denoting amount of a particular species that passes per given time through a unit area normal to the vector,

given by Fick’s First Law, for basic molecular diffusion

$$\mathbf{J}_A = -D_{AB} \nabla c_A$$

or, in the z-direction,

$$J_{A,z} = -D_{AB} \frac{dc_A}{dz}$$

For a general relation in a non-isothermal, isobaric system,

$$J_{A,z} = -cD_{AB} \frac{dy_A}{dz}$$

– Since mass is transferred by two means:
  - concentration differences
  - and convection differences from density differences
  - For binary system with constant V_z,

$$J_{A,z} = c_A(v_{A,z} - V_z)$$

  - Thus,

$$J_{A,z} = c_A(v_{A,z} - V_z) = -cD_{AB}\frac{dy_A}{dz}$$

  - Rearranging to

$$c_A v_{A,z} = -cD_{AB}\frac{dy_A}{dz} + c_A V_z$$

- As the total velocity,

$$V_z = \frac{1}{c}(c_A v_{A,z} + c_B v_{B,z})$$

- Or

$$c_A V_z = y_A (c_A v_{A,z} + c_B v_{B,z})$$

- Which substituted, becomes

$$c_A v_{A,z} = - cD_{AB} \frac{dy_A}{dz} + y_A (c_A v_{A,z} + c_B v_{B,z})$$

- Defining molar flux, **N** as flux relative to a fixed z,

$$\mathbf{N}_A = c_A \mathbf{v}_A$$

- And finally,

$$N_{A,z} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

- Or generalized,

$$\boxed{\mathbf{N}_A = -cD_{AB}\nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B)}$$

The four equations defining the fluxes, $\mathbf{J}_A$, $\mathbf{j}_A$, $\mathbf{N}_A$, and $\mathbf{n}_A$ are equivalent statements of the Fick rate equation. The diffusion coefficient, D_{AB}, is identical in all four equations. Any one of these equations is adequate to describe molecular diffusion; however, certain fluxes are easier to use for specific cases. The mass fluxes, $\mathbf{n}_A$ and $\mathbf{j}_A$, are used when the Navier-Stokes equations are also required to describe the process. Since chemical reactions are described in terms of moles of the participating reactants, the molar fluxes, $\mathbf{J}_A$ and $\mathbf{N}_A$, are used to describe mass-transfer operations in which chemical reactions are involved. The fluxes relative to coordinates fixes in space, $\mathbf{n}_A$ and $\mathbf{N}_A$, are often used to describe engineering operations within process equipment. The fluxes $\mathbf{J}_A$ and $\mathbf{j}_A$ are used to describe the mass transfer in diffusion cells used for measuring the diffusion coefficient. Table 24.2 summarizes the equivalent forms of the Fick rate equation.

Table 24.2 Equivalent forms of the Mass Flux Equation for Binary System *A* and *B*

Flux	Gradient	Fick rate equation	Restrictions
$\mathbf{n}_A$	$\nabla\omega_A$	$\mathbf{n}_A = -\rho D_{AB}\nabla\omega_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	
	$\nabla\rho_A$	$\mathbf{n}_A = -D_{AB}\nabla\rho_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	Constant ρ
$\mathbf{N}_A$	∇y_A	$\mathbf{N}_A = -cD_{AB}\nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	
	∇c_A	$\mathbf{N}_A = -D_{AB}\nabla c_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	Constant c
$\mathbf{j}_A$	$\nabla\omega_A$	$\mathbf{j}_A = -\rho D_{AB}\nabla\omega_A$	
	$\nabla\rho_A$	$\mathbf{j}_A = -D_{AB}\nabla\rho_A$	Constant ρ
$\mathbf{J}_A$	∇y_A	$\mathbf{J}_A = -cD_{AB}\nabla y_A$	
	∇c_A	$\mathbf{J}_A = -D_{AB}\nabla c_A$	Constant c

- Related molecular mass transfer
  - Defined in terms of chemical potential:

$$v_{A,z} - V_z = u_A \frac{d\mu_c}{dz} = -\frac{D_{AB}}{RT}\frac{d\mu_c}{dz}$$

  - Nernst-Einstein relation

$$\boxed{J_{A,z} = c_A(v_{A,z} - V_z) = -c_A \frac{D_{AB}}{RT}\frac{d\mu_c}{dz}}$$

Diffusion Coefficient

- Fick’s law proportionality/constant

$$D_{AB} = \frac{-J_{A,z}}{dc_A / dz} = \left(\frac{M}{L^2 t}\right)\left(\frac{1}{M / L^3 \times 1 / L}\right) = \frac{L^2}{t}$$

- Similar to kinematic viscosity, � , and thermal diffusivity, ↦

- Gas mass diffusivity
  - Based on Kinetic Gas Theory

$$D_{AA^*} = \frac{1}{3}\lambda u$$

  - ℓ = mean free path length, *u* = mean speed

$$D_{AA^*} = \frac{2T^{3/2}}{3\pi^{3/2}\sigma_A^2 P}\left(\frac{\kappa^3 N}{M_A}\right)^{1/2}$$

  - Hirschfelder's equation:

$$\boxed{D_{AB} = \frac{0.001858T^{3/2}\left(\dfrac{1}{M_A}+\dfrac{1}{M_B}\right)^{1/2}}{P\sigma_{AB}^2\Omega_D}}$$

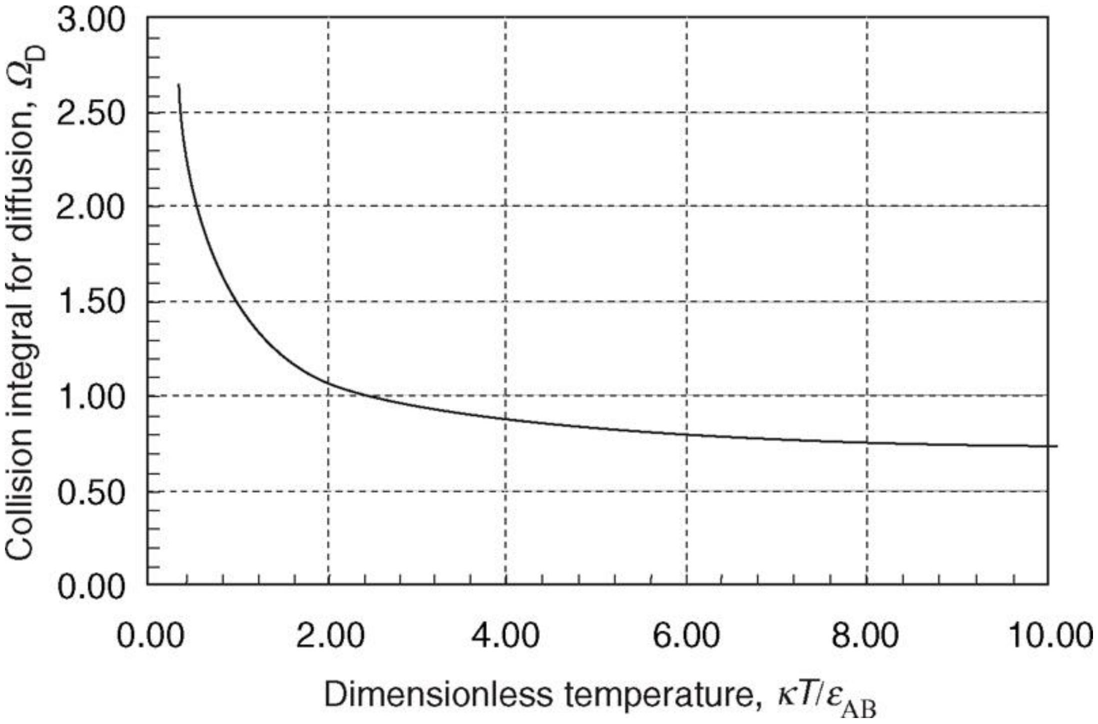
- Lennard-Jones parameters ← and ⊙ from tables, or from empirical relations
- for binary systems, (non-polar,non-reacting)

$$s_{AB} = \frac{s_A + s_B}{2} \qquad e_{AB} = \sqrt{e_A e_B}$$

- Extrapolation of diffusivity up to 25 atmospheres

$$D_{AB_{T_2,P_2}} = D_{AB_{T_1,P_1}} \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)^{3/2} \frac{D|_{T_1}}{D|_{T_2}}$$

Binary gas-phase Lennard-Jones "collisional integral"



Evaluate the diffusion coefficient of carbon dioxide in air at 20°C and atmos pressure. Compare this value with the experimental value reported in Appendix J.1.

From Appendix Table K.2 the values of σ and ϵ/κ are obtained

	σ, in Å	ϵ_A/κ, in K
Carbon dioxide	3.996	190
Air	3.617	97

The various parameters for equation (24-33) may be evaluated as follows:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{3.996 + 3.617}{2} = 3.806\ \mathring{A}$$

$$\epsilon_{AB}/\kappa = \sqrt{(\epsilon_A/\kappa)(\epsilon_B/\kappa)} = \sqrt{(190)(97)} = 136$$

$$T = 20 + 273 = 293\ \text{K}$$

$$P = 1\ \text{atm}$$

$$\frac{\epsilon_{AB}}{\kappa T} = \frac{136}{293} = 0.463$$

$$\frac{\kappa T}{\epsilon_{AB}} = 2.16$$

$$\Omega_D\ (\text{Table K.1}) = 1.047$$

$$M_{CO_2} = 44$$

and

$$M_{\text{Air}} = 29$$

Substituting these values into equation (24-33), we obtain

$$D_{AB} = \frac{0.001858T^{3/2}(1/M_A + 1/M_B)^{1/2}}{P\sigma_{AB}^2\Omega_D}$$

$$= \frac{(0.001858)(293)^{3/2}(1/44 + 1/29)^{1/2}}{(1)(3.806)^2(1.047)} = 0.147 \text{ cm}^2/\text{s}$$

From Appendix Table J.1 for CO_2 in air at 273 K, 1 atmosphere, we have

$$D_{AB} = 0.136 \text{ cm}^2/\text{s}$$

Equation (24-41) will be used to correct for the differences in temperature

$$\frac{D_{AB,T_1}}{D_{AB,T_2}} = \left(\frac{T_1}{T_2}\right)^{3/2}\left(\frac{\Omega_D|_{T_2}}{\Omega_D|_{T_1}}\right)$$

Values for Ω_D may be evaluated as follows:

at $T_2 = 273$ $\quad \epsilon_{AB}/\kappa T = \frac{136}{273} = 0.498 \quad \Omega_D|_{T_2} = 1.074$

at $T_1 = 293$ $\quad \Omega_D|_{T_1} = 1.047$ (previous calculations)

The corrected value for the diffusion coefficient at 20°C is

$$D_{AB,T_1} = \left(\frac{293}{273}\right)^{3/2}\frac{(1.074)}{(1.047)}(0.136) = 0.155 \text{ cm}^2/\text{s} \quad (1.55 \times 10^{-5} \text{ m}^2/\text{s})$$

- With no reliable ← or ⊙, we can use the Fuller correlation,

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

- For binary gas with polar compounds, we calculate □ by

$$\circ = \circ_{D_0} + \frac{0.196 d_{AB}^2}{T^*}$$

where

$$d_{AB} = \left(d_A d_B\right)^{1/2}, d = \frac{1.94 \times 10^3 m_p^2}{V_b T_b}$$

$$T^* = kT / e_{AB}$$

$$\frac{e_{AB}}{k} = \left(\frac{e_A}{k}\frac{e_B}{k}\right)^{1/2}$$

$$e/k = 1.18\left(1 + 1.3d^2\right)T_b$$

$$\circ_{D_0} = \frac{A}{\left(T^*\right)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

and

$$\sigma_{AB} = \left(\sigma_A \sigma_B\right)^{1/2} \qquad \sigma = \left(\frac{1.585 V_b}{1 + 1.3\delta^2}\right)^{1/3}$$

- For gas mixtures with several components,

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

- with

$$y'_2 = \frac{y_2}{y_2 + y_3 + \ldots + y_n}$$

In the chemical vapor deposition of silane (SiH_4) on a silicon wafer, a process gas stream rich in an inert nitrogen (N_2) carrier gas has the following composition:

$$y_{SiH_4} = 0.0075,\ y_{H_2} = 0.015,\ y_{N_2} = 0.9775$$

The gas mixture is maintained at 900 K and 100 Pa total system pressure. Determine the diffusivity of silane through the gas mixture. The Lennard-Jones constants for silane are $\varepsilon_A/\kappa = 207.6$ K and $\sigma_A = 4.08$ Å.

The binary diffusion coefficients at 900 K and 100 Pa total system pressure estimated by the Hirschfelder equation (24-33) are

$$D_{SiH_4-N_2} = 1.09 \times 10^3\ \text{cm}^2/\text{s} \quad \text{and} \quad D_{SiH_4-H_2} = 4.06 \times 10^3\ \text{cm}^2/\text{s}$$

The binary diffusion coefficients are relatively high because the temperature is high the total system pressure is low. The composition of nitrogen and hydrogen on a sil free basis are

$$y'_{N_2} = \frac{0.9775}{1 - 0.0075} = 0.9849 \quad \text{and} \quad y'_{H_2} = \frac{0.015}{1 - 0.0075} = 0.0151$$

Upon substituting these values into the Wilke equation (24-49), we obtain

$$D_{SiH_4-\text{mixture}} = \frac{1}{\dfrac{y'_{N_2}}{D_{SiH_4-N_2}} + \dfrac{y'_{H_2}}{D_{SiH_4-H_2}}} = \frac{1}{\dfrac{0.9849}{1.09 \times 10^3} + \dfrac{0.0151}{4.06 \times 10^3}} = 1.10 \times 10^3\ \frac{\text{cm}^2}{\text{s}}$$

This example verifies that for a dilute multicomponent gas mixture, the diffusion co cient of the diffusing species in the gas mixture is approximated by the binary diffu coefficient of the diffusing species in the carrier gas.

- Liquid mass diffusivity
  - No rigorous theories
  - Diffusion as molecules or ions
  - Eyring theory
  - Hydrodynamic theory
    - Stokes-Einstein equation

$$D_{AB} = \frac{kT}{6\pi r \mu_B}$$

  - Equating both theories, we get Wilke-Chang eq.

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

Table 24.4 Molecular Volumes at Normal Boiling Point for Some Commonly Encountered Compounds

Compound	Molecular volume, cm^3/g mole	Compound	Molecular volume, in cm^3/g mole
Hydrogen, H_2	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, N_2	31.2	Ammonia, NH_3	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H_2S	32.9
Carbon dioxide, CO_2	34.0	Bromine, Br_2	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl_2	48.4
Sulfur dioxide, SO_2	44.8	Iodine, I_2	71.5

Estimate the liquid diffusion coefficient of ethanol, C_2H_5OH, in a dilute solution of wat at 10°C. The molecular volume of ethanol may be evaluated by using values from Tab 24.5 as follows:

$$V_{C_2H_5OH} = 2V_C + 6V_H + V_O$$

$$V_{C_2H_5OH} = 2(14.8) + 6(3.7) + 7.4 = 59.2 \text{ cm}^3/\text{mol}$$

At 10°C, the viscosity of a solution containing 0.05 mole of alcohol/liter of water is 1.45 centipoises; the remaining parameters to be used are

$$T = 283 \text{ K}$$

$$\Phi_B \text{ for water} = 2.26$$

and

$$M_B \text{ for water} = 18$$

Substituting these values into equation (24-52), we obtain

$$D_{C_2H_5OH-H_2O} = \left(\frac{7.4 \times 10^{-8}(2.26 \times 18)^{1/2}}{(59.2)^{0.6}}\right)\left(\frac{283}{1.45}\right)$$

$$= 7.96 \times 10^{-6} \text{ cm}^2/\text{s} \qquad (7.96 \times 10^{-10} \text{ m}^2/\text{s})$$

This value is in good agreement with the experimental value of 8.3×10^{-10} m²/s reported in Appendix J.

- For infinite dilution of non-electrolytes in water, W-C is simplified to Hayduk-Laudie eq.

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

- Scheibel’s equation eliminates ⌟ B,

$$\frac{D_{AB}\mu_B}{T} = \frac{K}{V_A^{1/3}}$$

$$K = (8.2 \times 10^{-8})\left[1 + \left(\frac{3V_B}{V_A}\right)^{2/3}\right]$$

- As diffusivity changes with temperature, extrapolation of D_{AB} is by

$$\frac{(D_{ABT_1})}{(D_{ABT_2})} = \left(\frac{T_c - T_2}{T_c - T_1}\right)^n$$

- For diffusion of univalent salt in dilute solution, we use the Nernst equation

$$D_{AB} = \frac{2RT}{(1/\lambda_+^0 + 1/\lambda_-^0)F^2}$$

- Pore diffusivity
  - Diffusion of molecules within pores of porous solids
  - Knudsen diffusion for gases in cylindrical pores
    - Pore diameter smaller than mean free path, and density of gas is low
    - Knudsen number

$$Kn = \frac{l}{d_{pore}}$$

    - From Kinetic Theory of Gases,

$$D_{AA^*} = \frac{l u}{3} = \frac{l}{3}\sqrt{\frac{8KNT}{pM_A}}$$

- But if Kn >1, then

$$\boxed{D_{KA} = \frac{d_{pore}}{3} u = \frac{d_{pore}}{3} \sqrt{\frac{8kNT}{\pi M_A}} = 4850 d_{pore} \sqrt{\frac{T}{M_A}}}$$

- If both Knudsen and molecular diffusion exist, then

$$\frac{1}{D_{Ae}} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

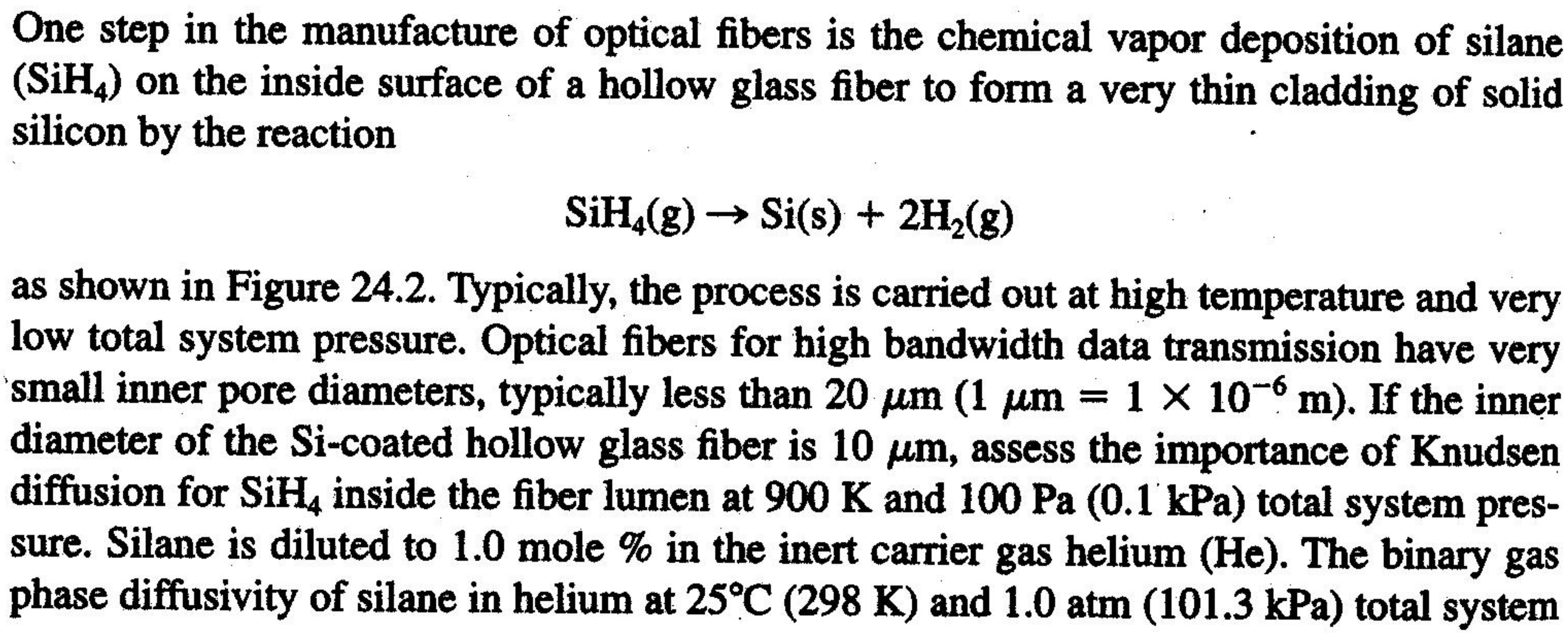
- with

$$\alpha = 1 + \frac{N_B}{N_A}$$

- For non-cylindrical pores, we estimate

$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

Example 6



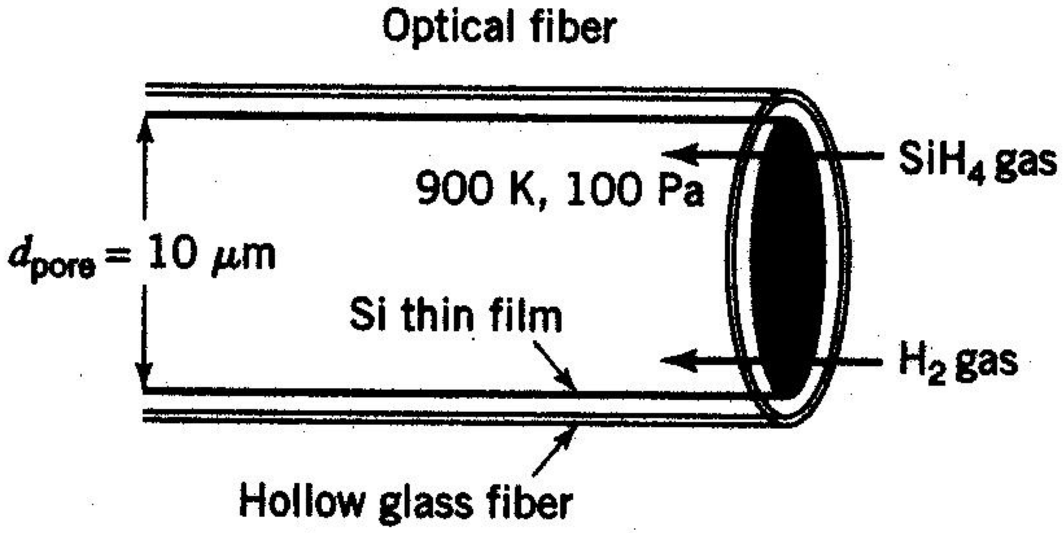
One step in the manufacture of optical fibers is the chemical vapor deposition of silane (SiH_4) on the inside surface of a hollow glass fiber to form a very thin cladding of solid silicon by the reaction

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$

as shown in Figure 24.2. Typically, the process is carried out at high temperature and very low total system pressure. Optical fibers for high bandwidth data transmission have very small inner pore diameters, typically less than 20 μm (1 μm = 1×10^{-6} m). If the inner diameter of the Si-coated hollow glass fiber is 10 μm, assess the importance of Knudsen diffusion for SiH_4 inside the fiber lumen at 900 K and 100 Pa (0.1 kPa) total system pressure. Silane is diluted to 1.0 mole % in the inert carrier gas helium (He). The binary gas phase diffusivity of silane in helium at 25°C (298 K) and 1.0 atm (101.3 kPa) total system pressure is 0.518 cm^2/s, with $\sigma_{\text{SiH}_4} = 4.08$ Å and $\varepsilon_{\text{SiH}_4}/\kappa = 207.6$ K. The molecular weight of silane is 32 g/mole.

The gas phase molecular diffusivity of SiH_4-He, Knudsen diffusivity for SiH_4, and effective diffusivity for SiH_4 at 900 K and 100 Pa total system pressure must be calculated. The gas phase molecular diffusivity of silane in helium is scaled to process temperature and pressure using the Hirschfelder extrapolation, equation (24-41)

$$D_{\text{SiH}_4-\text{He}}\Big|_{0.1\text{ kPa}}^{900\text{ K}} = 0.518\,\frac{\text{cm}^2}{\text{s}}\left(\frac{900\text{ K}}{298\text{ K}}\right)^{1.5}\left(\frac{101.3\text{ kPa}}{0.1\text{ kPa}}\right)\left(\frac{0.885}{0.668}\right) = 3.66\times 10^3\,\frac{\text{cm}^2}{\text{s}}$$



It is left to the reader to show that the collision integral Ω_D is equal to 0.885 at 298 K and 0.668 at 900 K for gaseous SiH_4-He mixtures. Note that the gas phase molecular diffusivity is high due to high temperature and very low system pressure. The Knudsen diffusivity of SiH_4 inside the optical fiber is calculated using equation (24-58), with $d_{pore} = 1 \times 10^{-3}$ cm (10 μm)

$$D_{K,SiH_4} = 4850\,d_{pore}\sqrt{\frac{T}{M_{SiH_4}}} = 4850(1 \times 10^{-3})\sqrt{\frac{900}{32}} = 25.7\,\frac{cm^2}{s}$$

Since the SiH_4 is significantly diluted in He, the process is dilute with respect to SiH_4 and so equation (24-60) can be used to estimate the effective diffusivity

$$D_{SiH_4,e} = \frac{1}{\dfrac{1}{D_{SiH_4-He}} + \dfrac{1}{D_{K,SiH_4}}} = \frac{1}{\dfrac{1}{3.66 \times 10^3} + \dfrac{1}{25.7}} = 25.5\,\frac{cm^2}{s}$$

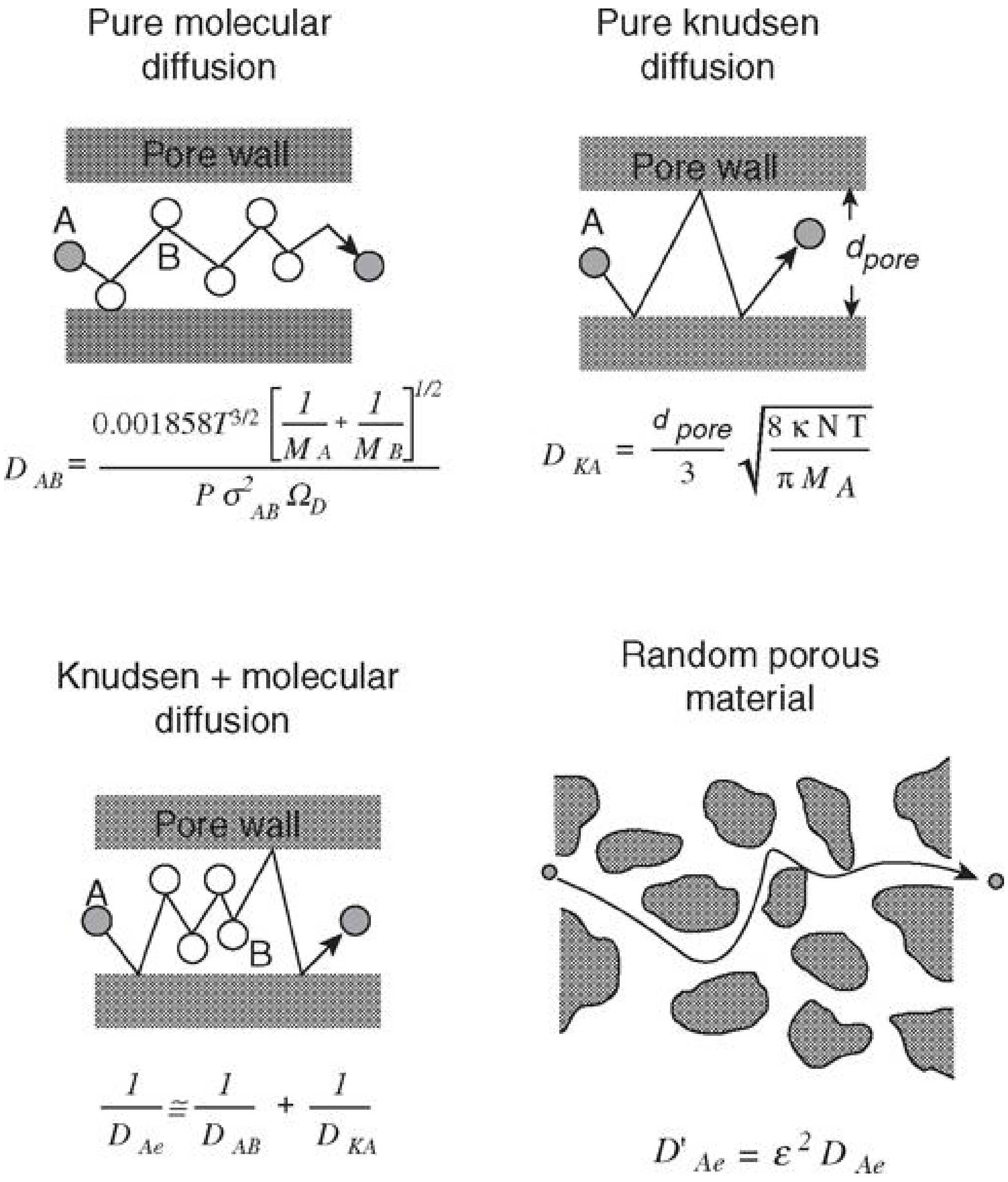
The effective diffusivity for SiH_4 is smaller than its Knudsen diffusivity, reflecting the resistance in series approach. Finally, we calculate the Knudsen number for SiH_4

$$\lambda = \frac{\kappa T}{\sqrt{2}\pi\sigma_A^2 P} = \frac{1.38 \times 10^{-16}\,\dfrac{\text{erg}}{K}\,\dfrac{1\,N\,\text{m}}{10^7\,\text{erg}}\,900\,K}{\sqrt{2}\pi\left(0.408\text{ nm}\,\dfrac{1\text{ m}}{10^9\text{ nm}}\right)^2 100\,\dfrac{N}{\text{m}^2}} = 1.68 \times 10^{-4}\text{ m} = 168\ \mu\text{m}$$

$$Kn = \frac{\lambda}{d_{\text{pore}}} = \frac{168\ \mu\text{m}}{10\ \mu\text{m}} = 16.8$$

Since $Kn \gg 1$ and the effective diffusivity is close to the Knudsen diffusivity, then Knudsen diffusion controls the silane transport inside the optical fiber if no external bulk transport is supplied.

Types of porous diffusion. Shaded areas represent nonpo



Pure molecular diffusion

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

Pure knudsen diffusion

$$D_{KA} = \frac{d_{pore}}{3} \sqrt{\frac{8 \kappa N T}{\pi M_A}}$$

Knudsen + molecular diffusion

$$\frac{1}{D_{Ae}} \cong \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

Random porous material

$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

- Hindered diffusion for solute in solvent-filled pores
  - A general model is

$$\boxed{D_{Ae} = D^{o}_{AB} F_1(\phi) F_2(\phi)}$$

  - F_1 and F_2 are correction factors, function of pore diameter,

$$\phi = \frac{d_s}{d_{pore}}$$

  - F_1 is the stearic partition coefficient

$$F_1(\phi) = \frac{\pi (d_{pore} - d_s)^2}{\pi d_{pore}^2} = (1 - \phi)^2$$

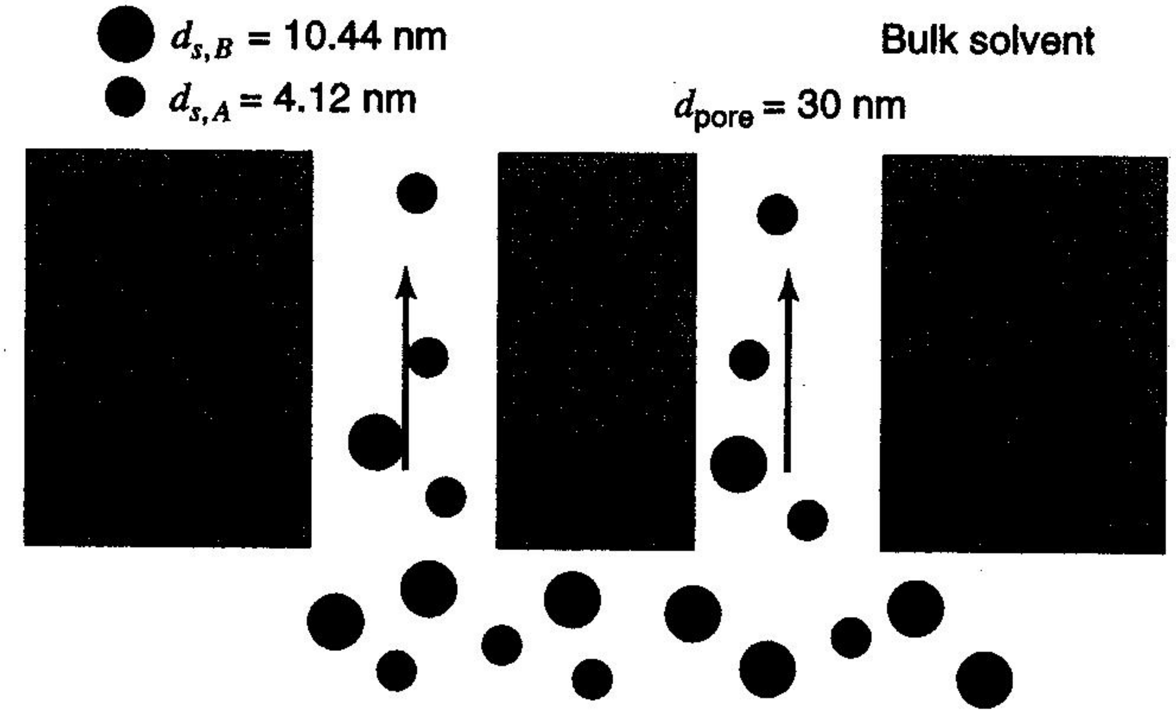
- F_2 is the hydrodynamic hindrance factor, one equation is by Renkin,

$$F_2(\varphi) = 1 - 2.104\varphi + 2.09\varphi^3 - 0.95\varphi^5$$

Example 7

It is desired to separate a mixture of two industrial enzymes, lysozyme and catalase, in a dilute, aqueous solution by a gel filtration membrane. A mesoporous membrane with cylindrical pores of 30 nm diameter is available (Figure 24.3). The following separation factor (α) for the process is proposed

$$\alpha = \frac{D_{Ae}}{D_{Be}}$$



Determine the separation factor for this process. The properties of each enzyme as reported by Tanford* are given below.

Lysozyme (species A)	**Catalase (species B)**
$M_A = 14\,100$ g/gmole	$M_B = 250\,000$ g/gmole
$d_{s,A} = 4.12$ nm	$d_{s,B} = 10.44$ nm
$D^{\circ}_{A-H_2O} = 1.04 \times 10^{-6}$ cm²/s	$D^{\circ}_{B-H_2O} = 4.10 \times 10^{-7}$ cm²/s

The transport of large enzyme molecules through pores filled with liquid water represents a hindered diffusion process. The reduced pore diameters for lysozyme and catalase are

$$\varphi_A = \frac{d_{s,A}}{d_{\text{pore}}} = \frac{4.12\text{ nm}}{30.0\text{ nm}} = 0.137 \qquad \text{and} \qquad \varphi_B = \frac{d_{s,B}}{d_{\text{pore}}} = \frac{10.44\text{ nm}}{30.0\text{ nm}} = 0.348$$

For lysozyme, $F_1(\varphi_A)$ by equation (24-64) and $F_2(\varphi_A)$ by the Renkin equation (24-65) are

$$F_1(\varphi_A) = (1 - \varphi_A)^2 = (1 - 0.137)^2 = 0.744$$

$$\begin{aligned} F_2(\varphi_A) &= 1 - 2.104\varphi_A + 2.09\varphi_A^3 - 0.95\varphi_A^5 \\ &= 1 - 2.104(0.137) + 2.09(0.137)^3 - 0.95(0.137)^5 = 0.716 \end{aligned}$$

The effective diffusivity of lysozyme in the pore, D_{Ae}, is estimated by equation (24-62)

$$D_{Ae} = D^{\circ}_{A-H_2O} F_1(\varphi_A) F_2(\varphi_A) = 1.04 \times 10^{-6}\,\frac{\text{cm}^2}{\text{s}}(0.744)(0.716) = 5.54 \times 10^{-7}\,\frac{\text{cm}^2}{\text{s}}$$

Likewise, for catalase $F_1(\varphi_B) = 0.425$, $F_2(\varphi_B) = 0.351$, and $D_{Be} = 6.12 \times 10^{-8}\ \text{cm}^2/\text{s}$. Finally, the separation factor is

$$\alpha = \frac{D_{Ae}}{D_{Be}} = \frac{5.54 \times 10^{-7}\ \text{cm}^2/\text{s}}{6.12 \times 10^{-8}\ \text{cm}^2/\text{s}} = 9.06$$

It is interesting to compare the value above with α', the ratio of molecular diffusivities at infinite dilution

$$\alpha' = \frac{D^\circ_{A-H_2O}}{D^\circ_{B-H_2O}} = \frac{1.04 \times 10^{-6}\ \text{cm}^2/\text{s}}{4.1 \times 10^{-7}\ \text{cm}^2/\text{s}} = 1.75$$

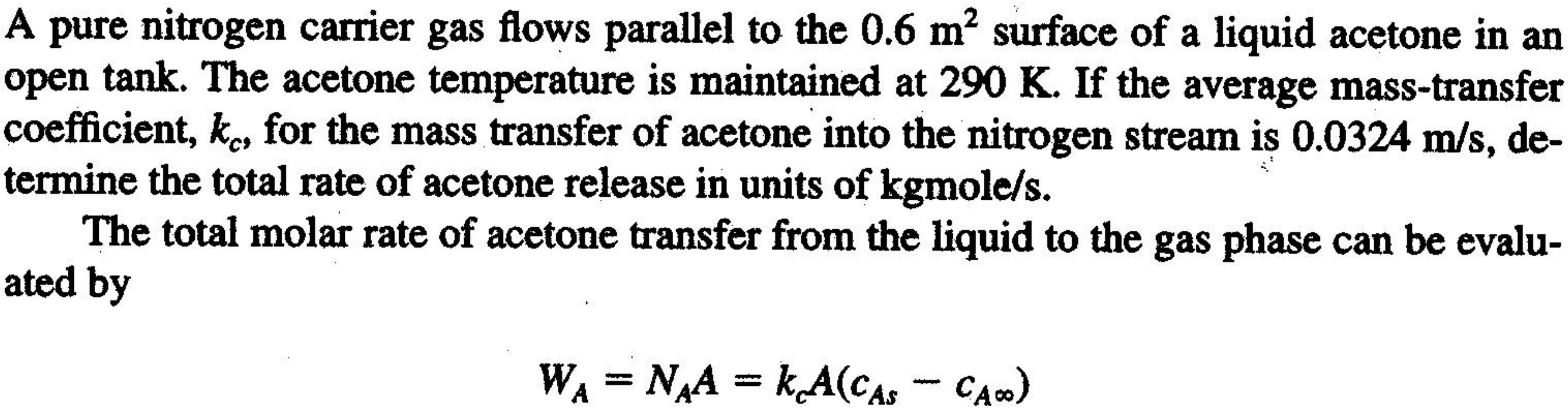
The small pore diameter enhances the value for α because the diffusion of the large catalase molecule is significantly hindered inside the pore relative to the smaller lysozyme molecule.

Convective Mass Transfer

- Mass transfer between moving fluid with surface or another fluid
- Forced convection
- Free/natural convection
- Rate equation analogy to Newton’s cooling equation

$$N_A = k_c - c_A$$

Example 8



A pure nitrogen carrier gas flows parallel to the 0.6 m^2 surface of a liquid acetone in an open tank. The acetone temperature is maintained at 290 K. If the average mass-transfer coefficient, k_c, for the mass transfer of acetone into the nitrogen stream is 0.0324 m/s, determine the total rate of acetone release in units of kgmole/s.

The total molar rate of acetone transfer from the liquid to the gas phase can be evaluated by

$$W_A = N_A A = k_c A(c_{As} - c_{A\infty})$$

The mass transfer area is specified as 0.6 m^2. At 290 K, acetone exerts a vapor pressure of 161 mm Hg or 2.148×10^4 Pa. Therefore, the concentration of acetone in the gas phase at the acetone surface is

$$c_{As} = \frac{P_A}{RT} = \frac{2.148 \times 10^4 \text{ Pa}}{\left(8.314 \frac{\text{Pa} \times \text{m}^3}{\text{kg mol} \times \text{K}}\right)(290 \text{ K})} = 8.91 \frac{\text{kg mol}}{\text{m}^3}$$

and the concentration of acetone in the nitrogen carrier gas is near zero, because the molar flowrate of the carrier gas is in a large excess relative to the rate of acetone transfer. Thus

$$W_A = k_c A(c_{As} - c_{A\infty}) = \left(0.0324 \frac{\text{m}}{\text{s}}\right)(0.6 \text{ m}^2)\left(8.91 \frac{\text{kg mol}}{\text{m}^3} - 0\right) = 0.1732 \frac{\text{kgmole}}{\text{s}}$$

Differential Equations

- Conservation of mass in a control volume:

$$\boxed{\iint_{c.s.} \rho \left(\mathbf{v} \cdot \mathbf{n} \right) dA + \frac{\partial}{\partial t} \iiint_{c.v.} \rho \, dV = 0}$$

- Or,

  in – out + accumulation – reaction = 0

- For in – out,
  - in x-dir, $n_{A,x}\Delta y\Delta z\big|_{x+\Delta x} - n_{A,x}\Delta y\Delta z\big|_{x}$
  - in y-dir, $n_{A,y}\Delta x\Delta z\big|_{y+\Delta y} - n_{A,y}\Delta x\Delta z\big|_{y}$
  - in z-dir, $n_{A,z}\Delta x\Delta y\big|_{z+\Delta z} - n_{A,z}\Delta x\Delta y\big|_{z}$
- For accumulation,

$$\frac{\partial \rho_A}{\partial t}\Delta x\Delta y\Delta z$$

- For reaction at rate r_A,

$$r_A \text{—} x \text{—} y \text{—} z$$

- Summing the terms and divide by λ x λ y λ z,

$$\frac{n_{A,x|x+\text{—}x} - n_{A,x|x}}{\text{—}x} + \frac{n_{A,y|y+\text{—}y} - n_{A,y|y}}{\text{—}y} + \frac{n_{A,z|z+\text{—}z} - n_{A,z|z}}{\text{—}z} + \frac{\P r_A}{\P t} - r_A = 0$$

  - with control volume approaching 0,

$$\frac{\P}{\P x} n_{A,x} + \frac{\P}{\P y} n_{A,y} + \frac{\P}{\P z} n_{A,z} + \frac{\P r_A}{\P t} - r_A = 0$$

- We have the continuity equation for component A, written as general form:

$$\boxed{\nabla \cdot \mathbf{n}_A + \frac{\partial \rho_A}{\partial t} - r_A = 0}$$

- For binary system;

$$\nabla \cdot \left(\mathbf{n}_A + \mathbf{n}_B \right) + \frac{\partial \left(\rho_A + \rho_B \right)}{\partial t} - \left(r_A + r_B \right) = 0$$

$$\mathbf{n}_A + \mathbf{n}_B = \rho_A \mathbf{v}_A + \rho_B \mathbf{v}_B = \rho \mathbf{v}$$

- but $r_A = -r_B$
- and

- So by conservation of mass,

$$\boxed{\cap \times r\,\mathbf{v} + \frac{\P r}{\P t} = 0}$$

- Written as substantial derivative,

$$\frac{Dr}{Dt} + r \cap \times \mathbf{v} = 0$$

  - For species A,

$$\frac{r\,Dw_A}{Dt} + \cap \times \mathbf{j}_A - r_A = 0$$

- In molar terms,

$$\nabla \cdot \mathbf{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0$$

  - For the mixture,

$$\nabla \cdot \left(\mathbf{N}_A + \mathbf{N}_B\right) + \frac{\partial \left(c_A + c_B\right)}{\partial t} - (R_A + R_B) = 0$$

  - And for stoichiometric reaction,

$$\nabla \cdot c\mathbf{V} + \frac{\partial c}{\partial t} - (R_A + R_B) = 0$$