Transport Phenomena

Mass Transfer

(1 Credit Hour)

$\mu\ \alpha\ k\ v\ D_{AB}\ U_i\ U_o\ U_D$

$h_i\ h_o\ Pr\ f\ Gr\ Re\ Le$

$Nu\ Sh\ Pe\ Sc\ k_c\ K_c\ \mathrm{d}$

$\Delta\ \rho\ \Sigma\ \Pi\ \partial\ \int\ \nabla$

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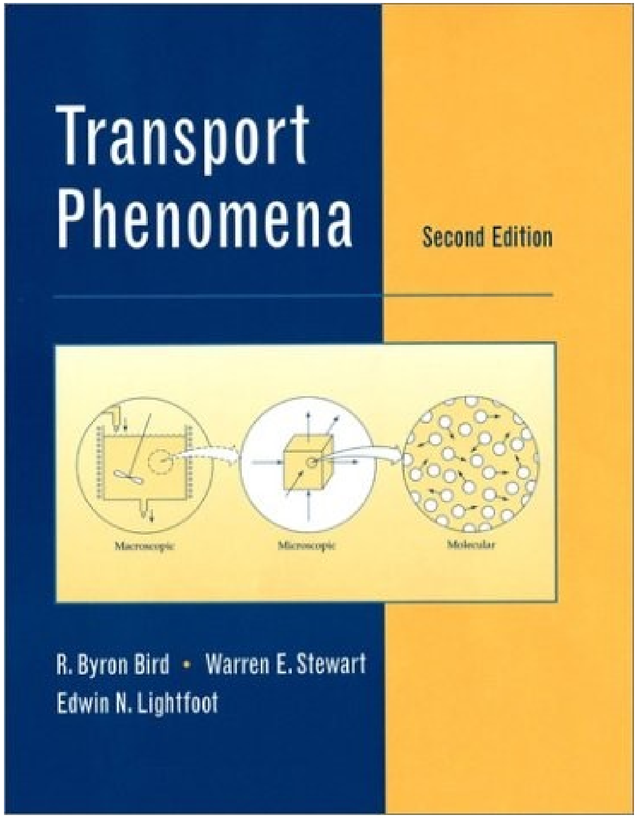
The Text Book

Please read through.



Bird, R.B. Stewart, W.E. and Lightfoot, E.N. (2002). Transport Phenomena. 2nd ed. John Wiley & Sons, Inc. Singapore.

Transfer processes

For a transfer or rate process

$$Rate\ of\ a\ quantity \propto driving\ force$$

$$Rate\ of\ a\ quantity \propto area\ for\ the\ flow\ of\ the\ quantity$$

$$Rate\ of\ a\ quantity = \left(\frac{1}{resistance}\right) \times Area \times driving\ force$$

$$Rate\ of\ a\ quantity = conductance \times Area \times driving\ force$$

$$Flux\ of\ a\ quantity = conductance \times driving\ force$$

Conductance is a transport property.

Compare the above equations with Ohm's law of electrical conductance

Transfer processes

$$Rate\,of\;\;a\;quantity = \frac{change\,in\;the\;quanity}{change\,in\;time}$$

$$Flux\;of\;\;a\;quantity = \frac{rate\,of\;\;the\;quantity}{area\;for\;\;flow\,of\;\;the\;quantity}$$

$$Gradient\,of\;\;a\;quantity = \frac{change\,in\;the\;quanity}{change\,in\;distance}$$

Transfer processes

In chemical engineering, we study three transfer processes (rate processes), namely

- Momentum transfer or Fluid flow
- Heat transfer
- Mass transfer

The study of these three processes is called as transport phenomena.

Transfer processes

Transfer processes are either:

- Molecular (rate of transfer is only a function of molecular activity), or
- Convective (rate of transfer is mainly due to fluid motion or convective currents)

Unlike momentum and mass transfer processes, heat transfer has an added mode of transfer called as radiation heat transfer.

Summary of transfer processes

Rate Process	Driving force	Conductance (Transport property)	Law for molecular transfer
Momentum transfer	Velocity gradient	Viscosity (Kinematic viscosity)	Newton's law of viscosity
Heat transfer	Temperature gradient	Thermal conductivity (Thermal diffusivity)	Fourier's law
Mass transfer	Concentration gradient (chemical potential gradient)	Mass diffusivity	Fick's law

Molecular rate laws

Newton’s law of viscosity (modified)

$$\tau_{zx} = -\nu \frac{d(u_x \rho)}{dz}$$

Fourier’s law of conduction heat transfer (modified)

$$\frac{q_z}{A} = -\alpha \frac{d(\rho c_p T)}{dz}$$

Fick’s law of molecular diffusion

$$J_{Az} = -D_A \frac{dc_A}{dz}$$

Molecular rate laws

The terms $(\rho \cdot u_x)$, $(\rho \cdot c_p \cdot T)$, c_A *are concentration terms and are momentum, heat, and mass (molar) concentrations having SI units of* $(\text{kg}\cdot\text{m}\cdot\text{s}^{-1})/\text{m}^3$, J/m^3, *and* mol/m^3, *respectively.*

μ, k, and D_A are called *transport properties.*

ν, α, and D_A are called *transport diffusivities.*

Each transport diffusivity has the SI unit of m^2/s.

Ratios of transport diffusivities

Prandtl number is the ratio of molecular diffusivity of momentum (kinematic viscosity) to molecular diffusivity of heat (thermal diffusivity).

Schmidt number is the ratio of molecular diffusivity of momentum (kinematic viscosity) to molecular diffusivity of mass.

Lewis number is the ratio of molecular diffusivity of heat (thermal diffusivity) to molecular diffusivity of mass.

Ratios of transport diffusivities

Group	Symbol	Definition	Formula	Applications
Prandtl number	Pr	$\dfrac{\text{molecular diffusivity of momentum}}{\text{molecular diffusivity of heat}}$ Note: Molecular diffusivity of momentum is also called as kinematic viscosity and molecular diffusivity of heat is also called as thermal diffusivity.	$\dfrac{\nu}{\alpha} = \dfrac{\mu/\rho}{k/(\rho \cdot c_p)}$ $= \dfrac{c_p \cdot \mu}{k}$	Simultaneous heat and momentum transfer
Schmidt number	Sc	$\dfrac{\text{molecular diffusivity of momentum}}{\text{molecular diffusivity of mass}}$ Note: Molecular diffusivity of mass is also called as mass diffusivity or diffusion coefficient.	$\dfrac{\nu}{D_{ij}} = \dfrac{\mu/\rho}{D_{ij}}$ $= \dfrac{\mu}{\rho \cdot D_{ij}}$	Simultaneous mass and momentum transfer
Lewis number	Le	$\dfrac{\text{molecular diffusivity of heat}}{\text{molecular diffusivity of mass}}$	$\dfrac{\alpha}{D_{ij}} = \dfrac{k/(\rho \cdot c_p)}{D_{ij}}$ $= \dfrac{k}{\rho \cdot c_p \cdot D_{ij}}$	Simultaneous heat and mass transfer

Rapid and brief introduction to mass transfer

Mass transfer is basically of two types

- Molecular mass transfer
- Convective mass transfer

Mass transfer can be within a single phase (homogeneous) or between phases. In the latter case it is called as "interphase mass transfer".

Rapid and brief introduction to mass transfer

Fick's Law of mass transfer

$$J_{Az} = -D_A \frac{dc_A}{dz}$$

A more general driving force is based on chemical potential gradient (μ_c)

$$J_{Az} = -c_A \frac{D_A}{RT} \frac{d\mu_c}{dz}$$

Rapid and brief introduction to mass transfer

Where,

$$\mu_c = \mu^o + RT \ln c_A$$

μ^o is the chemical potential at the standard state.

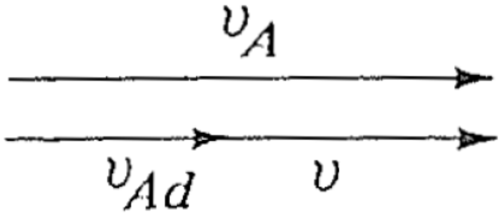
Apart from difference in concentration, a chemical potential gradient can also be obtained by temperature difference (thermal diffusion or Soret effect), pressure difference, differences in gravity forces, magnetic forces, etc. See Ref. 5, Chapter 24.

Rapid and brief introduction to mass transfer

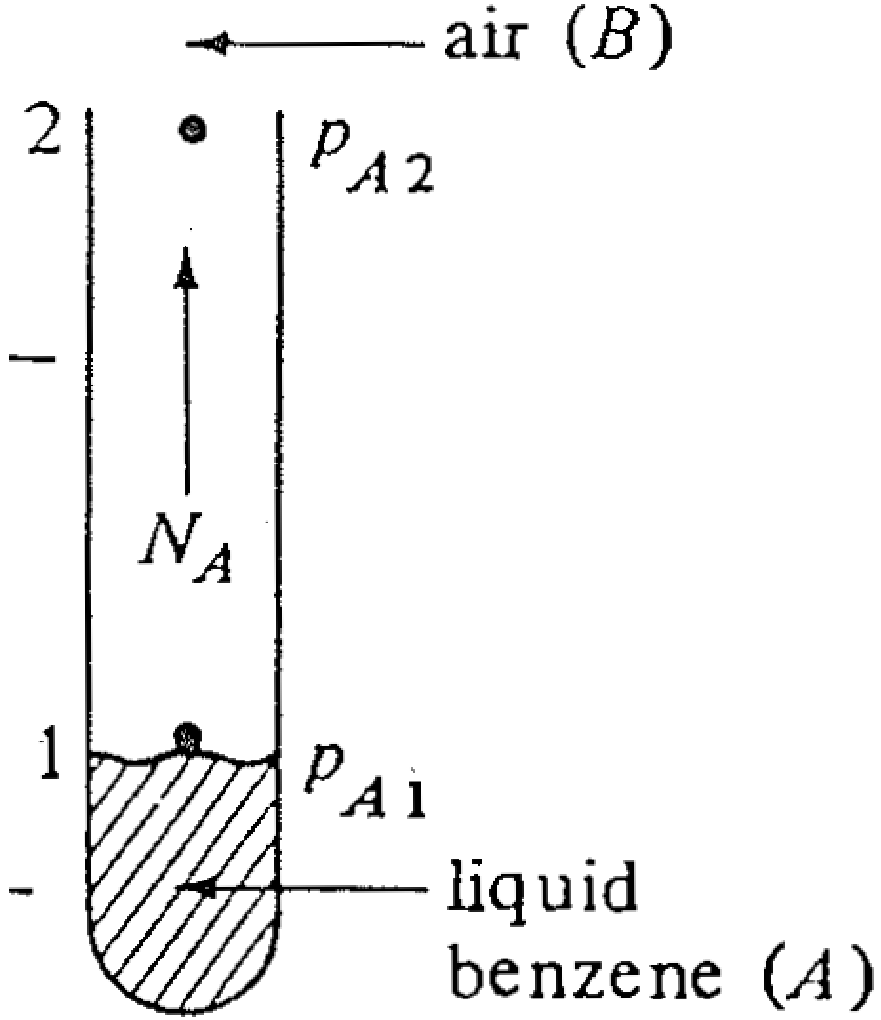
Mass is often transferred simultaneously by molecular phenomenon which is described by Fick's law and by convective flow (occurs say due to concentration or pressure differences). In these situations, one may write

Total velocity of A = diffusional velocity of A + average bulk velocity

$$u_A = u_{AD} + u$$



Rapid and brief introduction to mass transfer [2]



Rapid and brief introduction to mass transfer

For a binary system (*A* and *B*) with a constant average velocity in the *z*-direction, the molar flux in the *z*-direction relative to the molar-average velocity may be expressed by:

$$J_{Az} = c_A(u_{Az} - u_z)$$

Turbulent mass diffusivities

Momentum transfer:

$$\tau_{zx} = -\left(\frac{\mu}{\rho} + \varepsilon_M\right)\frac{d(u_x\rho)}{dz}$$

Heat transfer:

$$\frac{q_z}{A} = -(\alpha + \varepsilon_H)\frac{d(\rho c_p T)}{dz}$$

Mass transfer:

$$J_{Az} = -(D_A + \varepsilon_D)\frac{dc_A}{dz}$$

ε_M , ε_H , and ε_D are momentum, heat, and mass turbulent or eddy diffusivities. Each has the units of m^2/s.

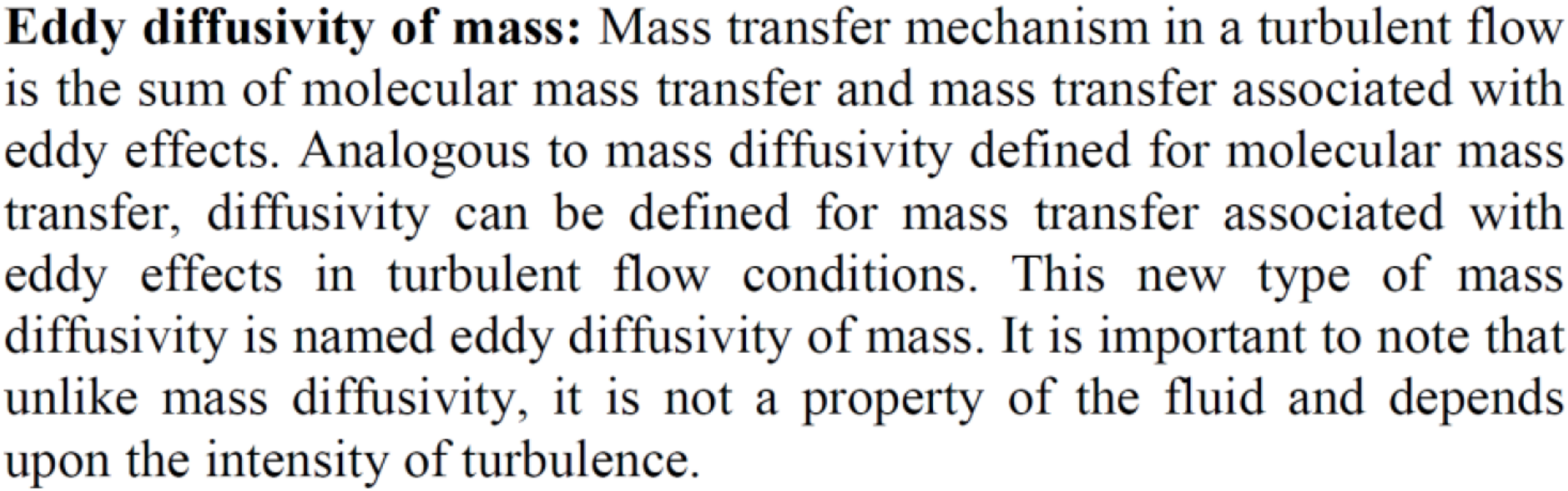
Turbulent mass diffusivities

Are you observing again a similarity among the various rate processes?

Turbulent mass diffusivities

These eddy diffusivities are unlike molecular diffusivities and depend upon the hydrodynamics and geometric factors of a system.

For example defining!



Eddy diffusivity of mass: Mass transfer mechanism in a turbulent flow is the sum of molecular mass transfer and mass transfer associated with eddy effects. Analogous to mass diffusivity defined for molecular mass transfer, diffusivity can be defined for mass transfer associated with eddy effects in turbulent flow conditions. This new type of mass diffusivity is named eddy diffusivity of mass. It is important to note that unlike mass diffusivity, it is not a property of the fluid and depends upon the intensity of turbulence.

Convective mass transfer

Similar to Newton's rate equation for convective heat transfer, one can define convective mass transfer equation as below:

$$N_A = k_c \cdot (c_{As} - c_A)$$

c_{As} is concentration of A (say benzoic acid) in solution at the solid (say benzoic acid pipe) surface and c_A is concentration within the bulk of the fluid flowing through the solid pipe. The units of k_c depend on the concentration units. Mass transfer coefficients are sometimes defined in terms of a, i.e., $k_c a$ where, a is interfacial area per unit volume of the contactor. The units of a are m^2/m^3.

Convective mass transfer

Like heat transfer coefficient, mass transfer coefficient depends upon various factors such as characteristic length (geometry), velocity, viscosity, density of the flowing fluid, product of acceleration due to gravity and concentration difference (buoyancy), and molecular mass diffusivity. Using dimensional analysis similar equation that can be derived for heat transfer can be obtained for mass transfer:

Convective mass transfer

Heat transfer: $Nu = f(Re, Pr, Gr)$

Mass transfer: $Sh = f(Re, Sc, Ar)$

Momentum transfer [4]: $Eu = f\left(Re, \frac{L}{d}, \frac{e}{d}\right)$

Convective mass transfer

Sherwood number: $Sh = \dfrac{k_c l}{D_A}$

Archimedes Number: $Ar = \dfrac{l^3 \rho g \Delta \rho_A}{\mu^2}$

Euler number: $Eu = \dfrac{\Delta p}{\rho u^2} = \dfrac{h_f}{u^2 / g}$

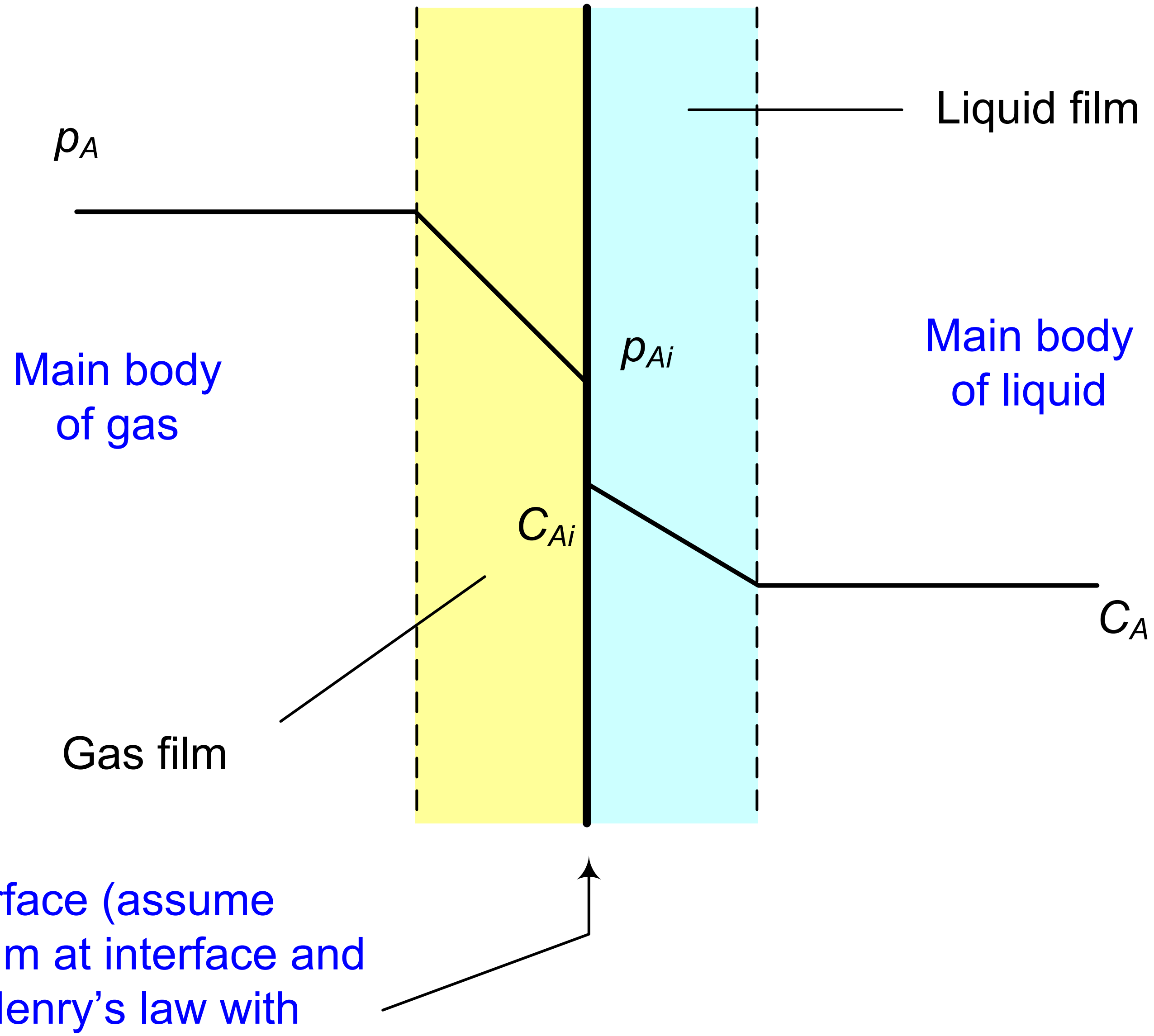
Convective mass transfer correlations

For turbulent flow inside pipes or tubes

$$Sh = 0.023 Re^{0.83} Sc^{1/3}$$

Compare the equation for heat transfer

Interphase mass transfer: Two film theory



Interface (assume equilibrium at interface and use Henry's law with constant value of Henry's constant)

Two-film theory: Overall mass transfer coefficient

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}$$

$$\frac{1}{K_L} = \frac{1}{mk_G} + \frac{1}{k_L}$$

Diffusion coefficient or mass diffusivity

- The proportionality coefficient for the Fick's law for molecular transfer is mass diffusivity or diffusion coefficient.
- Like viscosity and thermal conductivity, diffusion coefficient is also measured under molecular transport conditions and not in the presence of eddies (turbulent flow).

The SI units of mass diffusivity are m^2/s.

$$1\ m^2/s = 3.875\times10^4\ ft^2/h$$

$$1\ cm^2/s = 10^{-4}\ m^2/s = 3.875\ ft^2/h$$

$$1\ m^2/h = 10.764\ ft^2/h$$

$$1\ \text{centistokes} = 10^{-2}\ cm^2/s$$

Diffusion coefficient or mass diffusivity

Why do we use a small diameter capillary for the measurement of viscosity of a liquid?

Bring to mind Ostwald’s viscometer.

Ranges of mass diffusivities

Diffusion coefficients are generally highest for gases, lower for liquids, and lowest for solids. The ranges are as follow [4]:

For gases: 5×10^{-6} to 1×10^{-5} m^2/s

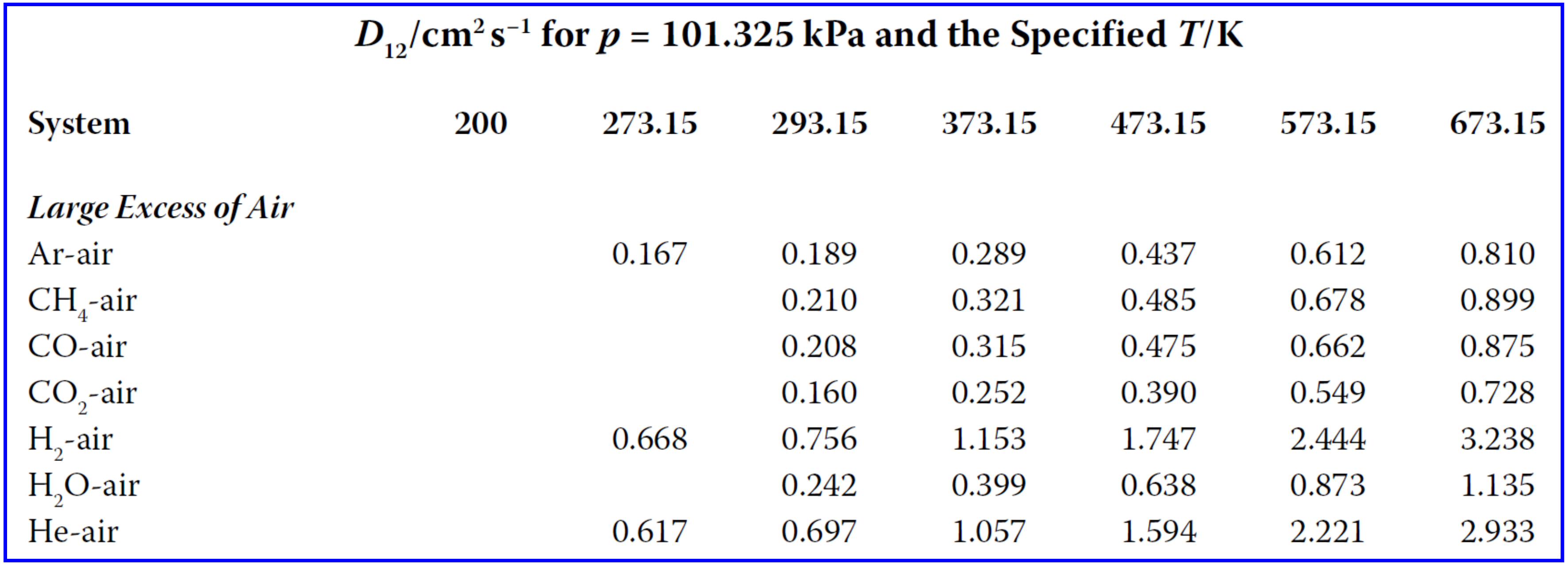
For liquids: 1×10^{-10} to 1×10^{-9} m^2/s

For solids: 1×10^{-14} to 1×10^{-10} m^2/s

Diffusion coefficient or mass diffusivity

- Diffusion coefficients may be obtained by doing experiments in the laboratory.
- Diffusion coefficients may be obtained from experimentally measured values by various researchers in the field. Many of these data is collected in handbooks, etc.
- When experimental values are not found, diffusion coefficients may be estimated using theoretical, semi-empirical (semi-theoretical), or empirical correlations.

Experimental diffusion coefficients [6]



D_{12}/cm^2 s^{-1} for p = 101.325 kPa and the Specified T/K

System	200	273.15	293.15	373.15	473.15	573.15	673.15
Large Excess of Air							
Ar-air		0.167	0.189	0.289	0.437	0.612	0.810
CH_4-air			0.210	0.321	0.485	0.678	0.899
CO-air			0.208	0.315	0.475	0.662	0.875
CO_2-air			0.160	0.252	0.390	0.549	0.728
H_2-air		0.668	0.756	1.153	1.747	2.444	3.238
H_2O-air			0.242	0.399	0.638	0.873	1.135
He-air		0.617	0.697	1.057	1.594	2.221	2.933

Experimental diffusion coefficients: References

- Lide, D.R. 2007. CRC Handbook of chemistry and physics. 87th ed. CRC Press.
- Poling, B.E.; Prausnitz, J.H.; O'Connell, J.P. 2000. The properties of gases and liquids. 5th ed. McGraw-Hill.
- Green. D.W.; Perry, R.H. 2008. Perry's chemical engineers' handbook. 8th ed. McGraw-Hill.

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Diffusion coefficient for gases at low pressure

For gases at low pressure (low density gases), the diffusion coefficient

- o decreases with pressure $D_{AB} \propto \frac{1}{P}$
- o increases with temperature, $D_{AB} \propto \mathrm{T}^{3/2}$ [4], and
- o virtually remains constant with gas composition.

Diffusion coefficient for gases at low pressure: Estimation

Based on kinetic theory and corresponding states principle the following equation [1] can be used for obtaining the mass diffusivity of gases at low pressures.

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

Here, D_{AB} is in cm²/s, T in K, and p in atm. See Table below.

Diffusion coefficient for gases at low pressure: Estimation

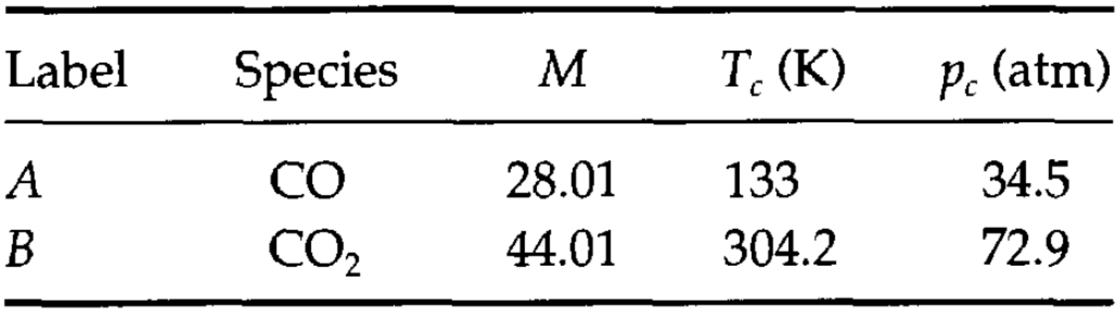
Situation	*a*	*b*
For non-polar gas pairs (excluding He and H_2)	2.745×10^{-4}	1.823
H_2O and a nonpolar gas	3.640×10^{-4}	2.334

The equation fits the experimental data well at atmospheric pressure within an average error of 6–8%.

Diffusion coefficient for gases at low pressure: Estimation

Example 17.2-1 [1]:

Estimate D_{AB} for the system CO-CO_2 at 296.1 K and 1 atm total pressure. Use the equation just described. *A* is CO and *B* is CO_2. The molecular weight and critical properties of the species are given as below:



Label	Species	M	T_c (K)	p_c (atm)
A	CO	28.01	133	34.5
B	CO_2	44.01	304.2	72.9

Homework problem

Estimate D_{AB} for the systems CO_2-N_2O, CO_2-N_2, CO_2-O_2 , N_2-O_2, and H_2-N_2 at 273.2 and 1 atm and compare the results with the experimental values given in Table 17.1-1 [1]. Also for H_2O-N_2 at 308 K and 1 atm and compare similarly.

Diffusion coefficient for gases at low pressure: Estimation

Based on the Chapman-Enskog theory, the following equation (sometimes called as Hirschfelder equation) using ideal gas law for the determination of total concentration "*c*" may be written:

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

$$= 0.0018583\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{p\sigma_{AB}^2\Omega_{\mathscr{D},AB}}$$

Here, D_{AB} is in cm^2/s, σ_{AB} is Å, and p in atm.

The mass diffusivity D_{AB} for binary mixtures of nonpolar gases is predictable within about 5% by kinetic theory.

Diffusion coefficient for gases at low pressure: Estimation

The parameters σ_{AB} and ε_{AB} could, in principle, be determined directly from accurate measurement of D_{AB} over a wide range of temperatures. Suitable data are not yet available for many gas pairs, one may have to resort to using some other measurable property, such as the viscosity of a binary mixture of *A* and *B*. In the event that there are no such data, then we can estimate them from the following combining rules for non-polar gas pairs.

$$\boxed{\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}}$$

$$\boxed{\sigma_{AB} = \tfrac{1}{2}(\sigma_A + \sigma_B)}$$

Use of these combining rules enables us to predict values of D_{AB} within about 6% by use of viscosity data on the pure species *A* and *B*, or within about 10% if the Lennard-Jones parameters for *A* and *B* are estimated from boiling point data as discussed in Chapter 1 of the text [1].

Diffusion coefficient for gases at low pressure: Estimation

The Lennard-Jones parameters can be obtained from the Appendix of the text book [1] and in cases when not known can be estimated as below:

$$\varepsilon/\kappa = 0.77T_c \qquad \sigma = 0.841\tilde{V}_c^{1/3} \quad \text{or} \quad \sigma = 2.44(T_c/p_c)^{1/3}$$

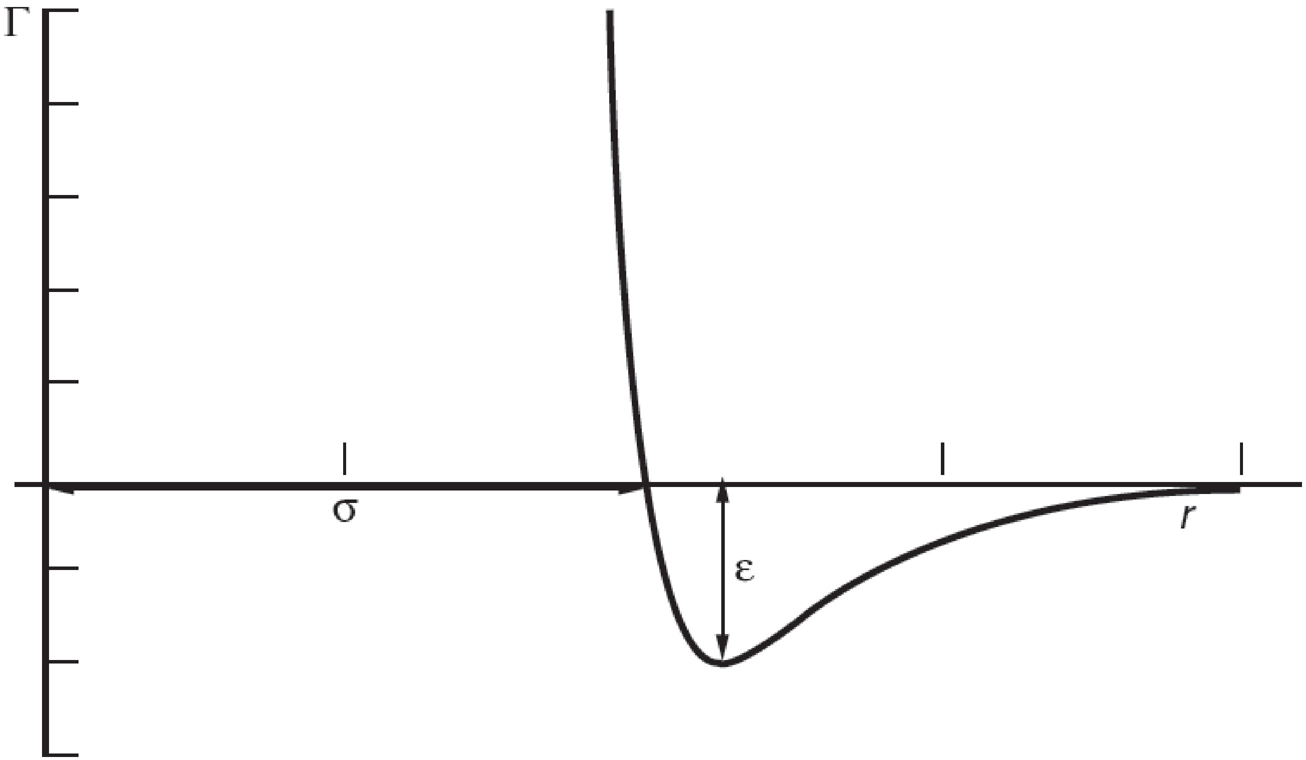
$$\varepsilon/\kappa = 1.15T_b \qquad \sigma = 1.166\tilde{V}_{b,\text{liq}}^{1/3}$$

$$\varepsilon/\kappa = 1.92T_m \qquad \sigma = 1.222\tilde{V}_{m,\text{sol}}^{1/3}$$

Here ε/κ and T are in K, σ is in Ångström units (1 Å = 10^{-10} m), $\tilde{V}$ is in cm^3/g-mole, and p_c is in atmospheres.

The boiling conditions are normal conditions, i.e., at 1 atm.

Lennard-Jones potential [7]



Plot of the Lennard-Jones potential as a function of distance between molecules.

Diffusion coefficient for gases at low pressure: Estimation

- The collision integral can be obtained using dimensionless temperature $\kappa T/\varepsilon_{AB}$ from the Appendix of the text book [1]. To avoid interpolation, a graphical relationship for collision integral is given in the next slide.
- A mathematical relationship by Neufeld is recommended for computational (spreadsheet) work [5].

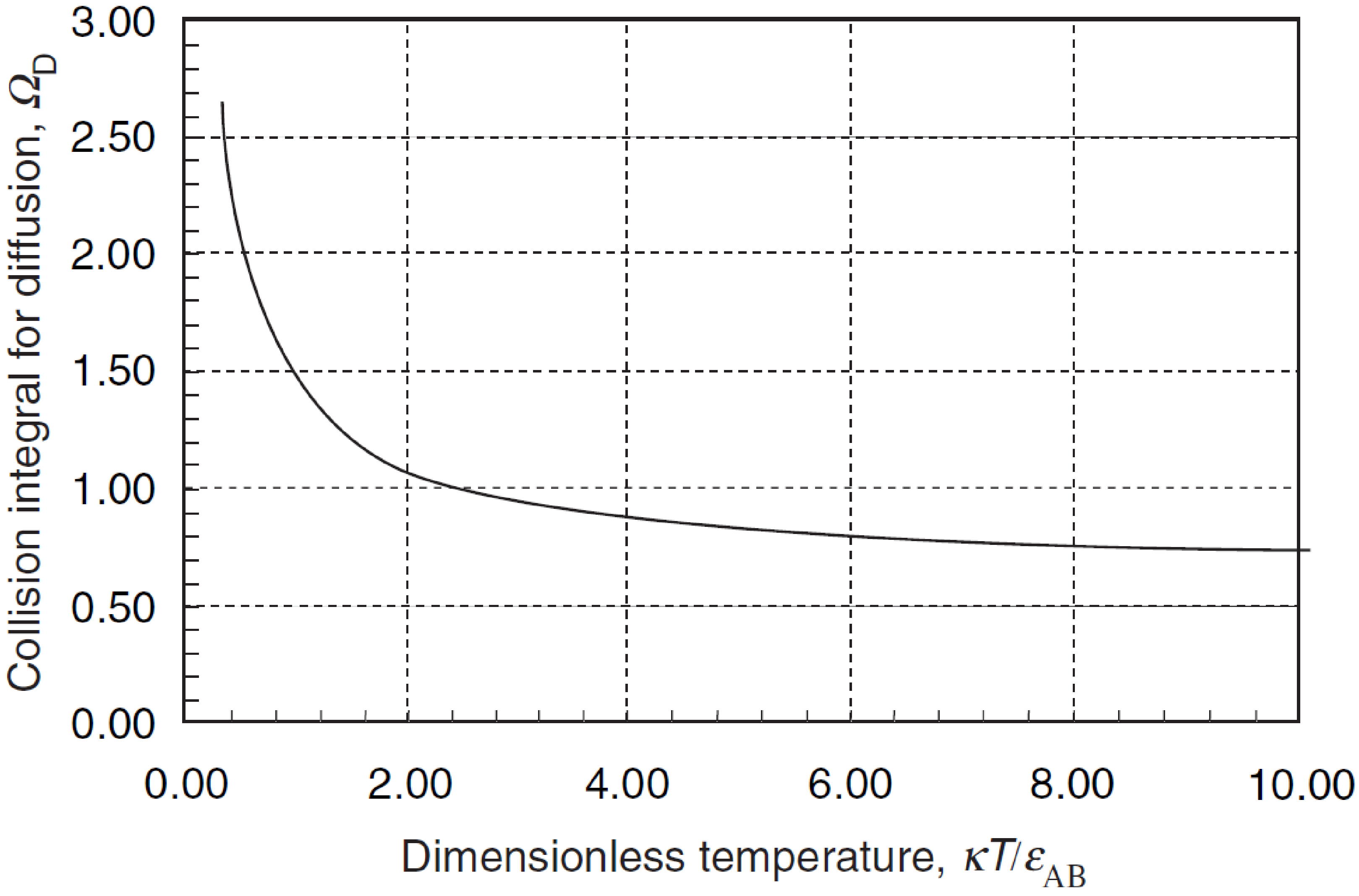
$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

$T^* = kT/\varepsilon_{AB}$ $\quad A = 1.06036$ $\quad B = 0.15610$

$C = 0.19300$ $\quad D = 0.47635$ $\quad E = 1.03587$

$F = 1.52996$ $\quad G = 1.76474$ $\quad H = 3.89411$

Diffusion coefficient for gases at low pressure: Estimation [4]



Diffusion coefficient for gases at low pressure: Estimation

The effect of composition (concentration) is not accommodated in the above equation. The effect of concentration in real gases is usually negligible and easily ignored, especially at low pressures. For high pressure gases, some effects, though small, are observed.

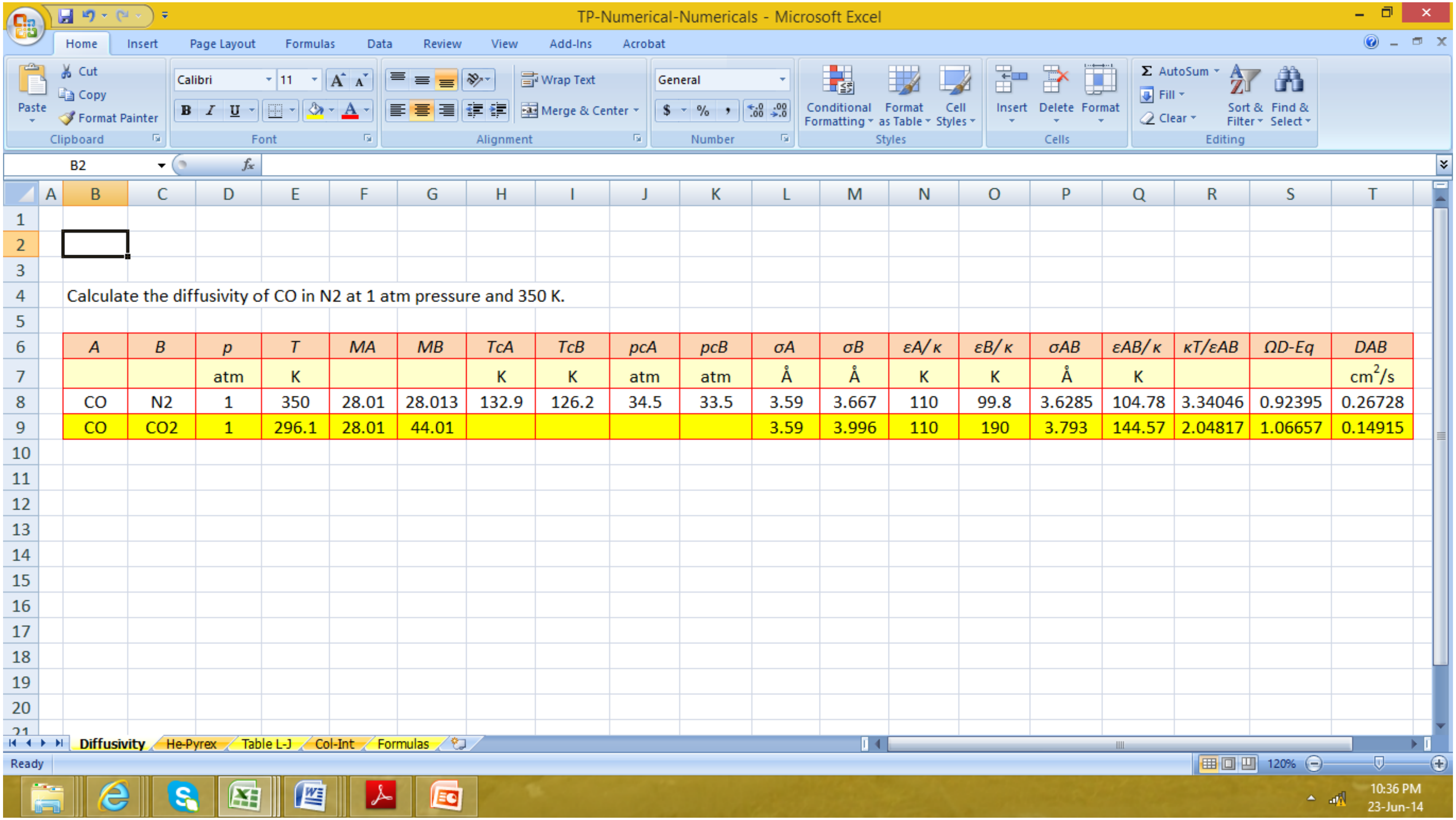
Diffusion coefficient for gases at low pressure: Estimation

Example 17.3-1 [1]:

Predict the value of D_{AB} for the system CO-CO_2 at 296.1 K and 1 atm total pressure.

Use the equation based on Chapman-Enskog theory as discussed above. The values of Lennard-Jones Potential and others may be found in Appendix E of the text [1].

Diffusion coefficient for gases at low pressure: Estimation



Calculate the diffusivity of CO in N2 at 1 atm pressure and 350 K.

A	B	p	T	MA	MB	TcA	TcB	pcA	pcB	σA	σB	εA/κ	εB/κ	σAB	εAB/κ	κT/εAB	ΩD-Eq	DAB
		atm	K			K	K	atm	atm	Å	Å	K	K	Å	K			cm^2/s
CO	N2	1	350	28.01	28.013	132.9	126.2	34.5	33.5	3.59	3.667	110	99.8	3.6285	104.78	3.34046	0.92395	0.26728
CO	CO2	1	296.1	28.01	44.01					3.59	3.996	110	190	3.793	144.57	2.04817	1.06657	0.14915

Diffusion coefficient for gases at low pressure: Estimation

The above equation (Hirschfelder equation) is used to extrapolate the experimental data. Using the above equation, the diffusion coefficient can be predicted at any temperature and any pressure below 25 atm [4] using the following equation.

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

Fuller's equation

Fuller's equation is an empirical equation that is also used at low pressures. The equation may be used for nopolar gas mixtures and polar-nonpolar mixtures [2]. The equation is less reliable than that of Hirschfelder equation described above.

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

Use T in K, p in atm, υ from the table given on the next slide. D_{AB} will be in cm^2/s.

Diffusion volumes to be used with Fuller's equation [4]

Atomic and structure diffusion-volume increments, v

C	16.5	Cl	19.5
H	1.98	S	17.0
O	5.48	Aromatic ring	−20.2
N	5.69	Heterocyclic ring	−20.2

Diffusion volumes for simple molecules, v

H_2	7.07	Ar	16.1	H_2O	12.7
D_2	6.70	Kr	22.8	$CCIF_2$	114.8
He	2.88	CO	18.9	SF_6	69.7
N_2	17.9	CO_2	26.9	Cl_2	37.7
O_2	16.6	N_2O	35.9	Br_2	67.2
Air	20.1	NH_3	14.9	SO_2	41.1

Use of Fuller's equation

Example problem [2]:

Normal butanol (*A*) is diffusing through air (*B*) at 1 atm abs. Using the Fuller's equation, estimate the diffusivity D_{AB} for the following conditions:

a) For 0 °C

b) 25.9 °C

c) 0 °C and 2.0 atm abs.

Homework Problems

1. Calculate the diffusion coefficient of methane in air at 20 oC and 1 atm. Use Fuller's equation.
2. Using Fuller's equation, calculate the diffusion coefficient of C_2H_5OH in air at 298 K and 1 atm.

Diffusion coefficient for multicomponent gas mixtures

Blanc's law:

$$D_{im} = \left(\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}} \right)^{-1}$$

May be good to ternary systems in which component *i* has very low concentration [5].

See Poling et al. [5] for additional discussion.

Diffusion coefficient for gases at high density

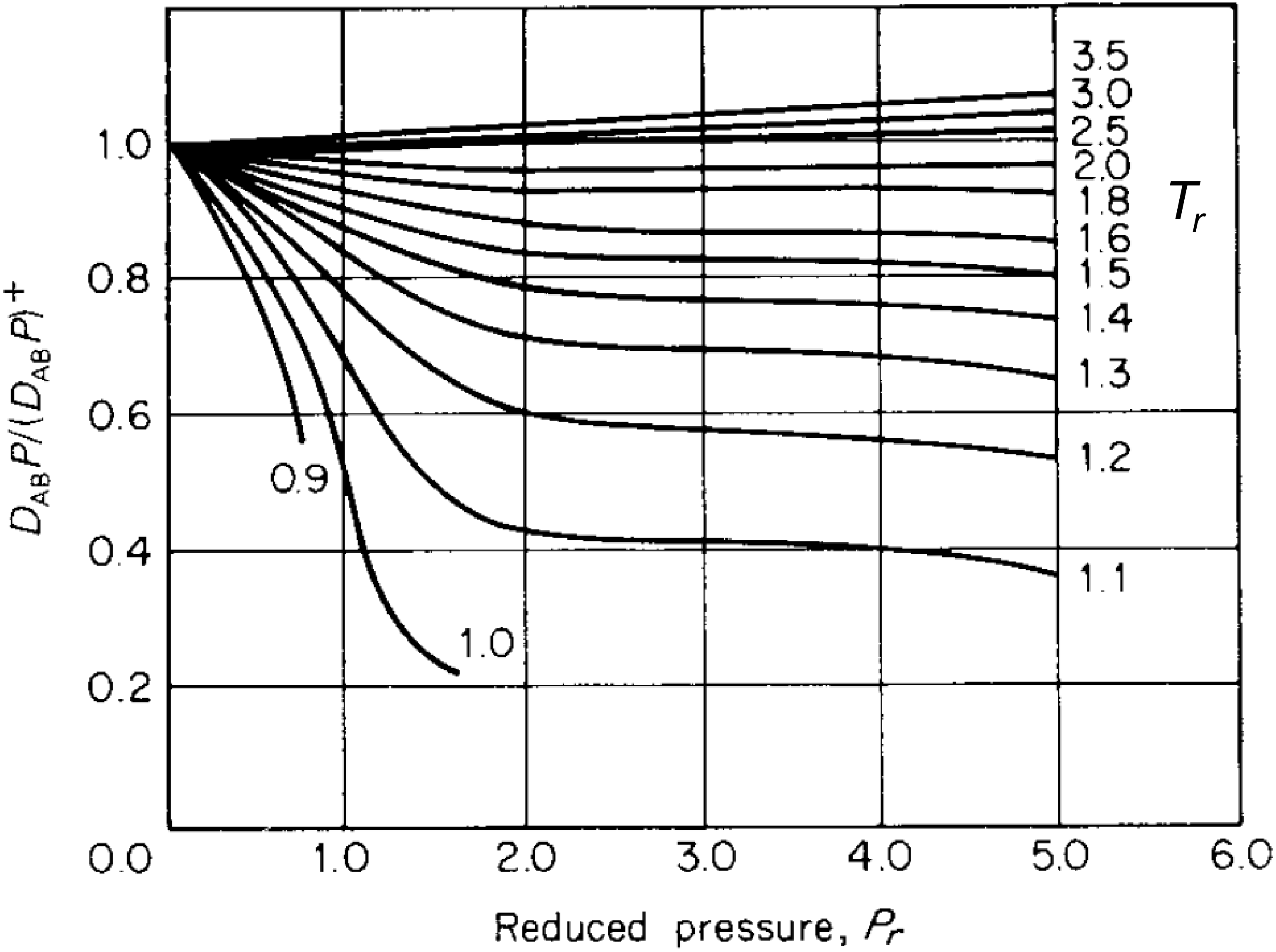
The behavior of gases at high pressures (dense gases) and of liquids is not well understood and difficult to interpret to a mathematical evaluation. The following approaches can be used for estimating the mass diffusivity of gases at high pressures.

Diffusion coefficient for gases at high density: Takahashi method [5]

$$\frac{D_{\mathrm{AB}}P}{(D_{\mathrm{AB}}P)^{+}} = f(T_r, P_r)$$

Here, T_r and p_r are pseudoreduced temperature and pseudoreduced pressure, respectively. p is in bar and D_{AB} is in cm^2/s. + sign suggests value at low pressure.

Diffusion coefficient for gases at high density: Takahashi method [5]



Diffusion coefficient for gas mixtures [1]

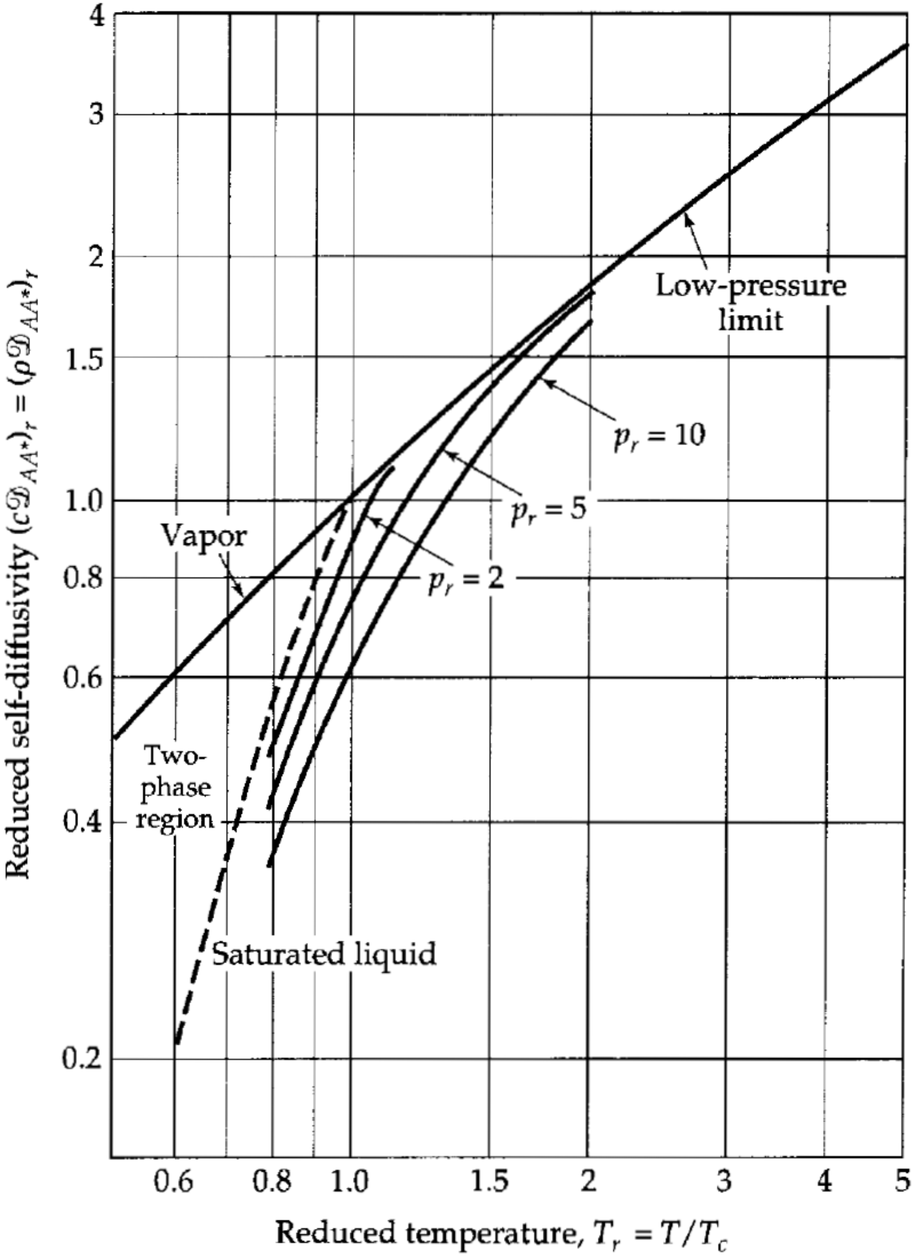


Fig. 17.2-1. A corresponding-states plot for the reduced self-diffusivity. Here $(c\mathscr{D}_{AA^*})_r = (\rho\mathscr{D}_{AA^*})_r$ for Ar, Kr, Xe, and CH_4 is plotted as a function of reduced temperature for several values of the reduced pressure. This chart is based on diffusivity data of J. J. van Loef and E. G. D. Cohen, *Physica A*, **156**, 522–533 (1989), the compressibility function of B. I. Lee and M. G. Kesler, *AIChE Journal*, **21**, 510–527 (1975), and Eq. 17.3-11 for the low-pressure limit.

Diffusion coefficient for gas mixtures [1]

$$c\mathscr{D}_{AB} = (c\mathscr{D}_{AB})_r (c\mathscr{D}_{AB})_c$$

The value of $(c\mathscr{D}_{AB})_r$ an be obtained from the graph above by knowing reduced temperature and reduced pressure.

$$T_r = \frac{T}{\sqrt{T_{cA} T_{cB}}}$$

$$p_r = \frac{p}{\sqrt{p_{cA} p_{cB}}}$$

$$(c\mathscr{D}_{AB})_c = 2.96 \times 10^{-6} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \frac{(p_{cA} p_{cB})^{1/3}}{(T_{cA} T_{cB})^{1/12}}$$

Where, D_{AB} is in cm^2/s, T in K, and p_c in atm.

Diffusion coefficient for gas mixtures

The above method is quite good for gases at low pressures. At high pressures, due to the lack of large number of experimental data, a comparison is difficult to make. The method is therefore suggested only for gases at low pressures.

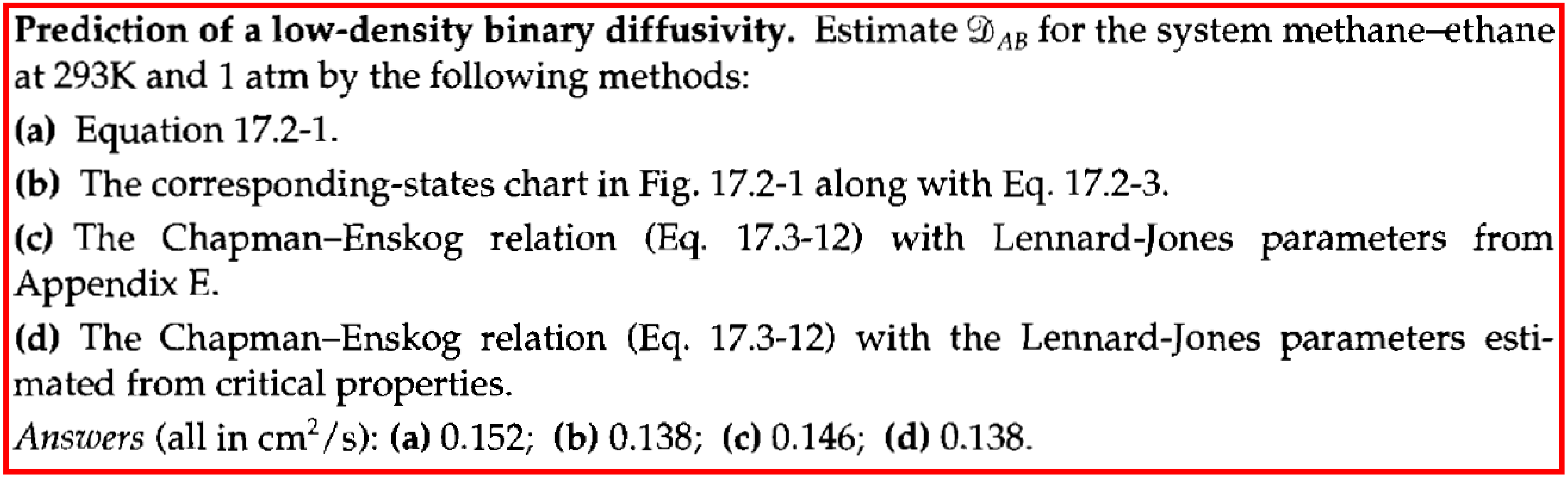
The value of cD_{AB} rather than D_{AB} is because cD_{AB} is usually found in mass transfer expressions and the dependence of pressure and temperature is simpler [1].

Diffusion coefficient for gas mixtures at high density

Example 17.2-3 [1]:

Estimate cD_{AB} for a mixture of 80 mol% CH_4 and 20 mol% C_2H_6 at 136 atm and 313 K. It is known that, at 1 atm and 293 K, the molar density is $c = 4.17 \times 10^{-5}$ gmol/cm^3 and D_{AB} 0.163 cm^2/s.

Problem 17 A.1 [1]



Prediction of a low-density binary diffusivity. Estimate $\mathscr{D}_{AB}$ for the system methane–ethane at 293K and 1 atm by the following methods:

(a) Equation 17.2-1.

(b) The corresponding-states chart in Fig. 17.2-1 along with Eq. 17.2-3.

(c) The Chapman–Enskog relation (Eq. 17.3-12) with Lennard-Jones parameters from Appendix E.

(d) The Chapman–Enskog relation (Eq. 17.3-12) with the Lennard-Jones parameters estimated from critical properties.

Answers (all in $\mathrm{cm^2/s}$): **(a)** 0.152; **(b)** 0.138; **(c)** 0.146; **(d)** 0.138.

Diffusion coefficient for liquid mixtures

Due to the not well defined theory for diffusion in liquids, empirical methods are required for the estimation of diffusion coefficients in liquids.

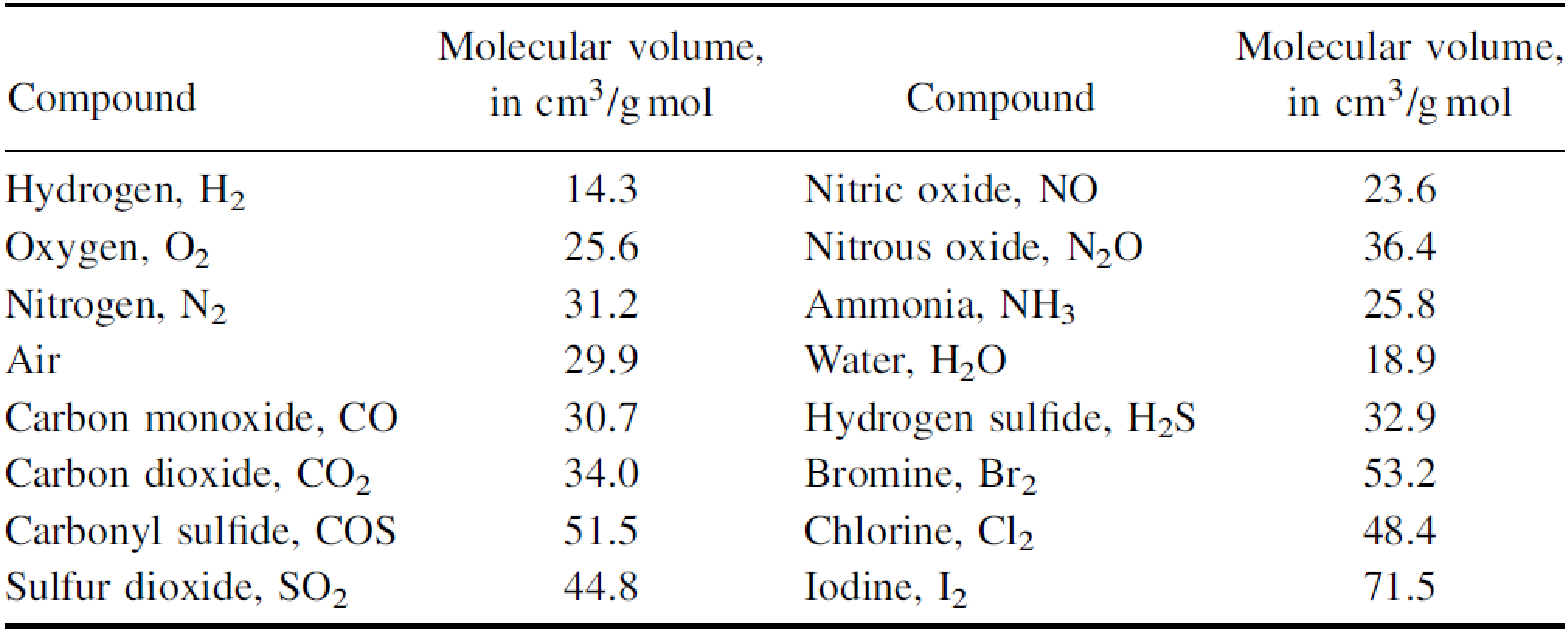
The following Wilke-Chang equation may be used for small concentration of *A* in *B* [1]:

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

Diffusion coefficient for liquid mixtures

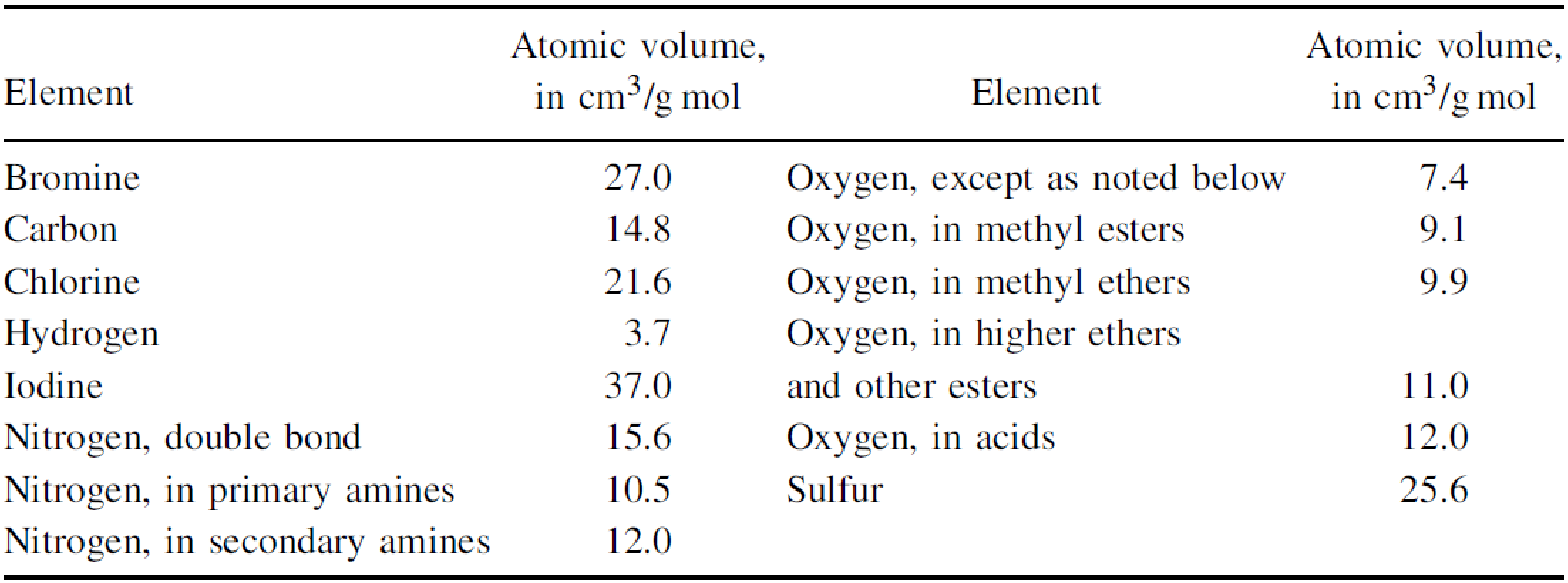
- In the above equation, $\tilde{V}$ is molar volume of solute A in cm^3/mol as liquid at its boiling point, μ is viscosity of solution in cP, ψ_B is an association parameter for the solvent, and T is absolute temperature in K. Recommended values of ψ_B are: 2.6 for water; 1.9 for methanol; 1.5 for ethanol; 1.0 for benzene, ether, heptane, and other unassociated solvents.
- The equation is good for dilute solutions of nondissociating solutes. For such solutions, it is usually good within ±10%.

Selected molar volumes at normal boiling points [4]

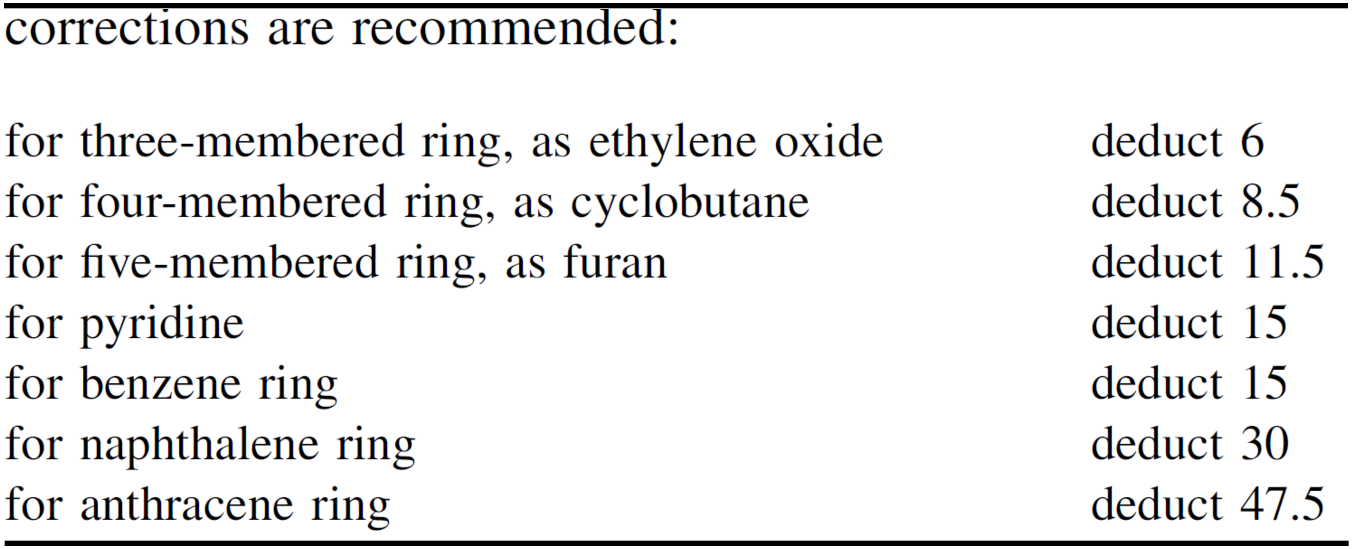


Compound	Molecular volume, in cm^3/g mol	Compound	Molecular volume, in cm^3/g mol
Hydrogen, H_2	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, N_2	31.2	Ammonia, NH_3	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H_2S	32.9
Carbon dioxide, CO_2	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

Atomic volumes for calculating molar volumes and corrections [4]



Element	Atomic volume, in $cm^3/g\,mol$	Element	Atomic volume, in $cm^3/g\,mol$
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers and other esters	11.0
Iodine	37.0	Oxygen, in acids	12.0
Nitrogen, double bond	15.6	Sulfur	25.6
Nitrogen, in primary amines	10.5		
Nitrogen, in secondary amines	12.0		



corrections are recommended:

for three-membered ring, as ethylene oxide	deduct 6
for four-membered ring, as cyclobutane	deduct 8.5
for five-membered ring, as furan	deduct 11.5
for pyridine	deduct 15
for benzene ring	deduct 15
for naphthalene ring	deduct 30
for anthracene ring	deduct 47.5

Diffusion coefficient for liquid mixtures

When molar volumes are not available, one may use the following equation after Tyn and Calus:

$$V_A = 0.285 V_c^{1.048}$$

V_c is critical volume in cm^3/gmol.

Diffusion coefficient for liquid mixtures

Example 17.4-1 [1]:

Estimate D_{AB} for a dilute solution of TNT (2,4,6-trinitrotoluene) in benzene at 15 °C. Take TNT as *A* and toluene as *B* component. Molar volume of TNT is 140 cm^3/mol.

Hint: As dilute solution, use viscosity of benzene instead of solution.

Example 5 [4, 418]:

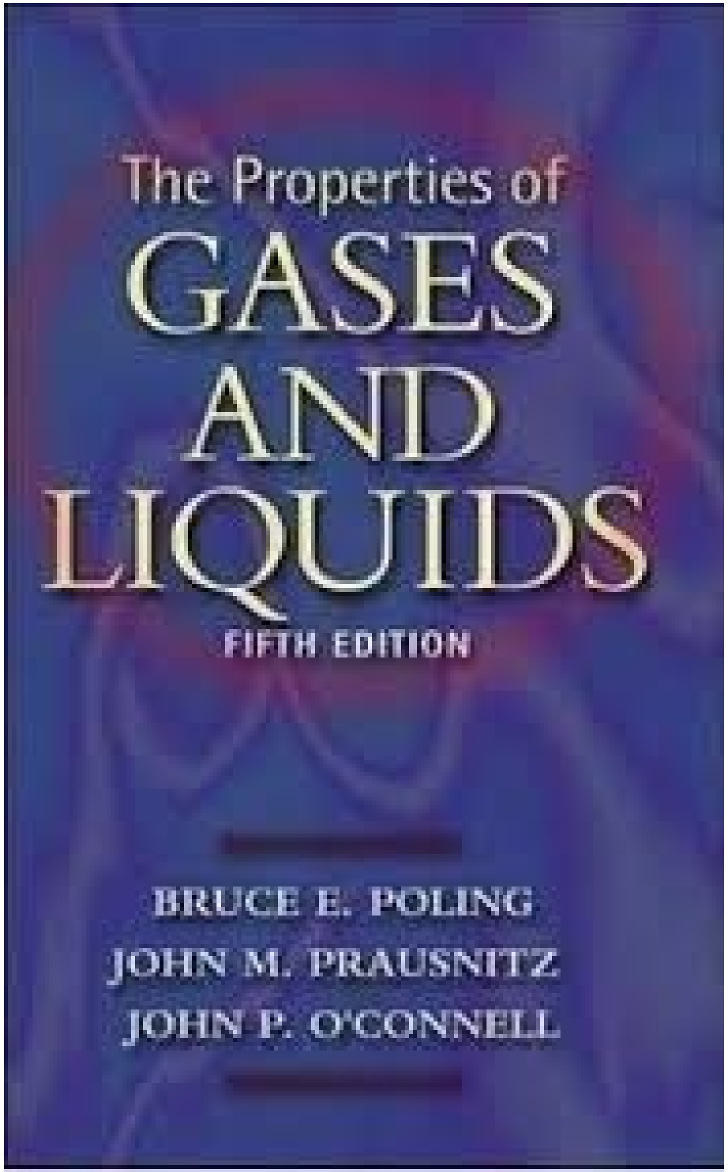
Estimate the diffusion coefficient of ethanol in a dilute solution of water at 10 °C.

Homework problem

Example 6.3-2 [2]:

Predict the diffusion coefficient of acetone (CH_3COCH_3) in water at 25 °C and 50 °C using the Wilke-Chang equation. The experimental value is 1.28 $\times 10^{-9}$ m^2/s at 25 °C.

Further reading



Poling, B.E.; Prausnitz, J.H.; O'Connell, J.P. 2000. The properties of gases and liquids. 5th ed. McGraw-Hill.

Excellent reference for the estimation of mass diffusivities. See Chapter 11 of the book.

Homework problems

Questions for discussions [1, pp. 538–539]:

1, 3, 4, and 7.

Problems [1, pp. 539–541]:

17A.4, 17A.5, 17A.6, 17A.9, and 17A.10.

Shell mass balance

Why do we need shell (small control element) mass balance?

Shell mass balance

We need, because, we desire to know what is happening inside. In other words, we want to know the differential or point to point molar flux and concentration distributions with in a system, i.e., we will represent the system in terms of differential equations. Macro or bulk balances such as that applied in material balance calculations only give input and output information and do not tell what happens inside the system.

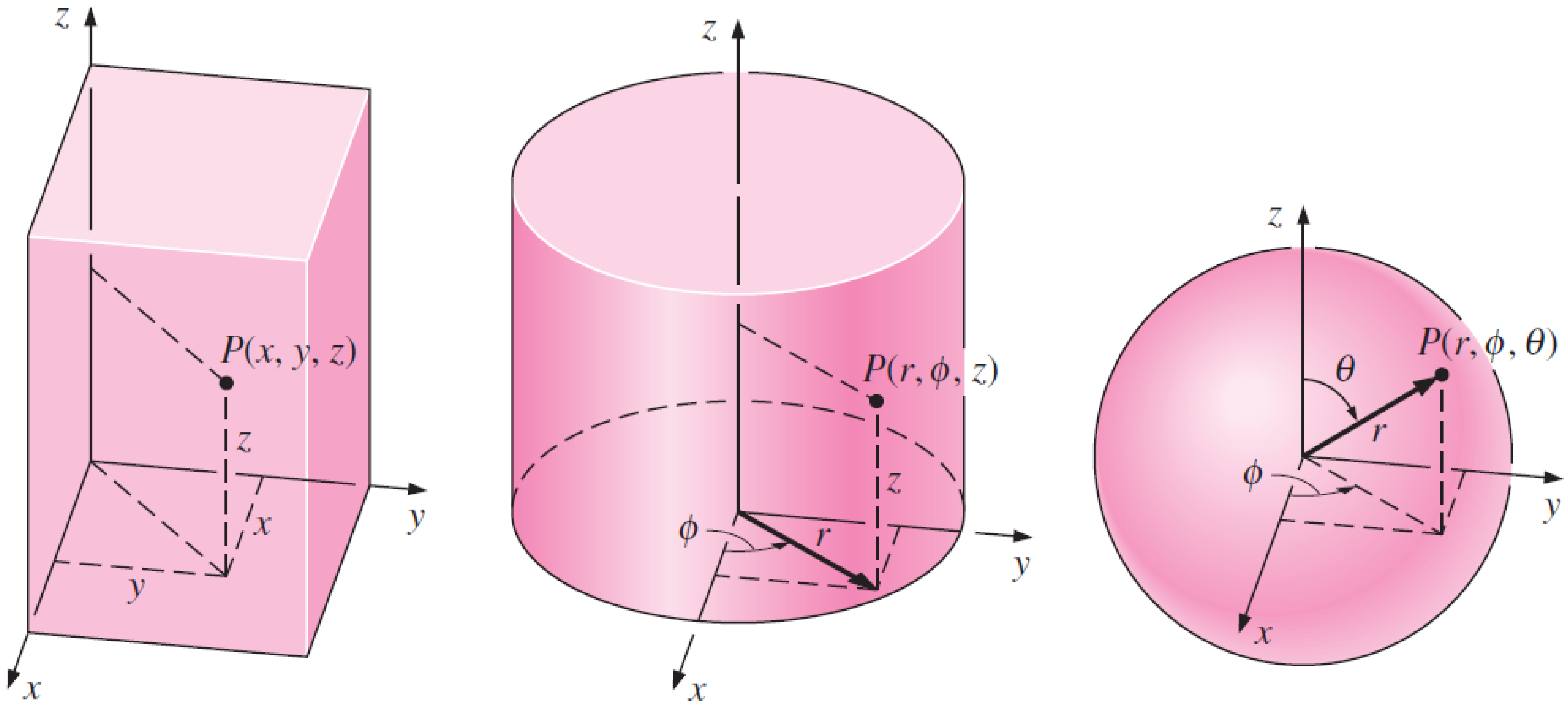
Steps involved in shell mass balance

- Select a suitable coordinate system (rectangular, cylindrical, or spherical) to represent the given problem.
- Accordingly, select a suitable small control element or thin shell of finite dimensions in the given system.
- Define the appropriate assumptions (steady-state, etc.) and apply mass balance over the shell geometry.
- Let the shell dimensions approach zero (differential dimensions) and using the definition of derivation, obtain the differential equations that describe the system. If only one direction is considered there will be one first order differential equation for a steady-state process. The solution of this equation gives the molar flux distribution.

Steps involved in shell mass balance

- Insert the definition of molar flux in the above differential equation, a second order differential equation will be the result.
- Define the appropriate boundary conditions and solve the second order differential equation to obtain the concentration profile and the values of the average flux.

Coordinate systems [8]



(*a*) Rectangular coordinates (*b*) Cylindrical coordinates (*c*) Spherical coordinates

See Appendix A.6 of the text [1].

General mass balance equation

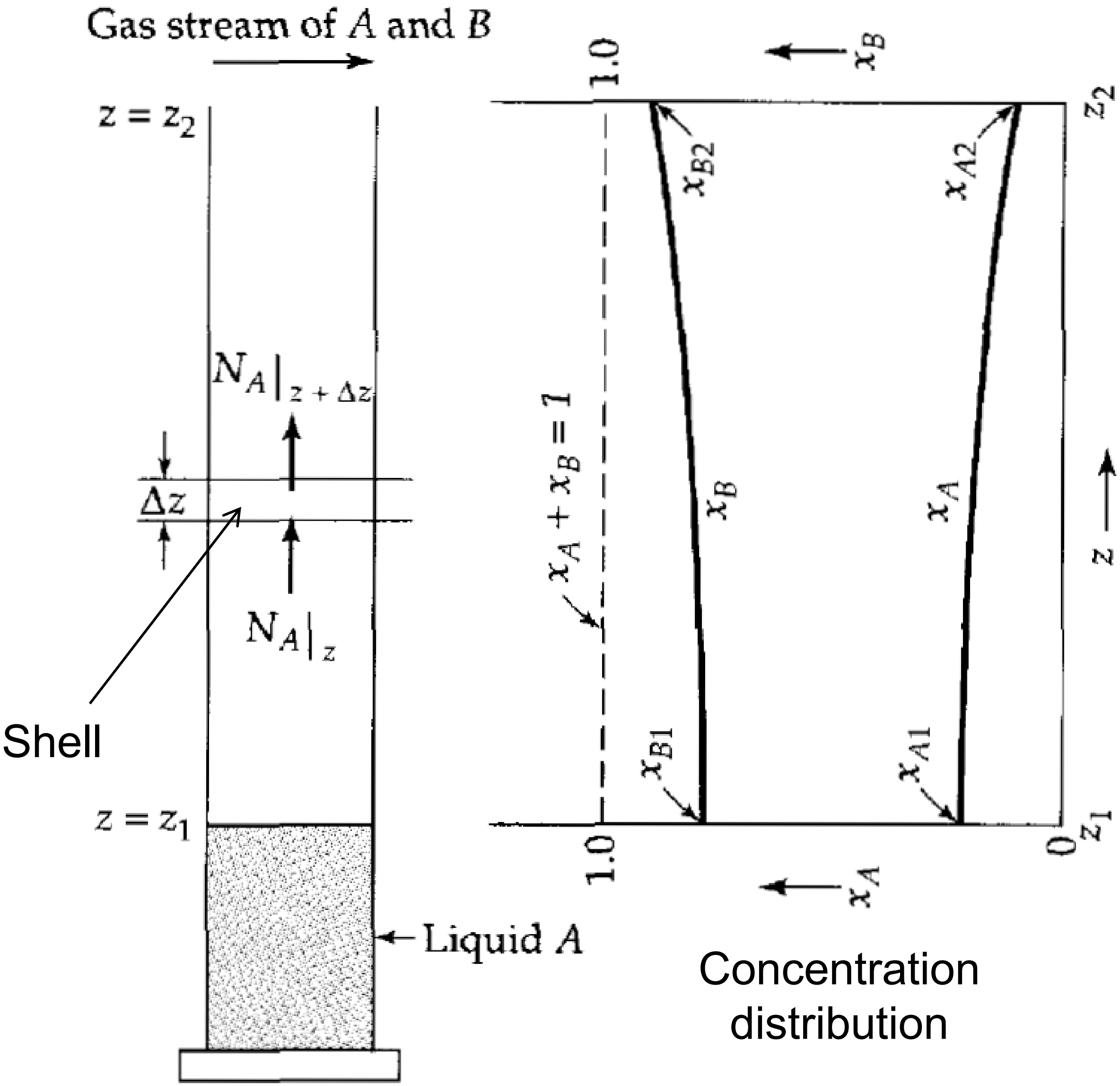
$$\boxed{\begin{aligned}&(Rate\ of\ mass\ in)-(Rate\ of\ mass\ out)+(Rate\ of\ mass\ generation)\\&-(Rate\ of\ mass\ consumption)=(Rate\ of\ accumulation\ of\ mass)\end{aligned}}$$

Rewrite the balance in
terms of number of moles

Modeling problem

Diffusion through a stagnant gas film

Diffusion through a stagnant gas film [1]



Concentration distribution

Diffusion through a stagnant gas film

The mass balance (law of conservation of mass) around the thin shell selected in the column of the gas may be written for steady-state conditions as:

$$\begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A\text{ in}\end{Bmatrix} - \begin{Bmatrix}\text{rate of}\\ \text{mass of}\\ A\text{ out}\end{Bmatrix} = 0$$

Diffusion through a stagnant gas film

As no reaction is occurring so the third term on the previous slide is not needed. The mass balance then can be written as

$$S \cdot N_{Az}\big|_{z} - S \cdot N_{Az}\big|_{z+\Delta z} = 0$$

Units of $S \cdot N_{Az}$ are $\mathrm{m}^2 \cdot \left(\dfrac{\mathrm{mol}}{\mathrm{m}^2 \cdot \mathrm{s}} \right) = \dfrac{\mathrm{mol}}{\mathrm{s}}$

Where, S is the cross-sectional area of the column and N_{AZ} is molar flux of A in z direction.

Diffusion through a stagnant gas film

Dividing throughput by Δz and taking $\Delta z \to 0$, it may be shown that

$$-\frac{dN_{Az}}{dz} = 0$$

We know for combined molecular and convective flux

$$N_{Az} = -cD_{AB}\frac{dx_A}{dz} + x_A(N_{Az} + N_{Bz})$$

As gas *B* is stagnant (non-diffusing), so $N_{Bz} = 0$ and the above equation becomes

$$N_{Az} = -cD_{AB}\frac{dx_A}{dz} + x_A N_{Az}$$

Diffusion through a stagnant gas film

$$N_{Az} = \frac{cD_{AB}}{1 - x_A} \frac{dx_A}{dz}$$

$$\frac{d}{dz}\left(\frac{cD_{AB}}{1 - x_A} \frac{dx_A}{dz} \right) = 0$$

Diffusion through a stagnant gas film: Concentration profile

$$\boxed{\left(\frac{1-x_A}{1-x_{A1}}\right)=\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\left(\frac{z-z_1}{z_2-z_1}\right)}}$$

$$\left(\frac{x_B}{x_{B1}}\right)=\left(\frac{x_{B2}}{x_{B1}}\right)^{\left(\frac{z-z_1}{z_2-z_1}\right)}$$

Diffusion through a stagnant gas film: **Molar flux**

$$N_{Az} = -\frac{cD_{AB}}{1 - x_A}\frac{dx_A}{dz}$$

$$\boxed{N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)}\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)}$$

$$N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)}\ln\left(\frac{x_{B2}}{x_{B1}}\right)$$

Diffusion through a stagnant gas film

$$\boxed{N_{Az} = \frac{cD_{AB}}{(z_2 - z_1)} \frac{x_{A1} - x_{A2}}{x_{B,lm}}}$$

Using ideal gas law

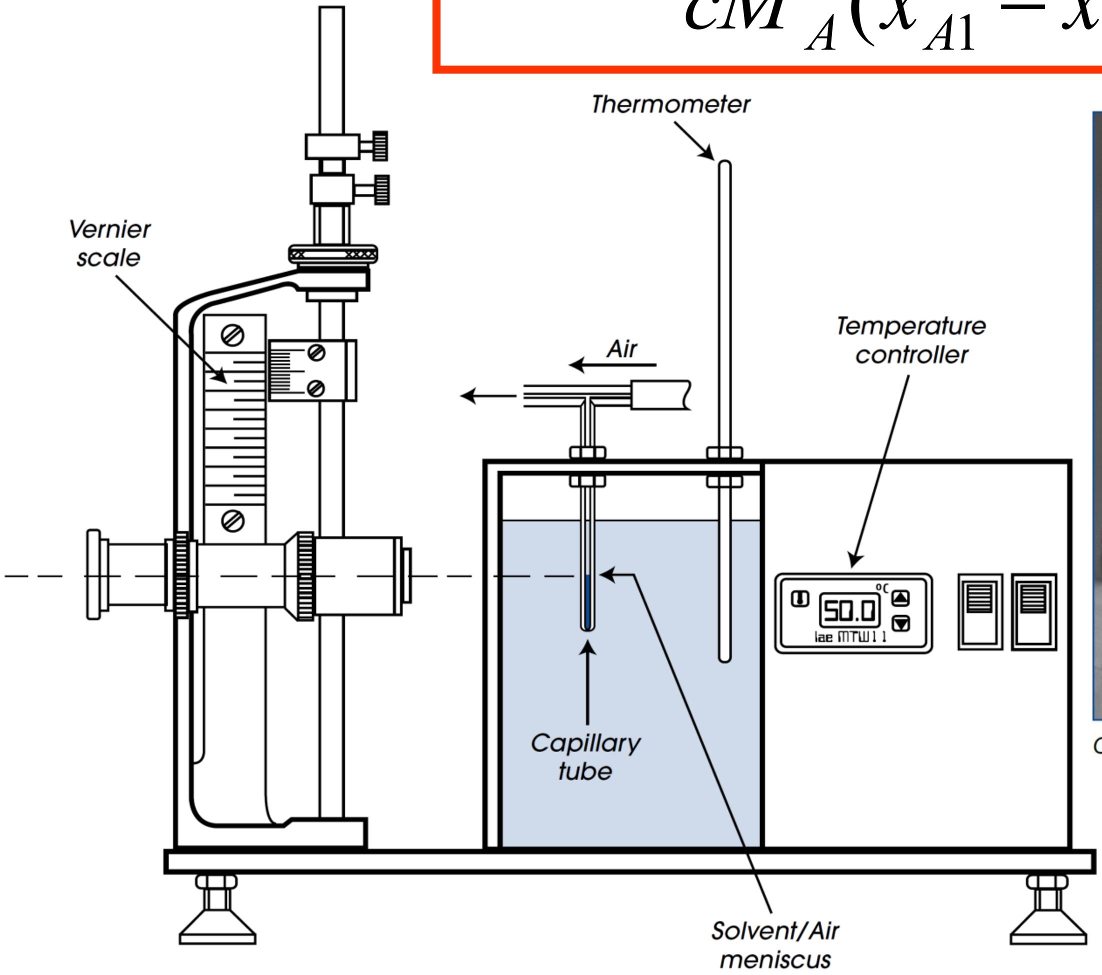
$$N_{Az} = \frac{D_{AB}p}{RT(z_2 - z_1)} \frac{p_{A1} - p_{A2}}{p_{B,lm}}$$

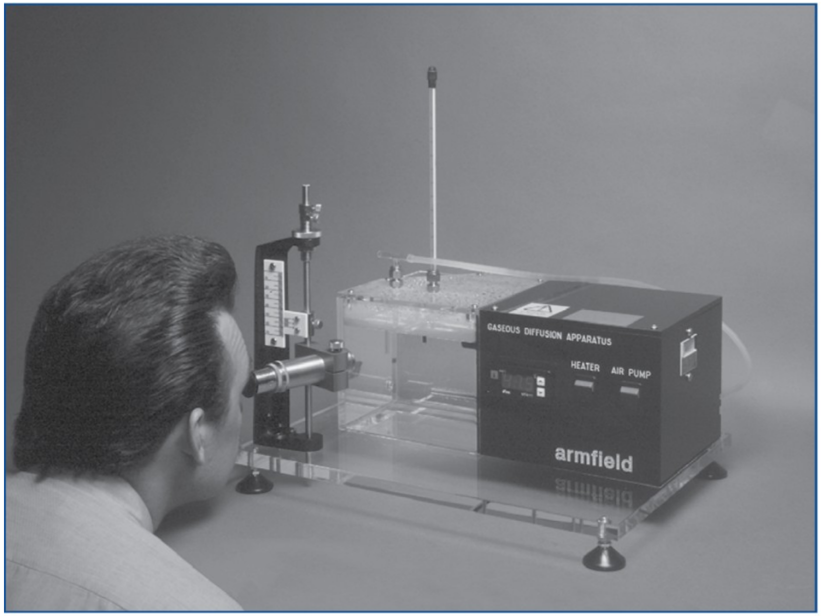
Where

$$x_{B,lm} = \frac{x_{A1} - x_{A2}}{\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)} \quad \text{or} \quad x_{B,lm} = \frac{x_{B2} - x_{B1}}{\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$$

Pseudosteady state diffusion through a stagnant gas film

$$D_{AB} = \frac{\rho_{A,L} x_{B,lm}}{c M_A (x_{A1} - x_{A2}) t} \frac{z_t^2 - z_{t0}^2}{2}$$





CERa Gaseous Diffusion Coefficients Apparatus

http://www.consultexim.hu/pdf/cer.pdf

[accessed on: 23-Aug-2015]

Diffusion through a stagnant gas film: Applications

The results are useful in:

- measuring the mass diffusion coefficient
- studying film models for mass transfer.

Diffusion through a stagnant gas film: Defects

In the present model, “it is assumed that there is a sharp transition from a stagnant film to a well-mixed fluid in which the concentration gradients are negligible. Although this model is physically unrealistic, it has nevertheless proven useful as a simplified picture for correlating mass transfer coefficients” [1]

The present method for measuring gas-phase diffusivities involves several defects:

- “the cooling of the liquid by evaporation
- the concentration of nonvolatile impurities at the interface
- the climbing of the liquid up the walls of the tube and curvature of the meniscus” [1]

Problem [9]

The water surface in an open cylindrical tank is 25 ft below the top. Dry air is blown over the top of the tank and the entire system is maintained at 65 °F and 1 atm. If the air in the tank is stagnant, determine the diffusion rate of the water. Use diffusivity as 0.97 ft^2/h at 65 °F water in air 1 atm.

[Universal gas constant = 0.73 ft^3-atm/lbmol-°R]

Hint: We need vapor pressure of water at 60^{o}F for this problem.

From where one can find the right value of vapor pressure of water?

Problem [9]

At the bottom of a cylindrical container is *n*-butanol. Pure air is passed over the open top of the container. The pressure is 1 atm and the temperature is 70 °F. The diffusivity of air-*n*-butanol is 8.57×10^{-6} m^2/s at the given conditions. If the surface of *n*-butanol is 6.0 ft below the top f the container, calculate the diffusion rate of *n*-butanol. Vapor pressure of n-butanol is 0.009 atm at the given conditions.

[Universal gas constant = 0.08205 m^3-atm/kmol-K]

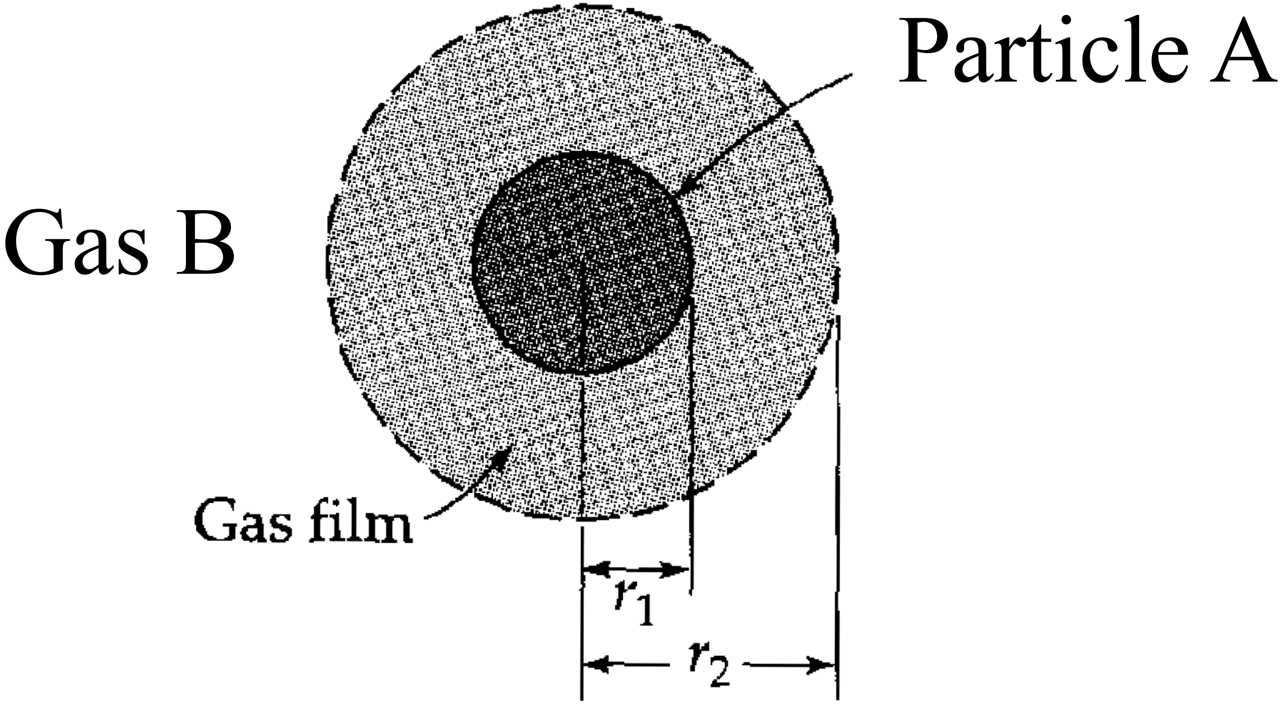
Homework problems

Example 18.2-2 [1]

Problem 18A.1 and 18A.6 [1]

Diffusion of *A* through stagnant gas film in spherical coordinates

A spherical particle *A* having radius r_1 is suspended in a gas *B*. The component *A* diffuses through the gas film having radius r_2. If the gas *B* is stagnant, i.e., not diffusing into *A*, derive an expression for molar flux of *A* into *B*.



Diffusion of *A* through stagnant gas film in spherical coordinates

Applying shell mass balance and taking limit when Δr approaches to zero:

$$\frac{d\left(r^2 N_{Ar}\right)}{dr} = 0$$

$$r^2 N_{Ar} = r_1^2 N_{Ar1} = r_2^2 N_{Ar2}$$

$$N_{Ar} = -cD_{AB}\frac{dx_A}{dr} + x_A(N_{Ar} + N_{Br})$$

$$N_{Ar} = -\frac{cD_{AB}}{1-x_A}\frac{dx_A}{dr}$$

Diffusion of *A* through stagnant gas film in spherical coordinates

$$\boxed{N_{Ar1} = \frac{cD_{AB}}{(r_2 - r_1)}\left(\frac{r_2}{r_1}\right)\ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right)}$$

$$\boxed{N_{Ar1} = \frac{cD_{AB}}{(r_2 - r_1)}\left(\frac{r_2}{r_1}\right)\ln\left(\frac{x_{B2}}{x_{B1}}\right)}$$

Diffusion of *A* through stagnant gas film in spherical coordinates

Derive concentration profile as shown below for the system just discussed in the previous slide.

$$\boxed{\left(\frac{1-x_A}{1-x_{A1}}\right)=\left(\frac{1-x_{A2}}{1-x_{A1}}\right)^{\frac{(1/r_1)-(1/r)}{(1/r_1)-(1/r_2)}}}$$

Diffusion of *A* through stagnant gas film in cylindrical coordinates

A cylindrical particle of benzoic acid *A* having radius r_1 is suspended in a gas *B*. The component *A* diffuses through the gas film having radius r_2. If the gas *B* is stagnant, i.e., not diffusing into *A*, derive an expression for molar flux of *A* into *B*. Also work out the concentration profile for the situation.

Diffusion of *A* through stagnant gas film in cylindrical coordinates: Pls confirm

Applying shell mass balance and taking limit when Δr approaches to zero:

$$\frac{d(rN_{Ar})}{dr} = 0$$

$$rN_{Ar} = r_1 N_{Ar1} = r_2 N_{Ar2}$$

$$N_{Ar} = -cD_{AB}\frac{dx_A}{dr} + x_A(N_{Ar} + N_{Br})$$

$$N_{Ar} = -\frac{cD_{AB}}{1-x_A}\frac{dx_A}{dr}$$

$$\boxed{r_1 N_{Ar1} = cD_{AB}\frac{\ln\left(\dfrac{1-x_{A2}}{1-x_{A1}}\right)}{\ln\left(\dfrac{r_2}{r_1}\right)}}$$

Diffusion of *A* through Pyrex glass tube

Method for separating helium from natural gas (Fig. 18B.8). Pyrex glass is almost impermeable to all gases but helium. For example, the diffusivity of He through pyrex is about 25 times the diffusivity of H_2 through pyrex, hydrogen being the closest "competitor" in the diffusion process. This fact suggests that a method for separating helium from natural gas could be based on the relative diffusion rates through pyrex.[7]

Suppose a natural gas mixture is contained in a pyrex tube with dimensions shown in the figure. Obtain an expression for the rate at which helium will "leak" out of the tube, in terms the diffusivity of helium through pyrex, the interfacial concentrations of the helium in the pyrex, and the dimensions of the tube.

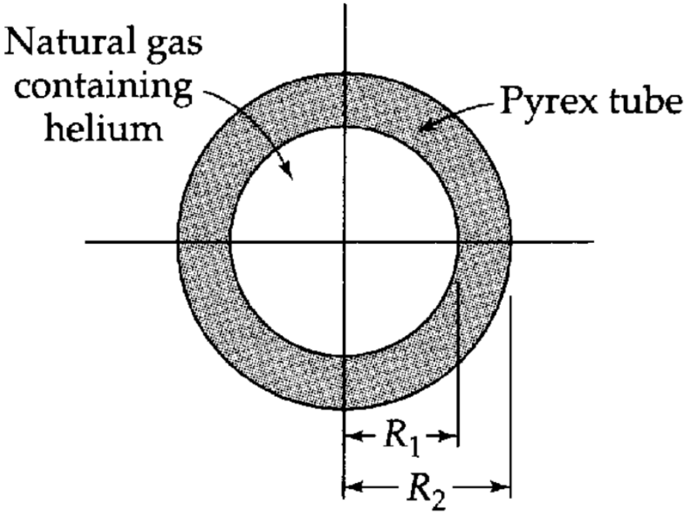


Fig. 18B.8. Diffusion of helium through pyrex tubing. The length of the tubing is *L*.

Diffusion of *A* through Pyrex glass tube

$$\frac{d\left(rN_{Ar}\right)}{d} = 0 \Rightarrow \boxed{N_{AR1} = \frac{cD_{AB}\left(x_{A1} - x_{A2}\right)}{R_1 \ln\left(R_2 / R_1\right)}}$$

$$N_{Ar} = -cD_{AB}\frac{dx_A}{dr}$$

$$\boxed{N_{AR1} = \frac{D_{AB}\left(c_{A1} - c_{A2}\right)}{R_1 \ln\left(R_2 / R_1\right)}}$$

$$\boxed{\frac{c_A - c_{A2}}{c_{A1} - c_{A2}} = \frac{\ln\left(R_2 / r\right)}{\ln\left(R_2 / R_1\right)}}$$

Separation of helium from gas mixture[4]

26.2 Helium gas is seperated from other components of a gas mixture by its selective diffusion through the wall of a Pyrex glass tube. Under steady-state conditions, the partial pressures of helium at the inner and outer surfaces of the Pyrex tube are 1.5 and 1.0 bar, respectively. If the wall thickness of the Pyrex tubing is 3 mm, determine

a. the flux of He through a tube having an inside diameter of 1.0 cm;

b. the concentration profile, $c_A(r)$, of helium within the wall.

Homework problems

Problem 18B.7 [1]

Problem 18B.9 [1]

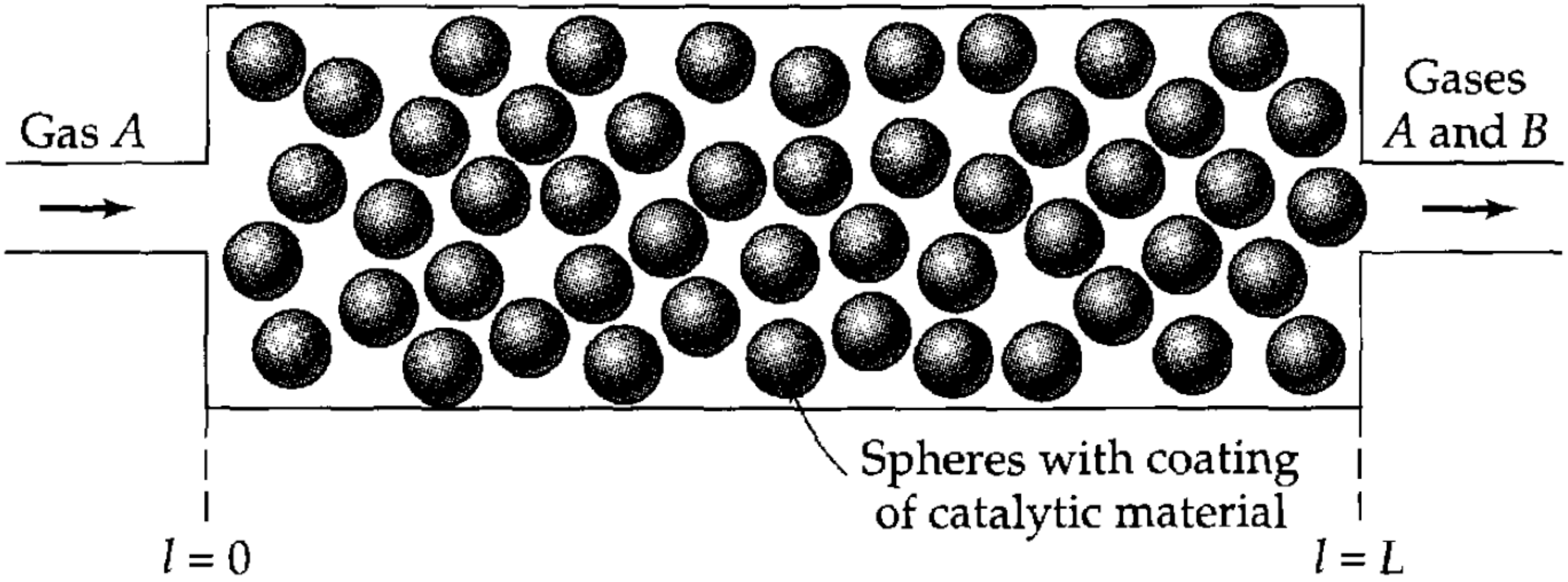
Diffusion with a heterogeneous chemical reaction [1]

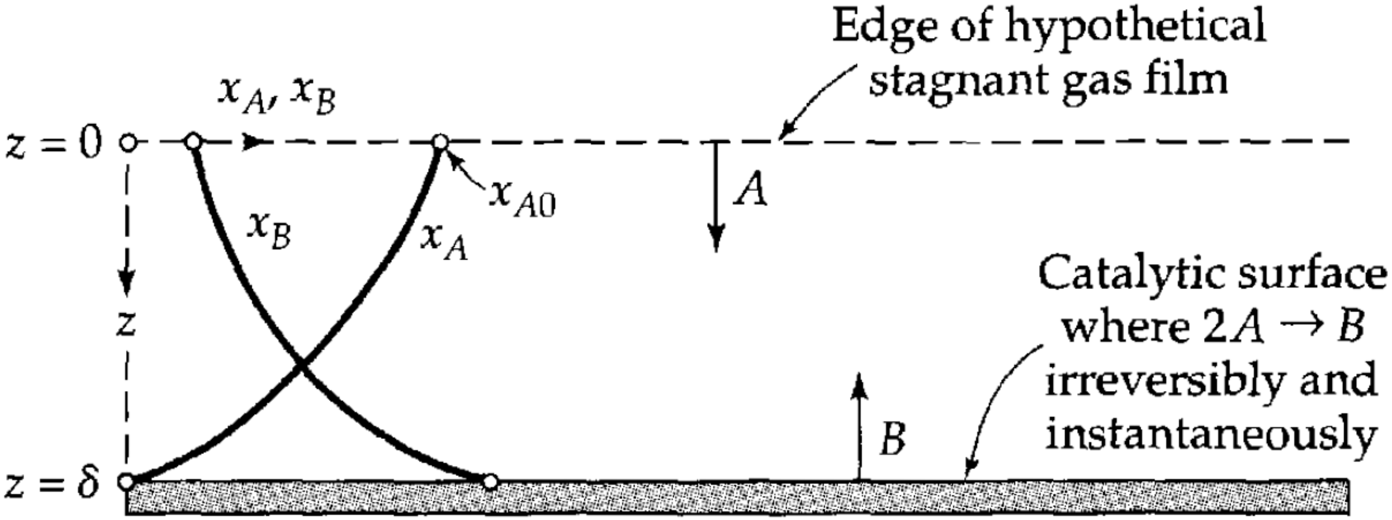
Consider a catalytic reactor shown on the next slide. At the catalyst surface the following reaction

$$2A \rightarrow B$$

occurs instantaneously. Each catalyst particle is surrounded by a stagnant gas film through which A has to diffuse to reach the catalyst surface. The component A and B diffuse back out through the gas film to the main bulk stream. Develop an expression for the rate of conversion of A to B when the effective gas film thickness and the main stream concentration x_{A0} and x_{B0} are known. The gas film is isothermal. Hint: $N_{Bz} = -\frac{1}{2}N_{Az}$ as moles of B are equal to half the moles of A, so the flux of B is half the flux of A.

Diffusion with a heterogeneous chemical reaction [1]





Diffusion with a heterogeneous chemical reaction

In the previous case, a very small portion (surface) of the catalyst is selected for the analysis which may be regarded as straight surface (being so small) instead of a curved surface. The curvature effects are negligible. Imagine Earth, a huge spherical body, but, for a small portion (area) we do not see any of that curvature.

For the reaction, $2A \rightarrow B$ stoichiometry suggets us that molar flux of A is two times the molar flux of B, i.e., molar flux of A is higher than molar flux of B.

Moreover, the molar flux of A is in opposite direction to the molar flux of B. Therefore N_{Bz} is not equal to 2 times of N_{Az} but the opposite, i.e.,. $N_{Bz} = -\frac{1}{2}N_{Az}$

Diffusion with a heterogeneous chemical reaction

$$\boxed{N_{AZ}=\frac{2cD_{AB}}{\delta}\ln\left(\frac{1}{1-\frac{1}{2}x_{A0}}\right)}$$

$$\boxed{\left(1-\frac{1}{2}x_A\right)=\left(1-\frac{1}{2}x_{A0}\right)^{1-(z/\delta)}}$$

Diffusion with a heterogeneous chemical reaction [2, 458]

Pure gas A diffuses from point 1 at a partial pressure of 101.32 kPa to point 2 a distance 2.0 mm away. At point 2 it undergoes a chemical reaction at the catalyst surface and $A \rightarrow 2B$. Component B diffuses back at steady-state. The total pressure is p = 101.32 kPa. The temperature is 300 K and $D_{AB} = 0.15\times10^{-4}$ m^2/s.

a) For instantaneous rate of reaction, calculate x_{A2} and N_A.

b) For a slow reaction where $k = 5.63\times10^{-3}$ m/s, calculate x_{A2} and N_A.

Hints:

$$N_B = -2N_A$$

$$\boxed{N_{AZ} = \frac{cD_{AB}}{\delta}\ln\left(\frac{1+x_{A1}}{1+x_{A2}}\right)}$$

Diffusion with a heterogeneous chemical reaction

Pseudo-homogeneous model of a vertical and cylindrical fixed bed reactor design is to be developed. The feed enters from the top and flows downwards and leave at the bottom. Consider isothermal conditions and negligible pressure.

Take *A* as reactant and apply shell mass balance for *A* to develop the differential equation involved in the reactor system.

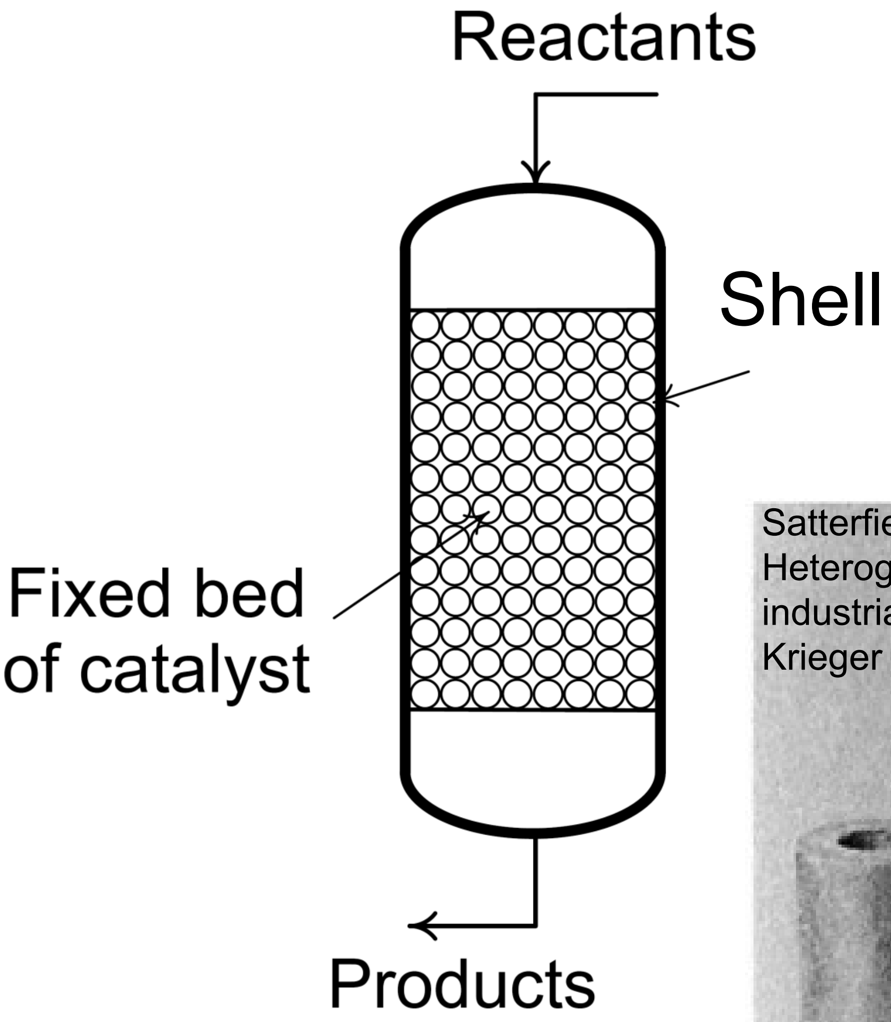
a) Consider axial direction only but include axial diffusivity

b) Consider also radial diffusion into Part (a)

c) How can you reduce Part (a) to simple plug flow rate equation.

d) Describe boundary conditions applied in each case.

Steady-state two-dimensional pseudo-homogeneous model for a fixed bed reactor



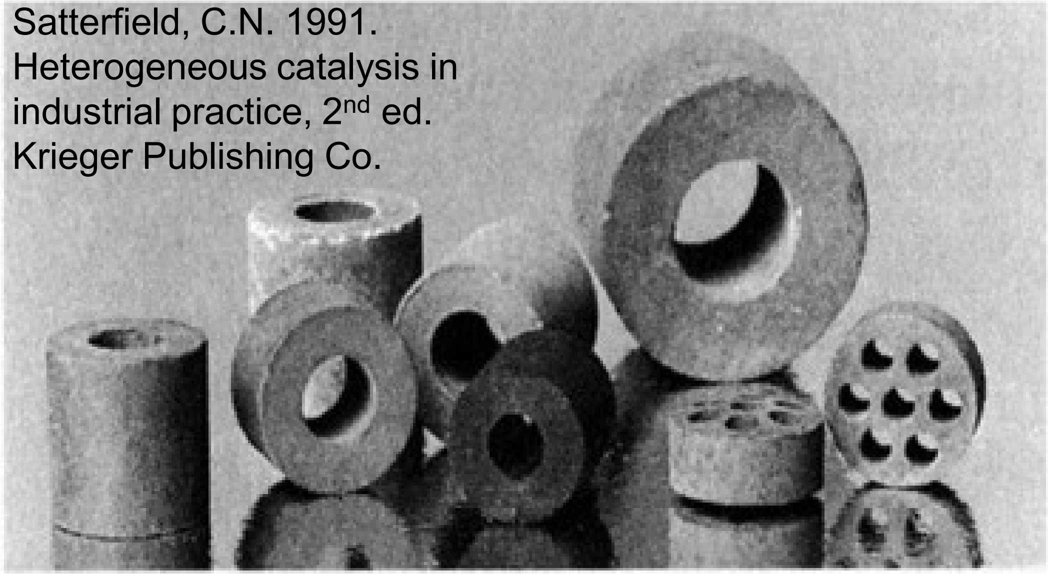
Reactants

Shell

Fixed bed of catalyst

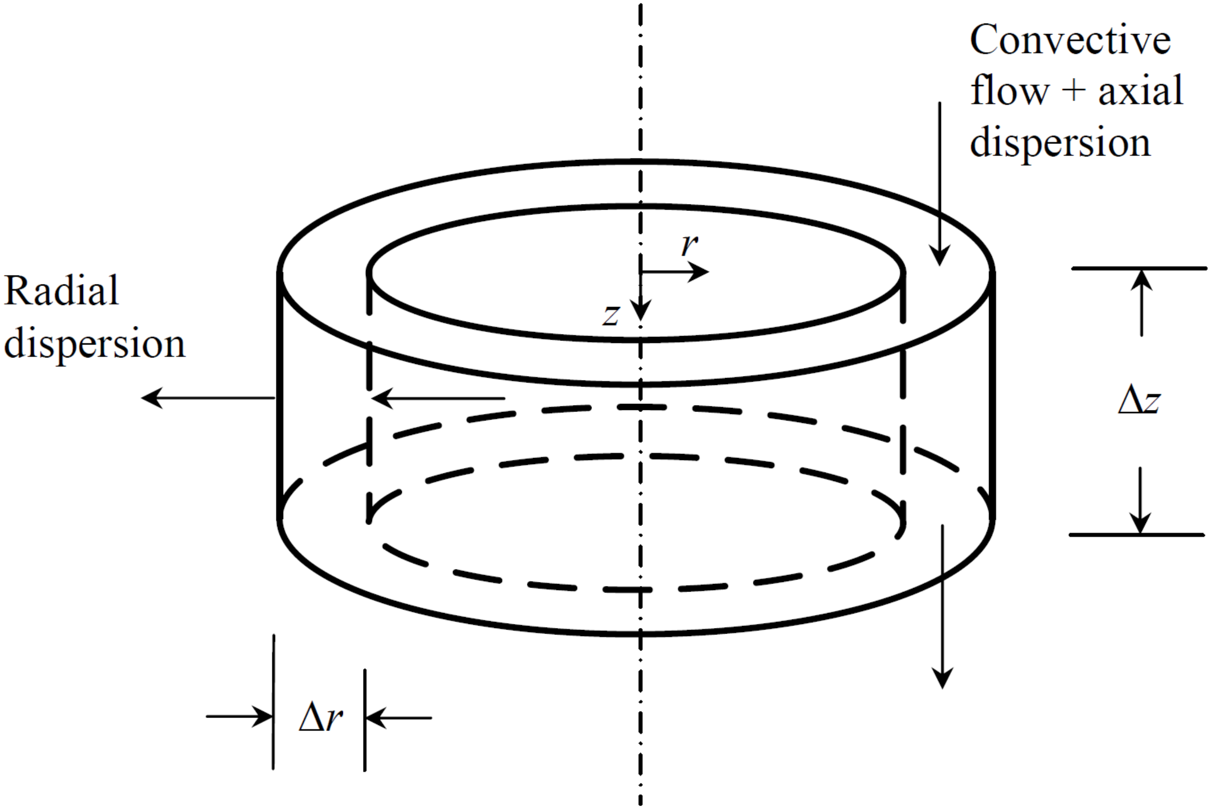
Products

http://www.sud-chemie-india.com/prod.htm



Satterfield, C.N. 1991. Heterogeneous catalysis in industrial practice, 2nd ed. Krieger Publishing Co.

Steady-state two-dimensional pseudo-homogeneous model for a fixed bed reactor



$$\begin{aligned}&Mass\,balance:\\&(Rate\,of\;mass\,in)-(Rate\,of\;mass\,out)+(Rate\,of\;mass\,generation)\\&-(Rate\,of\;mass\,consumption)=(Rate\,of\;accumulation\,of\;mass)\end{aligned}$$

Steady-state two-dimensional pseudo-homogeneous model

Continuity equation (constant D_r and D_a):

$$\boxed{-\frac{\partial(uc_A)}{\partial z}+D_a\frac{\partial^2 c_A}{\partial z^2}+D_r\left(\frac{\partial^2 c_A}{\partial r^2}+\frac{1}{r}\frac{\partial c_A}{\partial r}\right)-(-r_A)\cdot\rho_B=0}$$

It is two-dimensional second order partial differential equation.

For the derivations, see class notes and book by Missen, Ref. 10.

Steady-state two-dimensional pseudo-homogeneous model

Boundary conditions:

The simplest boundary conditions are that of Dirichlet, derivative boundary conditions are called as Neumann boundary conditions. With possible axial diffusion, Danckwerts boundary conditions are the correct one. Though Danckwerts boundary conditions are proposed earlier by Langmuir, but, they are commonly known after Danckwerts.

Steady-state two-dimensional pseudo-homogeneous model

Boundary conditions:

$$F'_{A0} = F'_A + \left(- D_a \frac{dc_A}{dz} \right) \qquad \text{at } z = 0$$

Where, F'_A is molar flux (molar flowrate per area) such as $F'_A = uc_A$

$$\frac{\partial c_A}{\partial z} = 0 \qquad \text{at } z = L$$

Danckwerts boundary conditions

$$\frac{\partial c_A}{\partial r} = 0 \qquad \text{at } r = 0$$

$$\frac{\partial c_A}{\partial r} = 0 \qquad \text{at } r = R$$

Where, R is inside radius of the cylindrical reactor body.

Steady-state two-dimensional pseudo-homogeneous model

Continuity equation (negligible axial diffusion, and constant D_r):

$$\boxed{-\frac{\partial(uc_A)}{\partial z}+D_r\left(\frac{\partial^2 c_A}{\partial r^2}+\frac{1}{r}\frac{\partial c_A}{\partial r}\right)-(-r_A)\cdot\rho_B=0}$$

It is two-dimensional parabolic second order partial differential equation.

For the derivations, see class notes and book by Missen, Ref. 10.

Steady-state two-dimensional pseudo-homogeneous model

Boundary conditions:

No need for Danckwerts boundary conditions.

$$\left.\begin{array}{ll} c_A = c_{A0} & \text{at } z = 0 \\ c_A = c_A & \text{at } z = L \end{array}\right\} \text{Dirichlet boundary conditions}$$

$$\frac{\partial c_A}{\partial r} = 0 \qquad \text{at } r = 0$$

$$\frac{\partial c_A}{\partial r} = 0 \qquad \text{at } r = R$$

Where, R is inside radius of the cylindrical reactor body.

Steady-state one-dimensional pseudo-homogeneous model

Continuity equation (negligible radial diffusion, and constant D_a):

$$\boxed{-\frac{\partial(uc_A)}{\partial z} + D_a \frac{\partial^2 c_A}{\partial z^2} - (-r_A)\cdot\rho_B = 0}$$

It is one-dimensional second order ordinary differential equation. It can be easily solved by splitting the second order equation to two first order ordinary differential equations.

For the derivations, see class notes and book by Missen, Ref. 10.

Steady-state one-dimensional pseudo-homogeneous model

Boundary conditions:

$$\left.\begin{array}{ll} F'_{A0} = F'_A + \left(- D_a \dfrac{dc_A}{dz} \right) & \text{at } z = 0 \\ \text{Where, } F'_A \text{ is molar flux (molar flowrate per area) such as } F'_A = uc_A & \\ \dfrac{\partial c_A}{\partial z} = 0 & \text{at } z = L \end{array}\right\} \begin{array}{l} \text{Danckwerts} \\ \text{boundary} \\ \text{conditions} \end{array}$$

Steady-state one-dimensional pseudo-homogeneous model

Continuity equation (negligible radial and axial diffusions):

$$\boxed{-\frac{\partial (u c_A)}{\partial z} - (-r_A)\cdot \rho_B = 0}$$

It is one-dimensional first order ordinary differential equation.

Boundary conditions:

No need for Danckwerts boundary conditions.

$$\left.\begin{array}{ll} c_A = c_{A0} & \text{at } z = 0 \\ c_A = c_A & \text{at } z = L \end{array}\right\} \text{Dirichlet boundary conditions}$$

For the derivations, see class notes and book by Missen, Ref. 10.

Formulation of the previous equation in terms of fractional conversion (X_A)

$$\frac{dX_A}{dz} = \frac{\rho_B \cdot (-r_A) \cdot M_{feed}}{G \cdot y_{A0}}$$

$$\frac{dX_A}{dz} = \frac{\pi \cdot D_i^2 \cdot \rho_B \cdot (-r_A)}{4 \cdot F_{A0}}$$

$$\frac{\partial X_A}{\partial \left(\frac{W}{F_{A0}} \right)} = (-r_A)$$

G is mass velocity and has SI unit of kg/s·m^2.

Boundary conditions:

$X_A = X_{A0} = 0$ at $z = 0$

$X_A = X_A$ at $z = L$

For the derivations, see class notes.

Significance of dimensionless numbers

It is convenient to write the above mentioned differential equations and their boundary conditions in terms of dimensionless groups. Dimensionless groups may have smaller numerical values which may facilitate a numerical solution. Also analysis of the system may be described in a more convenient manner.

The above equations are usually written in terms of Peclet number.

Significance of dimensionless numbers

Peclet number for radial mass transfer

$$Peclet\ number = \frac{Mass\ trasnferrate\ by\ convection}{Mass\ transferrate\ by\ diffusion}$$

$$Pe_{r,m} = \frac{u \cdot d_p}{D_r} = \frac{G \cdot d_p}{\rho \cdot D_r}$$

Particle (catalyst) diameter

Solution of partial differential equations

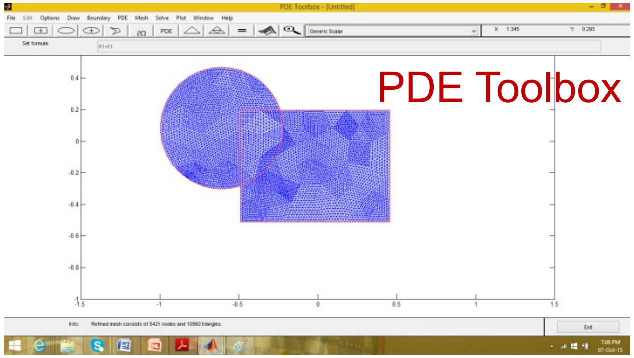
- Finite difference approach
- Finite element approach

Finite difference:

- Explicit methods

  (Easy to put but beware of convergence and stability)
- Implicit methods

  The Crank-Nicolson method



Generic Scalar

Set formula: R1+E1

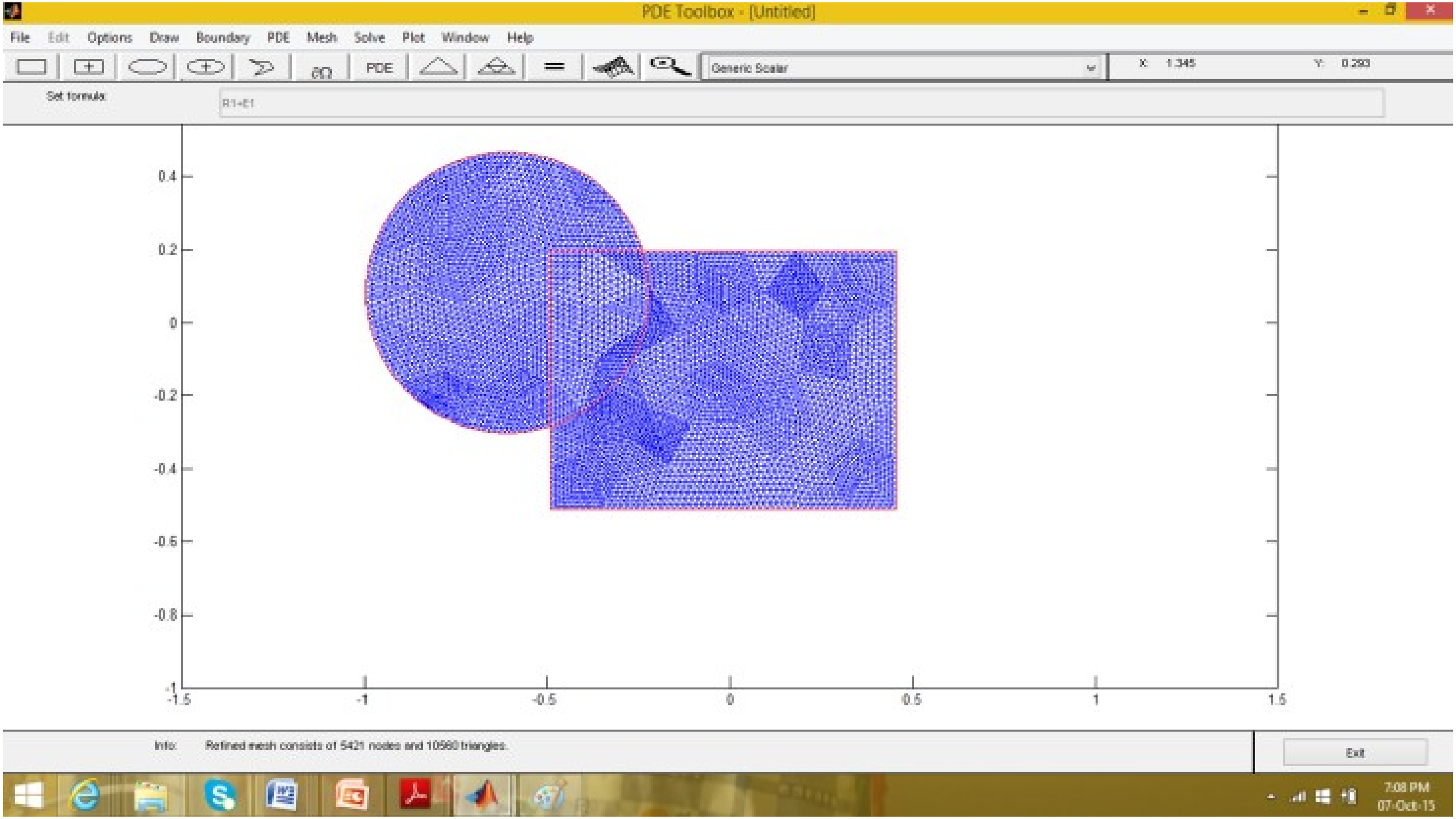
Info: Refined mesh consists of 5421 nodes and 10560 triangles.

PDE Toolbox

Finite element:

- Comsol Multiphysics (old name Femlab based on MATLAB PDE Toolbox), Fluent etc.

Workshop MATLAB PDE Toolbox

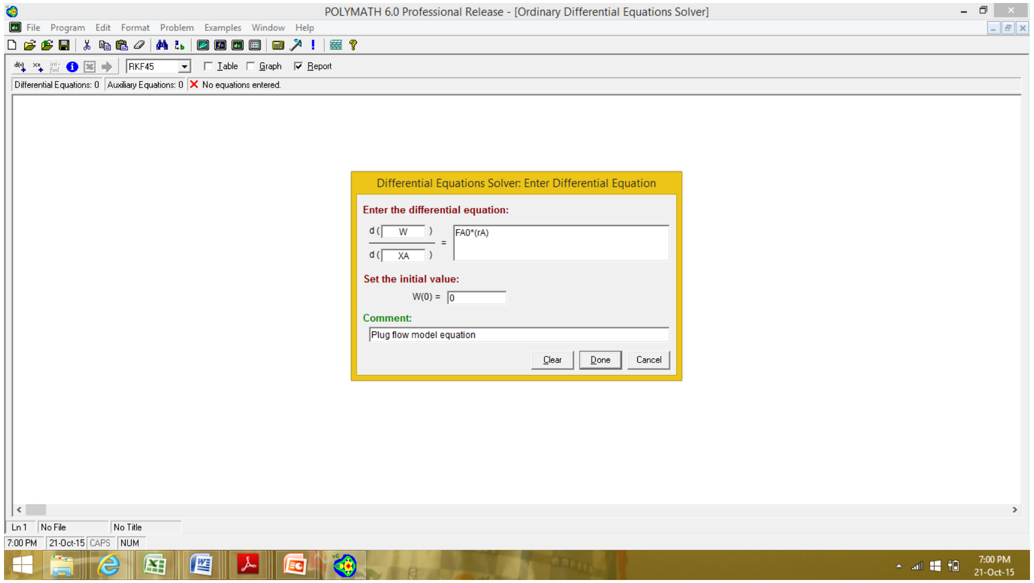


Set formula: R1+E1

Info: Refined mesh consists of 5421 nodes and 10560 triangles.

Polymath software

Polymath software is an excellent source for solving single and simultaneous ordinary differential equations.



Differential Equations: 0 | Auxiliary Equations: 0 | No equations entered.

Differential Equations Solver: Enter Differential Equation

Enter the differential equation:

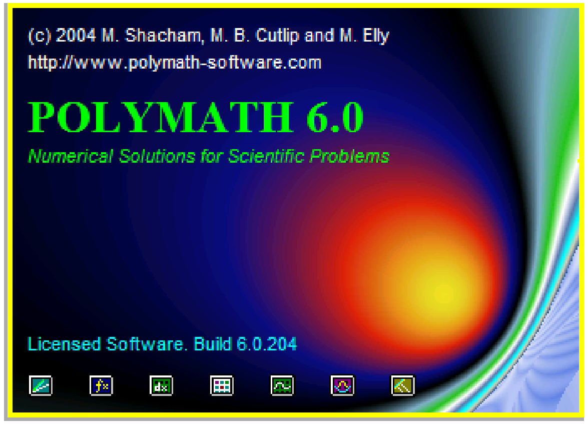
d(W) / d(XA) = FA0*(rA)

Set the initial value:

W(0) = 0

Comment:

Plug flow model equation



(c) 2004 M. Shacham, M. B. Cutlip and M. Elly
http://www.polymath-software.com

POLYMATH 6.0

Numerical Solutions for Scientific Problems

Licensed Software. Build 6.0.204

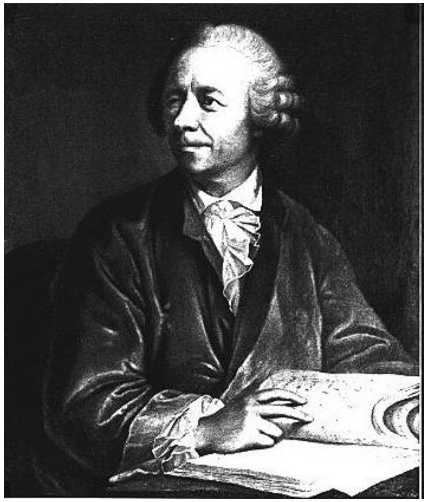
Instead of using POLYMATH software, you can prepare an excel spreadsheet using Euler’s method or Runge-Kutta method

Euler’s method

Euler’s method is employed for approximate solution of ordinary differential equations with initial value problems.

$$y_{n+1} = y_n + h \cdot f(x_n, y_n)$$

$$h = x_{n+1} - x_n$$



Euler (1707-1783)

Take interval “*h*” as low as possible.

Take at least 100 steps for the Euler’s method for a better accuracy.

Runge-Kutta 4th order method has better efficiency than Euler’s method. You can easily setup these methods in **Excel** or **MATLAB**.

4th Order RK method in MATLAB

```matlab
% Solve dy/dt=-0.005*CA with CA0=0.2, 4th order Runge Kutta
CA0 = 0.2;                  % Initial Condition
h=20;                       % h is interval
t = 0:h:600;                % t goes from 0 to 600 s
CA = zeros(size(t));   % Preallocate array (good coding practice)
CA(1) = CA0;           % Initial condition gives solution at t=0
for i=1:(length(t)-1)

  f1 = -0.005*CA(i);     % Approx derivative
  CA1 = CA(i)+f1*h/2;    % Intermediate value (using f1)

  f2 = -0.005*CA1;       % Approx derivative
  CA2 = CA(i)+f2*h/2;    % Intermediate value (using f2)

  f3 = -0.005*CA2;       % Approx derivative
  CA3 = CA(i)+f3*h;      % Endpoint value (using f3)

  f4 = -0.005*CA3;       % Approx derivative at endpoint value

  CA(i+1) = CA(i) + (f1+2*f2+2*f3+f4)*h/6; % Solution
end
plot(t,CA);
```

Weight of catalyst in a fixed bed reactor (Use of Polymath)

A fixed bed reactor is to be designed for the dehydrogenation of methylcyclohexane to toluene to obtain 90% conversion of the reactant. The feed is pure MCH and reaction is clean with no side reactions.

Initial molar flowrate of MCH = 100 mol/s

Reactor pressure = 1.013 bar

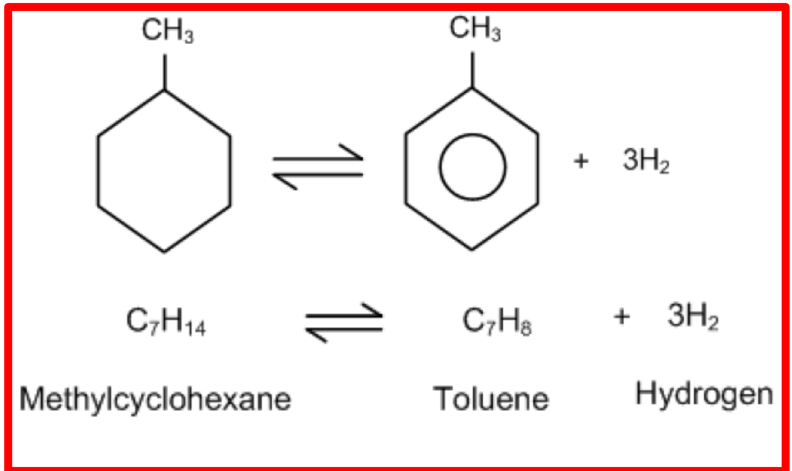
Reactor temperature = 661.8 K (isothermal conditions)

Density of the catalyst bed = 860 kg/m^3

$(-r_A) = k \cdot p_A^n$, mol/s.g-cat ($n = 1$)

Where, $k = 1.65 \times 10^{-5}$ mol/s.g-cat-Pa

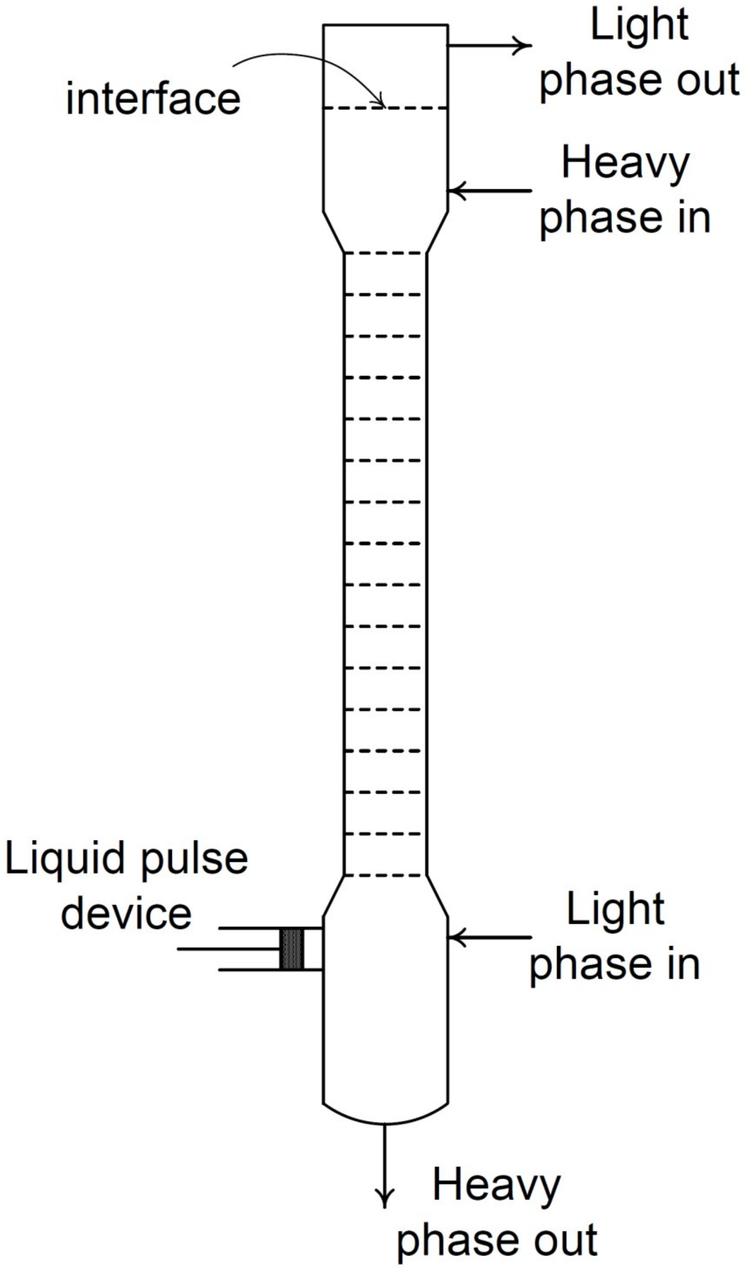
$$yA = \frac{y_{A0} \cdot (1 - X)}{1 + 3 \cdot y_{A0} \cdot X}$$



Mathematical modeling of a liquid-liquid extractor

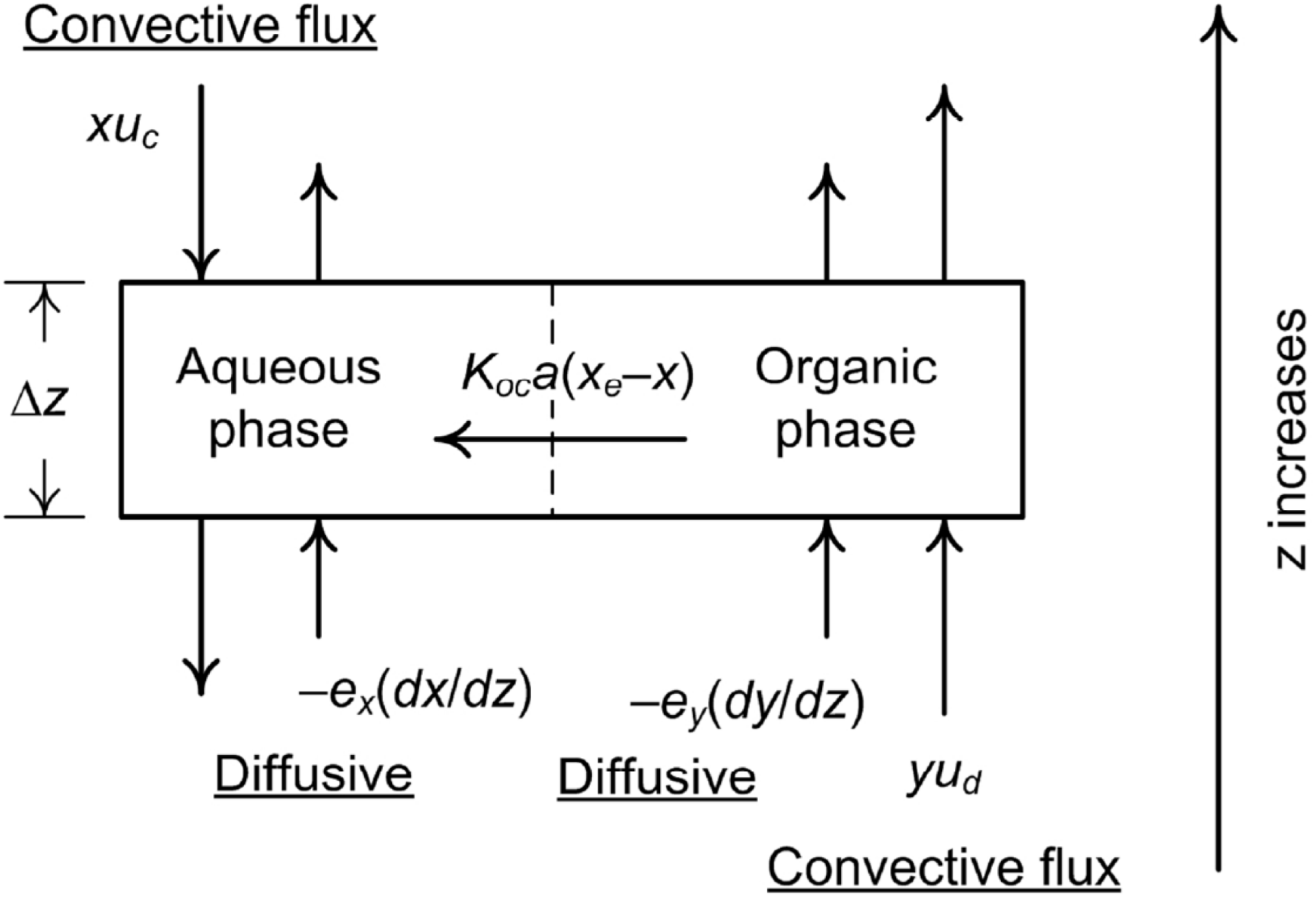
Acetic acid (*A*) is to be extracted from an organic solution (say in ethylacetate) using a suitable solvent such as water. The extraction is to be carried out in a differential extractor such as liquid pulsed extraction column (installed in our unit operations laboratory) as shown on the next slide. Apply shell mass balance and develop the differential equations applied to the extractor. The light phase, i.e., organic phase which is behaving as dispersed phase enters from the bottom while heavy phase (continuous phase) which is aqueous phase enters from the top and flows towards bottom. Consider isothermal conditions and negligible pressure drop.

Liquid pulsed extraction column [11]



Installed at unit operations laboratory

Mathematical modeling of a differential extraction column



Mathematical modeling of a differential extraction column

For dispersed phase moving from bottom and losing "*A*"

$$\boxed{-\frac{\partial\left(u_d y_A\right)}{\partial z}+\frac{\partial^2\left(E_d y_A\right)}{\partial z^2}-K_{oc}a\cdot(x_{Ae}-x_A)=0}$$

For continuous phase coming from top and gaining "*A*"

$$\boxed{+\frac{\partial\left(u_c x_A\right)}{\partial z}+\frac{\partial^2\left(E_c x_A\right)}{\partial z^2}+K_{oc}a\cdot(x_{Ae}-x_A)=0}$$

For the derivations, see class notes.

Mathematical modeling of a differential extraction column

What are the boundary conditions?

Hint: Go to

Smoot, L.D. and Babb, A.L., **1962**. Mass transfer studies in a pulsed extraction column: longitudinal concentration profiles. Ind. Eng. Chem. Fundam. 1, 93–103.

Homework Problem

Acetic acid is required to be removed from an organic phase using water as the solvent. A 400 cm tall liquid pulsed column is used for the purpose. 5.0 wt% acetic acid in the organic carrier enters the column from the bottom (having lower density) and moves upwards in the column. The solvent (water) enters the column at the top and flows downward countercurrently to the organic phase.

a) Develop a mathematical model for the column assuming radial dispersion is negligible. Reduce the model equations for the condition of negligible axial dispersions in each phase.

b) The experimental data for the column is given below. Using the given correlation find out the experimental mass transfer coefficient (apparent mass transfer coefficient) based on continuous phase and obtain the unknown concentration and concentration profile of acetic acid in each phase in the column.

c) If apparent mass transfer coefficient is not given, how can one find the mass transfer coefficient? What type of data is missing in the table below?

Homework Problem

d) If axial dispersion is important in each phase. How can axial diffusivities be calculated using experimental data and what experimental data is required?

Use the following data:

$$K_{ocp}a = 0.1145 \cdot (Af)^{0.2578} \cdot u_d^{1.062}$$

$Af = 19.33 \times 10^{-3}$ m/s

$u_c = 3.803 \times 10^{-3}$ m/s

$u_d = 1.647 \times 10^{-3}$ m/s

Solute	y_i (mol/L)	y_o (mol/L)	x_i (mol/L)	x_o (mol/L)	m
Acetic acid	0.6661	?	?	0.24	0.0708

Repeat part (b) for the following conditions, when propionic acid is present is the organic phase and has to be removed using water as the solvent.

Homework Problem

Data:

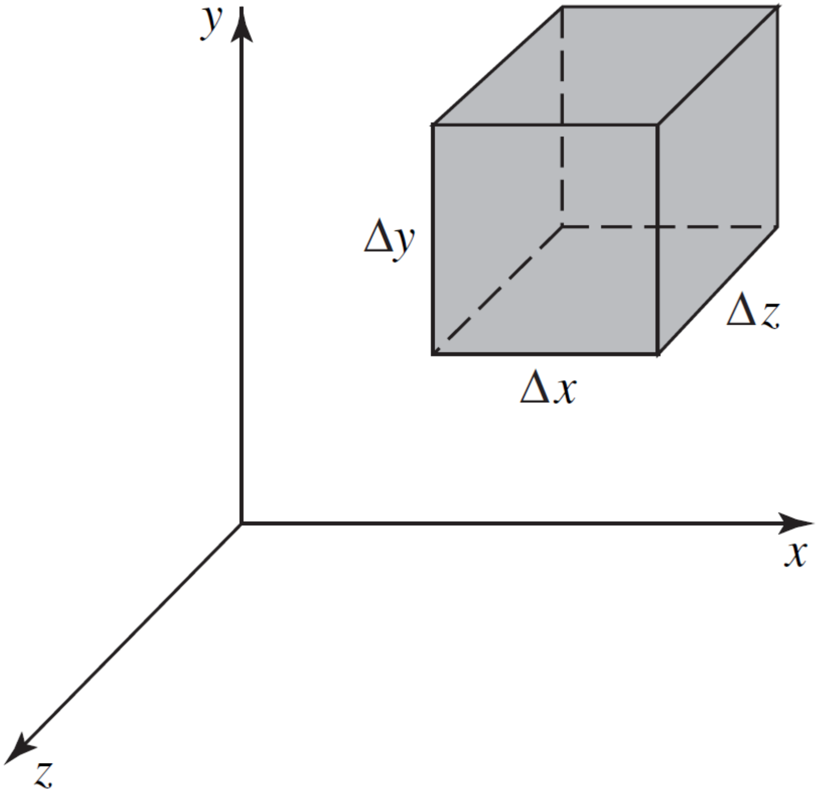
$Af = 19.33 \times 10^{-3}$mm/s
$u_c = 3.803 \times 10^{-3}$ m/s
$u_d = 1.647 \times 10^{-3}$ m/s

Solute	y_i (mol/L)	y_o (mol/L)	x_i (mol/L)	x_o (mol/L)	m	$K_{ocp}a$ (s^{-1})
Propionic acid	0.54	?	?	0.22	0.2801	3.47×10^{-3}

Where,
y_i is inlet molar concentration of solute in organic phase, mol/L
y_o is outlet molar concentration of solute in organic phase, mol/L
x_i is inlet molar concentration of solute in aqueous phase, mol/L
y_o is outlet molar concentration of solute in aqueous phase, mol/L
m is distribution coefficient ($y = mx$) at the conditions of experimentation, –
$K_{ocp}a$ is apparent overall mass transfer coefficient based on continuous phase, 1/s.

Differential equation for mass transfer

A control volume in a body of a fluid is shown below:



Differential equation for mass transfer

For the control volume shown

$$\boxed{\begin{aligned}&(\mathit{Rate\ of\ mass\ in}) - (\mathit{Rate\ of\ mass\ out}) + (\mathit{Rate\ of\ mass\ generation})\\&- (\mathit{Rate\ of\ mass\ consumption}) = (\mathit{Rate\ of\ accumulation\ of\ mass})\end{aligned}}$$

The net rate of mass transfer through the control volume may be worked out by considering mass to be transferred across the control surfaces.

Differential equations for mass transfer in terms of N_A (molar units) [4]

In rectangular coordinates

$$\frac{\partial c_A}{\partial t} + \left[\frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z}\right] = R_A$$

in cylindrical coordinates is

$$\frac{\partial c_A}{\partial t} + \left[\frac{1}{r}\frac{\partial}{\partial r}(rN_{A,r}) + \frac{1}{r}\frac{\partial N_{A,\theta}}{\partial \theta} + \frac{\partial N_{A,z}}{\partial z}\right] = R_A$$

and in spherical coordinates is

$$\frac{\partial c_A}{\partial t} + \left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 N_{A,r}) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(N_{A,\theta}\sin\theta) + \frac{1}{r\sin\theta}\frac{\partial N_{A,\phi}}{\partial \phi}\right] = R_A$$

For the derivations, see class notes.

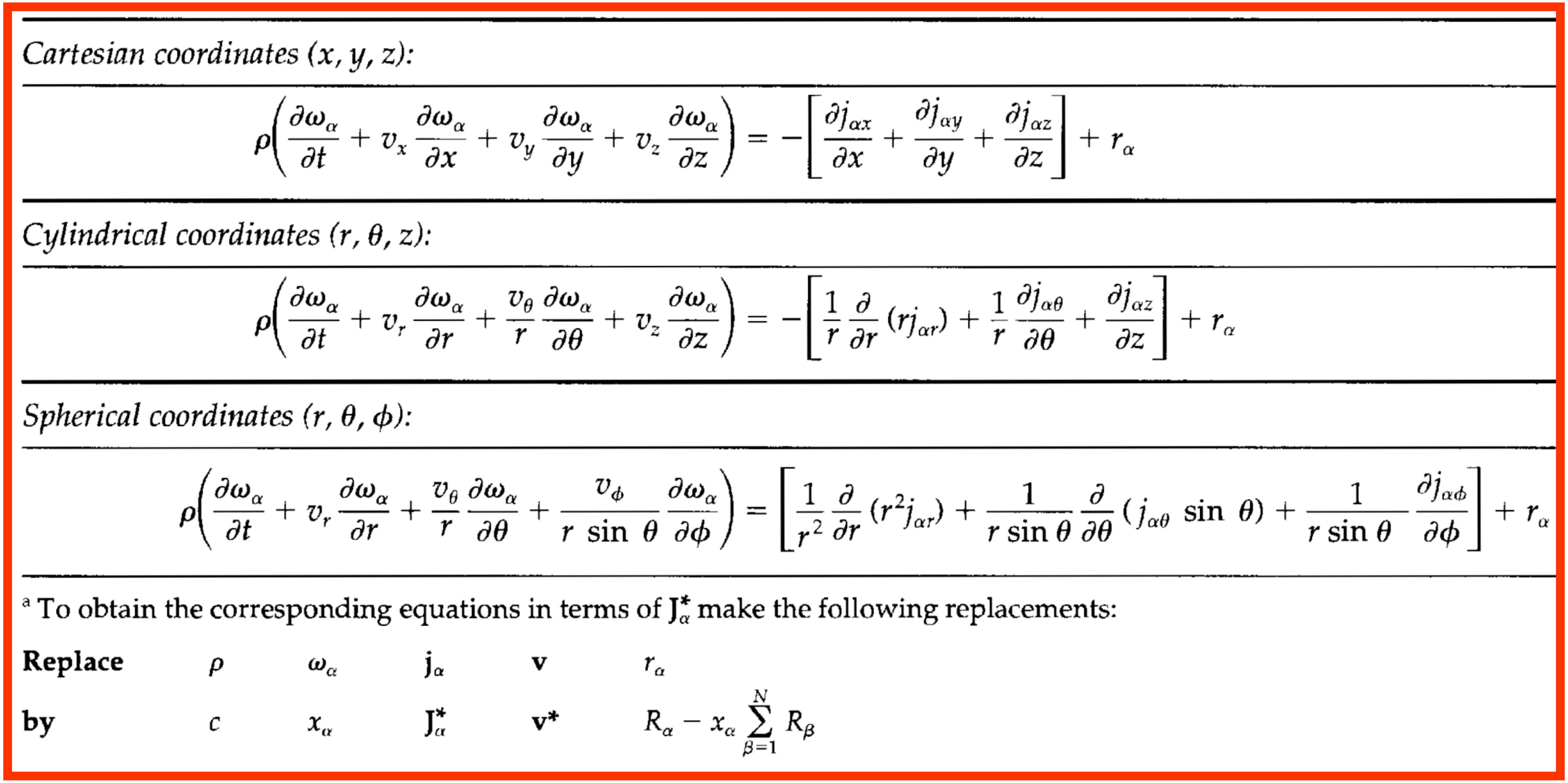
Differential equation for mass transfer in rectangular coordinates (mass units)

For the control volume shown before

$$\boxed{\frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z} \right) + r_A}$$

The net rate of mass transfer through the control volume may be worked out by considering mass to be transferred across the control surfaces.

Differential equations for mass transfer in terms of j_{Az} [1]



Cartesian coordinates (x, y, z):

$$\rho\left(\frac{\partial \omega_\alpha}{\partial t} + v_x \frac{\partial \omega_\alpha}{\partial x} + v_y \frac{\partial \omega_\alpha}{\partial y} + v_z \frac{\partial \omega_\alpha}{\partial z}\right) = -\left[\frac{\partial j_{\alpha x}}{\partial x} + \frac{\partial j_{\alpha y}}{\partial y} + \frac{\partial j_{\alpha z}}{\partial z}\right] + r_\alpha$$

Cylindrical coordinates (r, θ, z):

$$\rho\left(\frac{\partial \omega_\alpha}{\partial t} + v_r \frac{\partial \omega_\alpha}{\partial r} + \frac{v_\theta}{r} \frac{\partial \omega_\alpha}{\partial \theta} + v_z \frac{\partial \omega_\alpha}{\partial z}\right) = -\left[\frac{1}{r}\frac{\partial}{\partial r}(r j_{\alpha r}) + \frac{1}{r}\frac{\partial j_{\alpha\theta}}{\partial \theta} + \frac{\partial j_{\alpha z}}{\partial z}\right] + r_\alpha$$

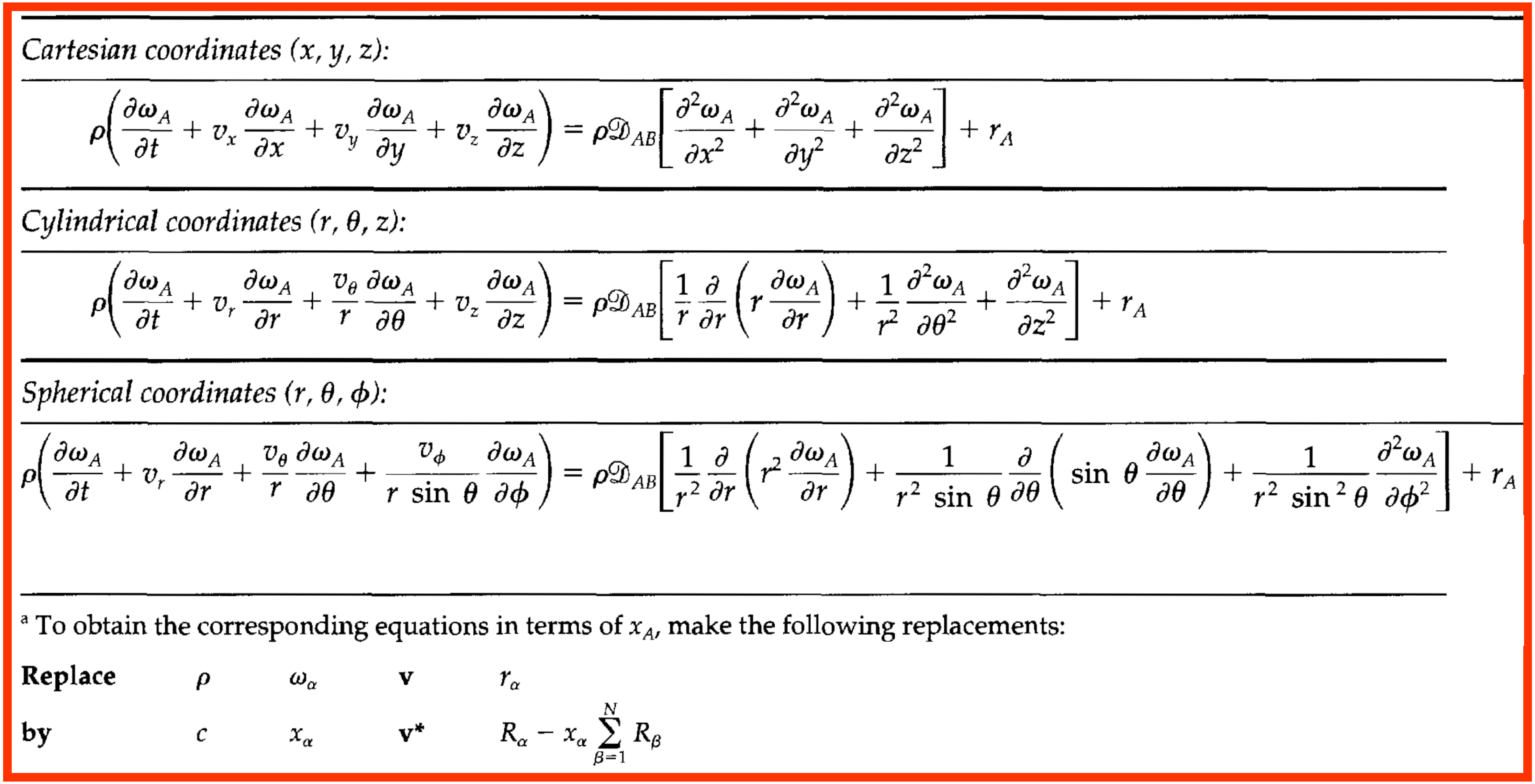
Spherical coordinates (r, θ, ϕ):

$$\rho\left(\frac{\partial \omega_\alpha}{\partial t} + v_r \frac{\partial \omega_\alpha}{\partial r} + \frac{v_\theta}{r} \frac{\partial \omega_\alpha}{\partial \theta} + \frac{v_\phi}{r\sin\theta} \frac{\partial \omega_\alpha}{\partial \phi}\right) = \left[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 j_{\alpha r}) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(j_{\alpha\theta}\sin\theta) + \frac{1}{r\sin\theta}\frac{\partial j_{\alpha\phi}}{\partial \phi}\right] + r_\alpha$$

[a] To obtain the corresponding equations in terms of $\mathbf{J}_\alpha^*$ make the following replacements:

Replace	ρ	ω_α	$\mathbf{j}_\alpha$	$\mathbf{v}$	r_α
by	c	x_α	$\mathbf{J}_\alpha^*$	$\mathbf{v}^*$	$R_\alpha - x_\alpha \sum_{\beta=1}^{N} R_\beta$

Differential equations for mass transfer in terms of ω_A [1]



Cartesian coordinates (x, y, z):

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_x \frac{\partial \omega_A}{\partial x} + v_y \frac{\partial \omega_A}{\partial y} + v_z \frac{\partial \omega_A}{\partial z}\right) = \rho \mathscr{D}_{AB}\left[\frac{\partial^2 \omega_A}{\partial x^2} + \frac{\partial^2 \omega_A}{\partial y^2} + \frac{\partial^2 \omega_A}{\partial z^2}\right] + r_A$$

Cylindrical coordinates (r, θ, z):

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_r \frac{\partial \omega_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial \omega_A}{\partial \theta} + v_z \frac{\partial \omega_A}{\partial z}\right) = \rho \mathscr{D}_{AB}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial \omega_A}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 \omega_A}{\partial \theta^2} + \frac{\partial^2 \omega_A}{\partial z^2}\right] + r_A$$

Spherical coordinates (r, θ, ϕ):

$$\rho\left(\frac{\partial \omega_A}{\partial t} + v_r \frac{\partial \omega_A}{\partial r} + \frac{v_\theta}{r}\frac{\partial \omega_A}{\partial \theta} + \frac{v_\phi}{r \sin\theta}\frac{\partial \omega_A}{\partial \phi}\right) = \rho \mathscr{D}_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \omega_A}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \omega_A}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \omega_A}{\partial \phi^2}\right] + r_A$$

---

[a] To obtain the corresponding equations in terms of x_A, make the following replacements:

Replace	ρ	ω_α	$\mathbf{v}$	r_α
by	c	x_α	$\mathbf{v}^*$	$R_\alpha - x_\alpha \sum_{\beta=1}^{N} R_\beta$

Class activity: Application of general mass balance equation

Write down the generalized equations given in slides in terms of mass quantities. Write down the model equations for the following cases using these generalized equations.

Question No. 1

Acetic acid from an aqueous solution is being extracted in a pulsed liquid-liquid extraction column using ethyl acetate as the solvent and the following conditions are prevailed:

- No drop in pressure in any of the phases.
- Isothermal conditions.
- The two phases are flowing in countercurrent flow direction.
- The two phases are in pure plug flow conditions. So there is no axial or radial diffusion in the extractor.
- Assume the process is at steady-state.

Class activity: Application of general mass balance equation

Question No. 2
Cyclohexane is dehydrogenated in gas phase catalytic fixed bed reactor and the following conditions are prevailed:

- No pressure drop.
- Isothermal conditions.
- The gas phase is flowing in a plug flow fashion.
- Assume the process is at steady-state.

Question No. 3
Cyclohexane is dehydrogenated in gas phase catalytic fixed bed reactor and the following conditions are prevailed:

- No pressure drop.
- Isothermal conditions.
- There is no axial diffusion, however, there is a possibility of radial diffusion.
- Assume the process is at steady-state.

Class activity: Application of general mass balance equation

Question No. 4

Cyclohexane is dehydrogenated in gas phase catalytic fixed bed reactor and the following conditions are prevailed:

- No pressure drop.
- Isothermal conditions.
- There are axial as well as radial diffusions.
- Assume the process is at startup.

Question No. 5

A pressurized gas is contained in a spherical tank with thick porous wall. The spherical wall is slowly rotating on its vertical axis.

- No pressure drop in the wall.
- Isothermal conditions.

Write model equations only for the wall region as well as region within the vessel, separately.

Class activity: Application of general mass balance equation

Question No. 6

Ammonia gas from air is absorbed in water (solvent) in a randomly packed column. The following conditions are prevailed:

- No drop in pressure in any of the phases.
- Isothermal conditions.
- The two phases are flowing in countercurrent flow direction.
- The two phases are in pure plug flow conditions. So there is no axial or rad diffusion in the absorber.
- Assume the process is at shut-down.

Question No. 7

Cyclohexane is dehydrogenated in gas phase catalytic fixed bed reactor and the followi conditions are prevailed:

- Appreciable pressure drop.
- Non-isothermal conditions.
- There are axial as well as radial diffusions.
- Assume the process is at startup.

Class activity: Application of general mass balance equation

Question No. 8

Cyclohexane is dehydrogenated in gas phase catalytic fixed bed reactor and the following conditions are prevailed:

- Appreciable pressure drop.
- Non-isothermal conditions.
- There are axial as well as radial diffusions.
- Assume the process is at startup.
- The reactor is rotating on its axial axis.

Question No. 9

A horizontal cylindrical reactor packed with spherical alumina particles is used for the conversion of hydrogen sulfide into elemental sulfur (Claus reactor). The reactants enter from the top of the reactor and the products leave at the bottom of the reactor. The following conditions are prevailed.

- Insignificant pressure drop.
- Isothermal conditions.
- No diffusion limitations in the axial direction. However, radial diffusivity is important.
- Assume the process is at steady-state.

Class activity: Application of general mass balance equation

Question No. 10

CO_2 is diffusing in still air contained in a rectangular duct. The diffusion is unidirectional.

Question No. 11

Ammonia gas from air is absorbed in water (solvent) in a randomly packed column. The following conditions are prevailed:

- No drop in pressure in any of the phases.
- Isothermal conditions.
- The two phases are flowing in countercurrent flow direction.
- There is a possibility of axial diffusion only.
- Assume the process is at steady-state.

Application of general mass balance equation

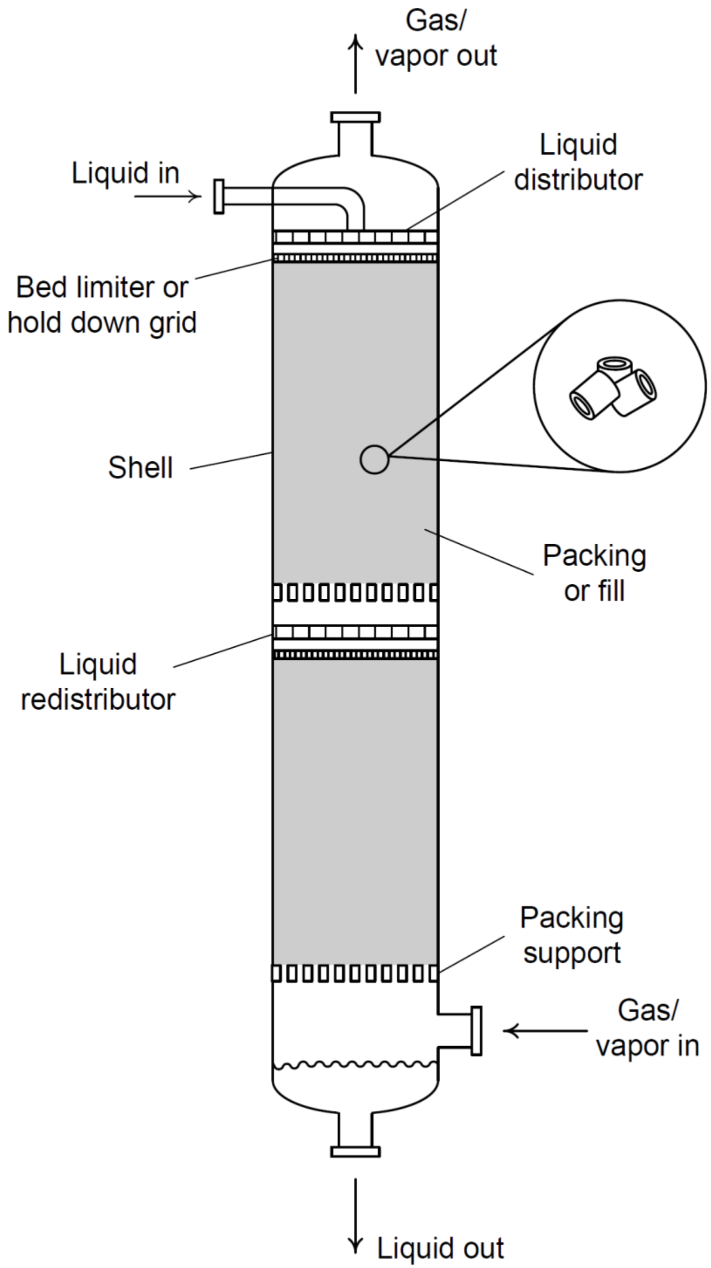
Apply the general continuity equations for various other systems described in the class.

Think other situations such as falling film problem discussed in Chapter 2 of the text book [1] and develop the model differential equations.

Mathematical modeling of a differential gas-absorber

Ammonia gas (*A*) is to be absorbed from an air-ammonia mixture using a suitable solvent, say, water. The gas absorption is to be carried out in a differential absorber such as packed column (installed in our unit operations laboratory) as shown on the next slide. Apply shell mass balance and develop the differential equations (for all possible conditions including and excluding diffusivities) applied to the gas absorber. The gas phase enters from the bottom and flows upwards and vice versa.

Packed column [11]



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