ChE 204
Introduction to Transport Phenomena

Module 4

Mass Transport: the Fick's law of molecular diffusion

4.0. Modes of mass transport

4.1. Fick's law of molecular diffusion

4.2 Diffusivity of gases and kinetic theory

4.3. Fick's law of molecular diffusion in binary systems

4.4. Equilibrium at interfaces: the Henry's Law

4.5. Convective-diffusion equation in binary systems

4.6. Mass transfer coefficient for molecular transport between two phases

ChE 204
Introduction to Transport Phenomena

Module 4

Mass Transport: the Fick’s law of molecular diffusion

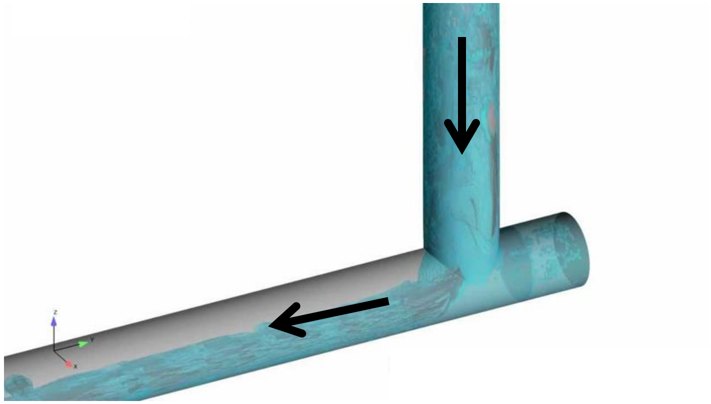
Objectives of this module:

- To describe the transport modes for mass
- To understand and apply the Fick’s first law
- To understand the meaning of diffusion from a macro and molecular point of view

4.0. Modes of mass transport

- Molecular diffusion (from high to low concentration)

- Advective mass transport (transport by bulk motion of the fluid)



Note: in most cases these two transport will be combined in convective mass transport

4.0. Modes of mass transport

- Molecular diffusion (from high to low concentration)

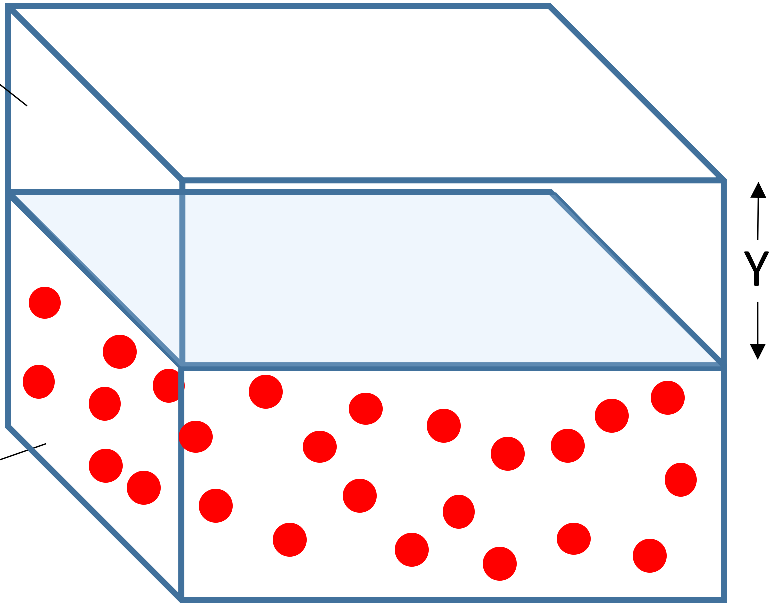
?

Diffusion is the process by which molecules, ions, or other small particles spontaneously mix, moving from regions of relatively high concentration into regions of lower concentration.

This process can be described in two ways:
1. Fick’s Law and diffusion coefficient, which is a more fundamental description
2.In terms of mass transfer coefficient, which is an approximate engineering idea offering a simpler and more practical solution to problems.

4.1. Fick’s law of molecular diffusion

t = 0



Container B

Low Conc

Container A

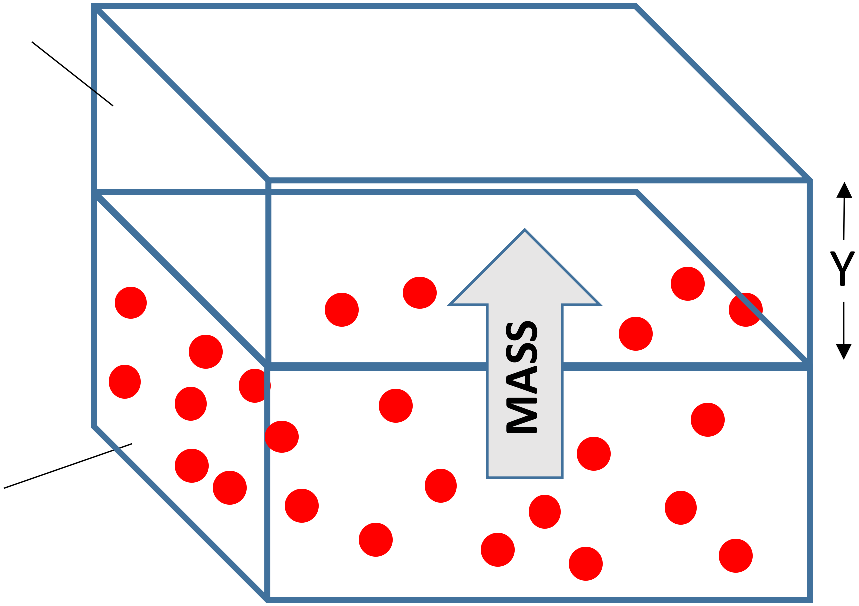
High Conc

4.1. Fick’s law of molecular diffusion

Small t

Container B

Low Conc



Container A

High Conc

4.1. Fick's law of molecular diffusion

SOME DEFINITIONS

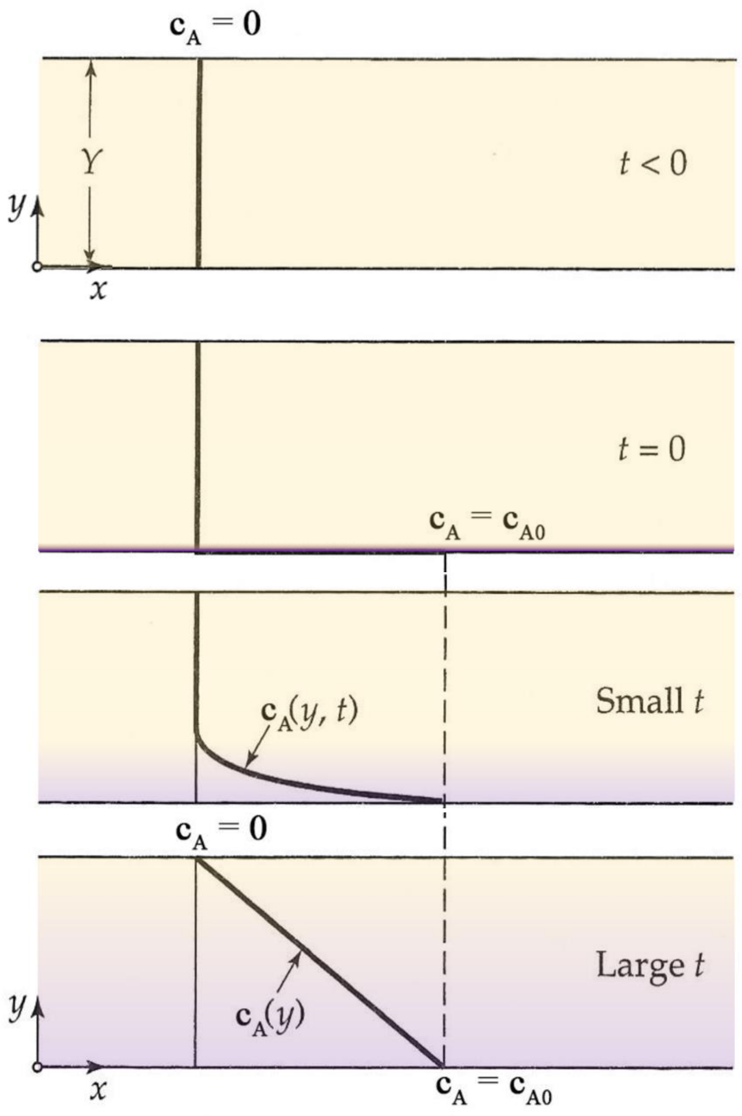
The **molar flow rate** indicates the moles of a compound transferred by diffusion per unit time

$$J = \frac{moles}{time} \qquad \left[\frac{mol}{s}\right]$$

The **molar flux** is the molar flow rate per unit area

$$j = \frac{J}{A} = \frac{moles}{Area \times time} \qquad \left[\frac{mol}{m^2\, s}\right]$$

4.1. Fick’s law of molecular diffusion



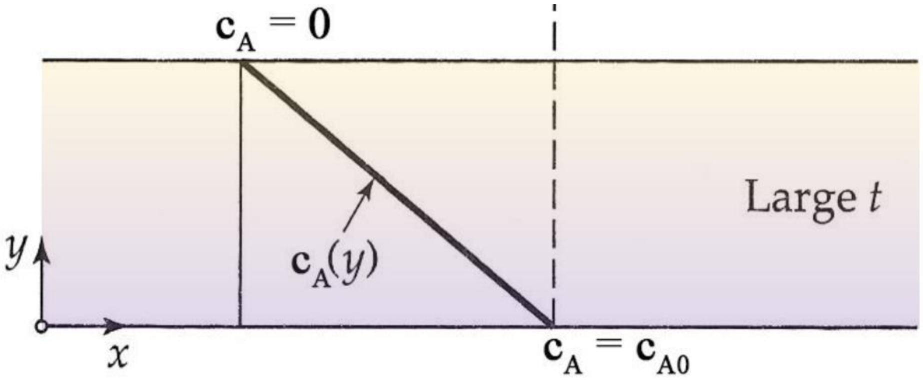
1) The two containers are separated (i.e. by impermeable membrane)

2) We position the two containers in contact (i.e. we remove the membrane)

3) A starts to diffuse into B

4) How is the concentration profile going to look like at steady state?

4.1. Fick's law of molecular diffusion



At large t (steady state):

$$\frac{J_A}{A} \propto \frac{c_{A0} - 0}{Y}$$

This is again a phenomenological relation

↑ area ↑ thickness of the window

$$\frac{J_A}{A} = \mathcal{D}_{AB}\frac{c_A}{Y}$$

$$\boxed{j_{A,y} = -\mathcal{D}_{AB}\frac{dc_A}{dy}}$$

(or molar)

$J = [\text{mol s}^{-1}]$ Molecular Flow via diffusion

$c = [\text{mol m}^{-3}]$ Molar concentration

$A = [\text{m}^2]$ Surface Area

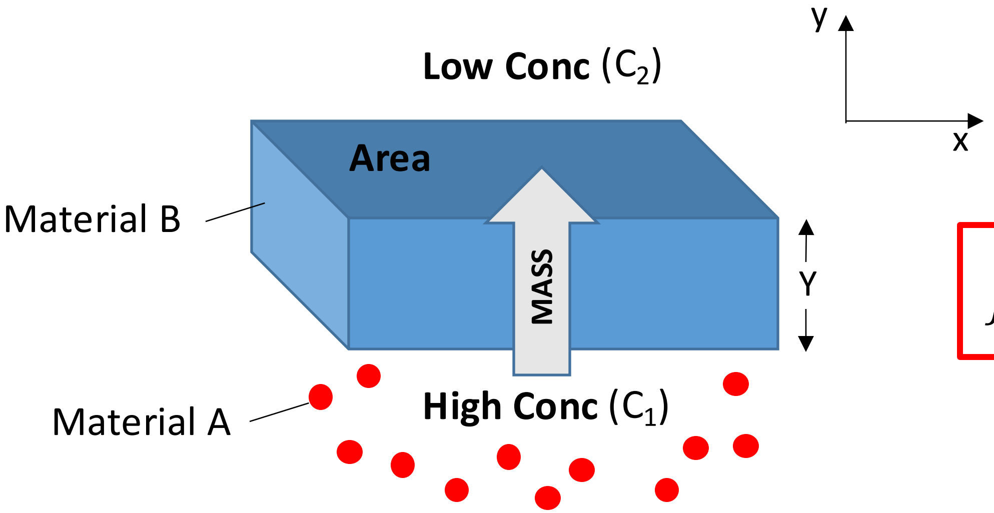
$\mathcal{D}_{AB} = [\text{m}^2\ \text{s}^{-1}]$

Molar diffusivity of A in B
"molar diffusion coefficient"

$j = \frac{J}{A} = [\text{mol m}^{-2}\text{s}^{-1}]$

Molecular flux via diffusion

4.1. Fick's law of molecular diffusion



$$\boxed{j_{A,y} = \frac{J_A}{Area} = -D_{AB}\frac{(C_2 - C_1)}{Y}}$$

- Equal concentration ⇨ no mass diffusion
- Mass diffuses from lower to higher concentration
- The greater the difference in concentration, the faster is the diffusion
- The diffusion coefficient is material dependent

"Mass diffusion is proportional to the negative concentration gradient between regions"

4.1. Fick's law of molecular diffusion

$$\boxed{j_{A,y} = -\mathcal{D}_{AB}\frac{dc_A}{dy}}$$

"The rate of mass transfer through a material is proportional to the negative gradient of the concentration and to the area"

Mass transfer by diffusion is analogous to heat transfer by conduction:

$$\boxed{q = -k\frac{dT}{dy}}$$

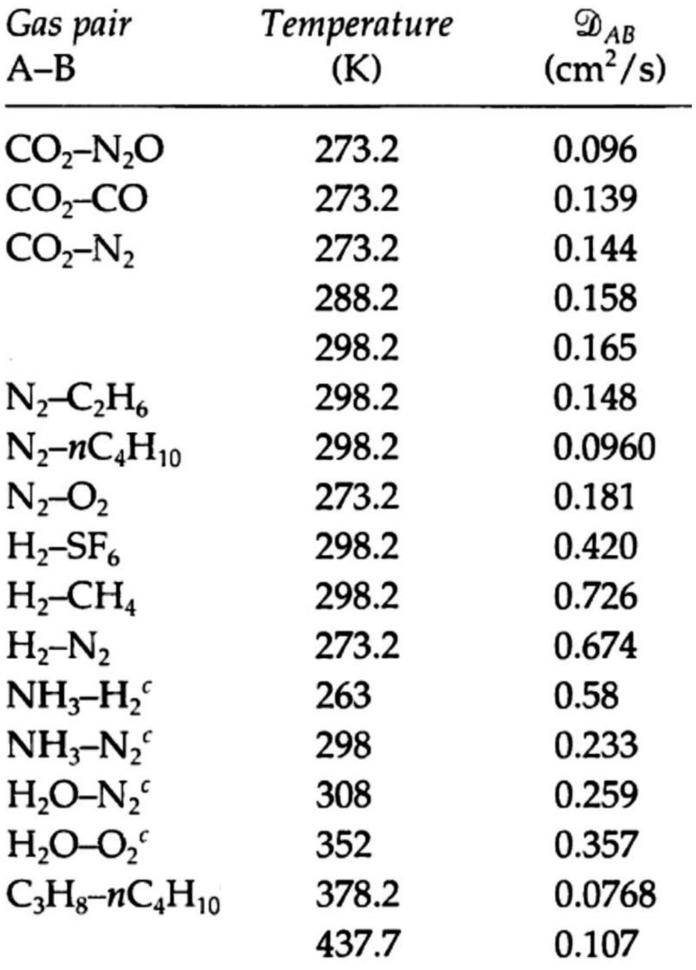
Assumptions:

- Steady state
- Solubility of A into B
- Diluted systems
- One dimensional diffusion
- Total molar concentration is constant
- No internal mass lost or generation

4.1. Fick’s law of molecular diffusion

Values of the Diffusion coefficient

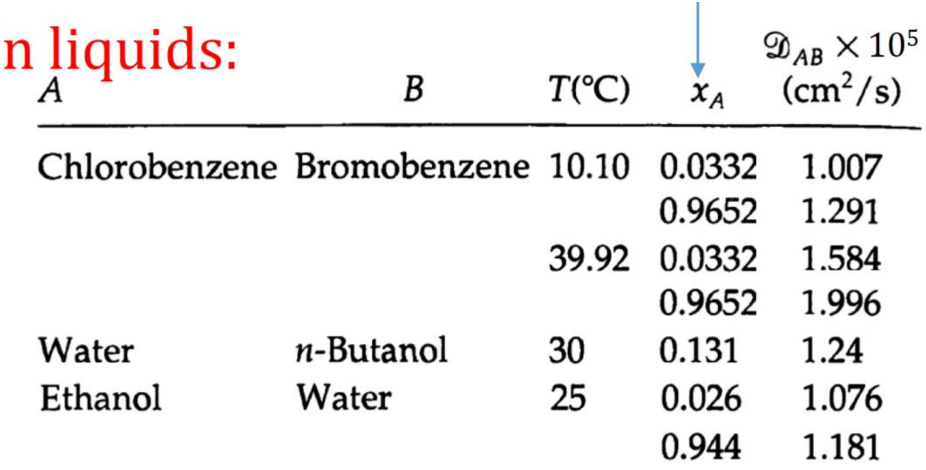
in gases:



Gas pair A–B	Temperature (K)	$\mathscr{D}_{AB}$ (cm^2/s)
CO_2–N_2O	273.2	0.096
CO_2–CO	273.2	0.139
CO_2–N_2	273.2	0.144
	288.2	0.158
	298.2	0.165
N_2–C_2H_6	298.2	0.148
N_2–nC_4H_{10}	298.2	0.0960
N_2–O_2	273.2	0.181
H_2–SF_6	298.2	0.420
H_2–CH_4	298.2	0.726
H_2–N_2	273.2	0.674
NH_3–H_2[c]	263	0.58
NH_3–N_2[c]	298	0.233
H_2O–N_2[c]	308	0.259
H_2O–O_2[c]	352	0.357
C_3H_8–nC_4H_{10}	378.2	0.0768
	437.7	0.107

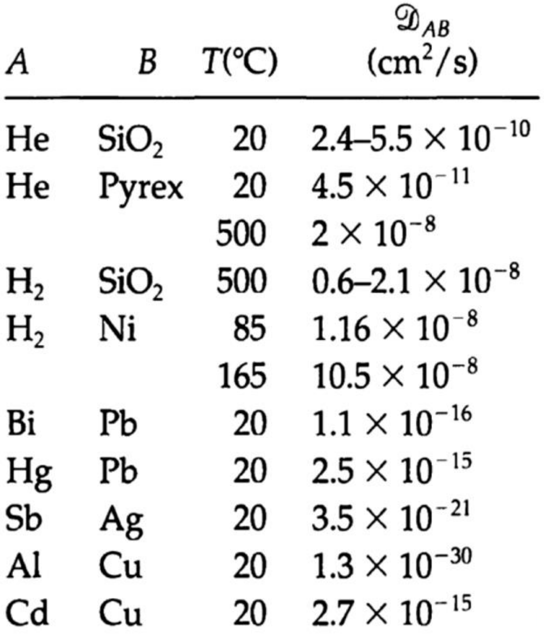
in liquids:

x_A (mol fraction of A)



A	B	T(°C)	x_A	$\mathscr{D}_{AB} \times 10^5$ (cm^2/s)
Chlorobenzene	Bromobenzene	10.10	0.0332	1.007
			0.9652	1.291
		39.92	0.0332	1.584
			0.9652	1.996
Water	*n*-Butanol	30	0.131	1.24
Ethanol	Water	25	0.026	1.076
			0.944	1.181

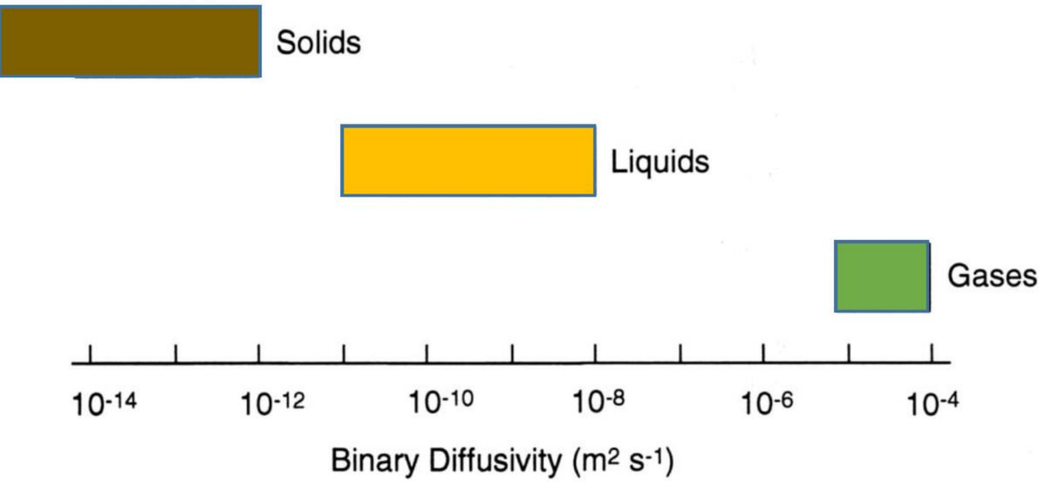
in solids:

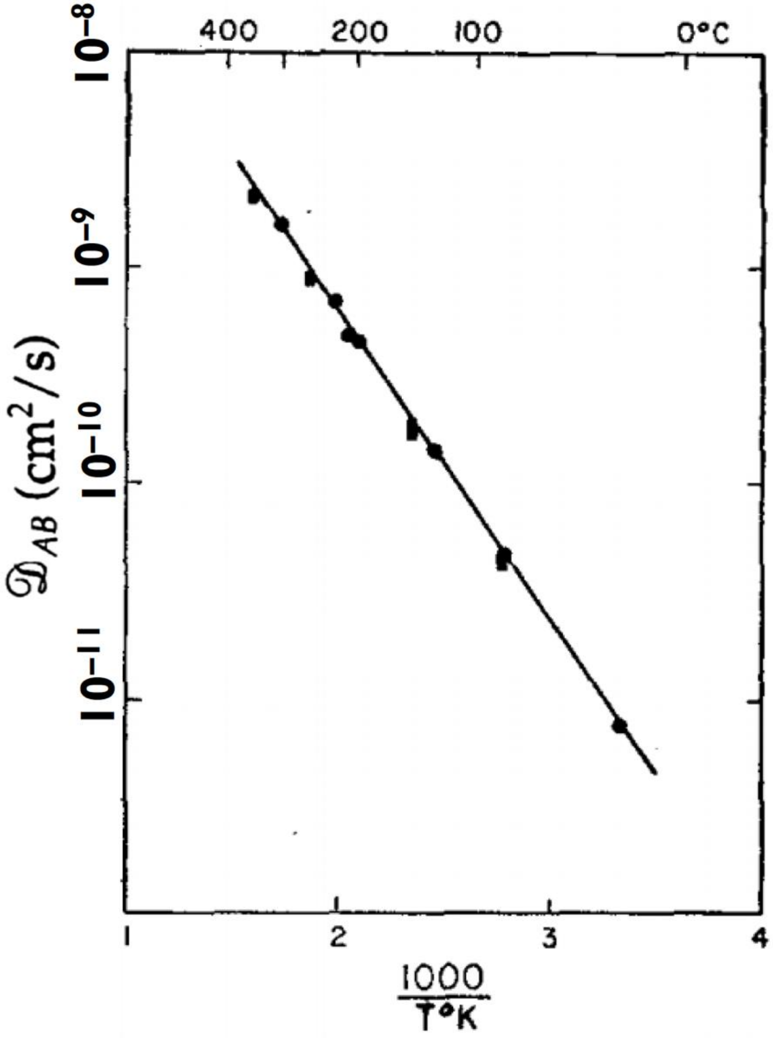


A	B	T(°C)	$\mathscr{D}_{AB}$ (cm^2/s)
He	SiO_2	20	$2.4–5.5 \times 10^{-10}$
He	Pyrex	20	4.5×10^{-11}
		500	2×10^{-8}
H_2	SiO_2	500	$0.6–2.1 \times 10^{-8}$
H_2	Ni	85	1.16×10^{-8}
		165	10.5×10^{-8}
Bi	Pb	20	1.1×10^{-16}
Hg	Pb	20	2.5×10^{-15}
Sb	Ag	20	3.5×10^{-21}
Al	Cu	20	1.3×10^{-30}
Cd	Cu	20	2.7×10^{-15}

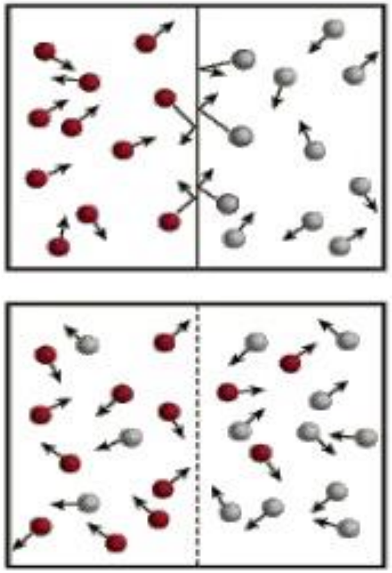
4.1. Fick’s law of molecular diffusion

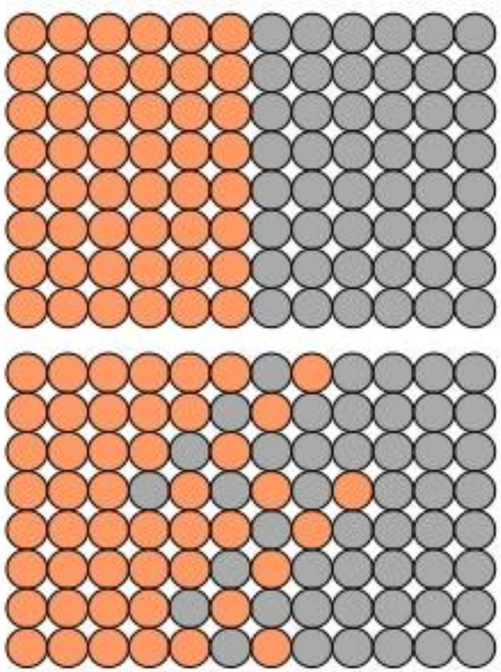
Values of the Diffusion coefficient



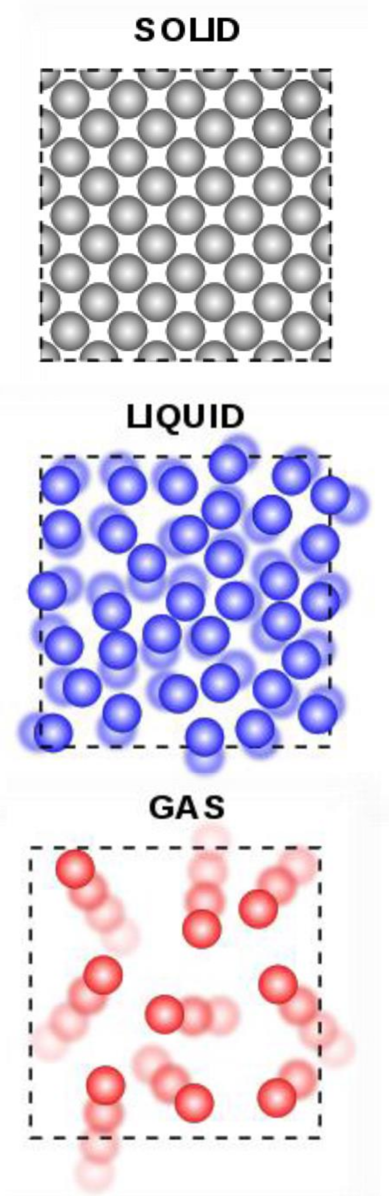


4.2. Diffusivity of gases and kinetic theory





- Diffusion is easy in liquids and gases where atoms are relatively free to move around:
- In solids, atoms are not fixed at its position but constantly moves (oscillates) . So, Diffusion is difficult in solids due to bonding and requires, most of the time, external energy to mobilize the atoms.

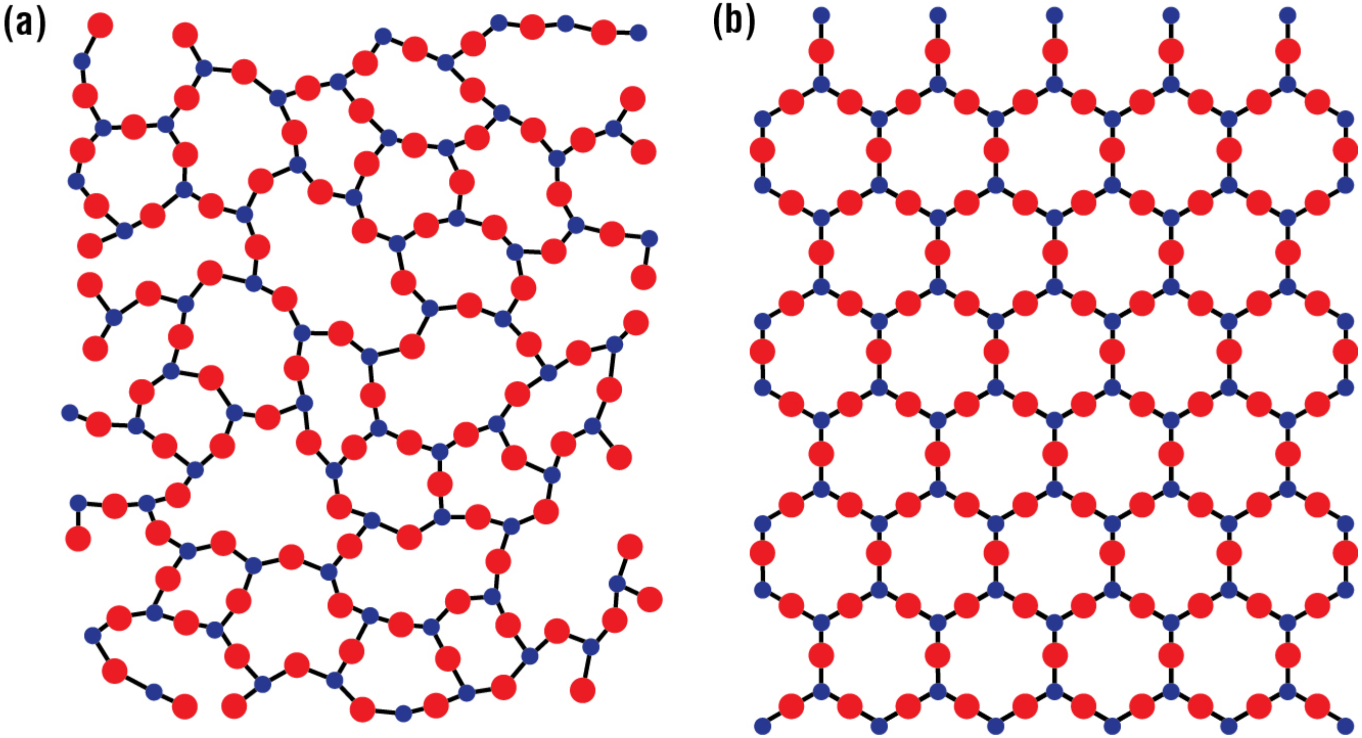


4.1. Fick’s law of molecular diffusion

Gas Diffusion in solids

SiO_2 amorphous
(glass)

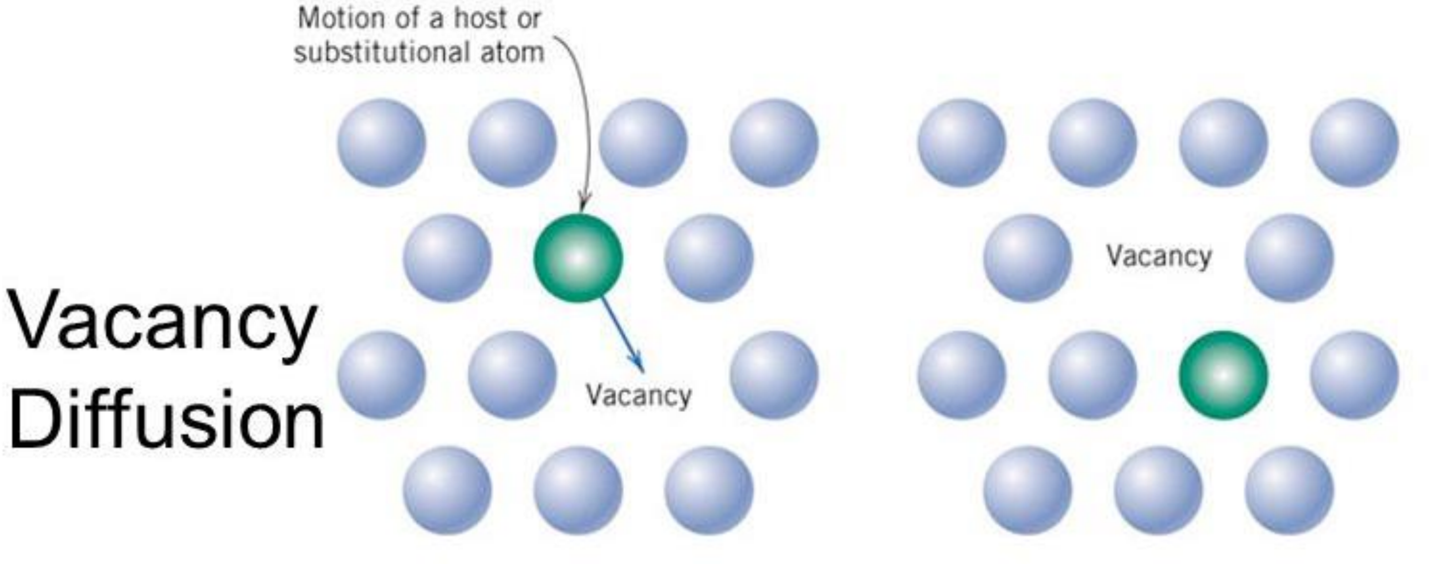
SiO_2 crystalline
(quartz)

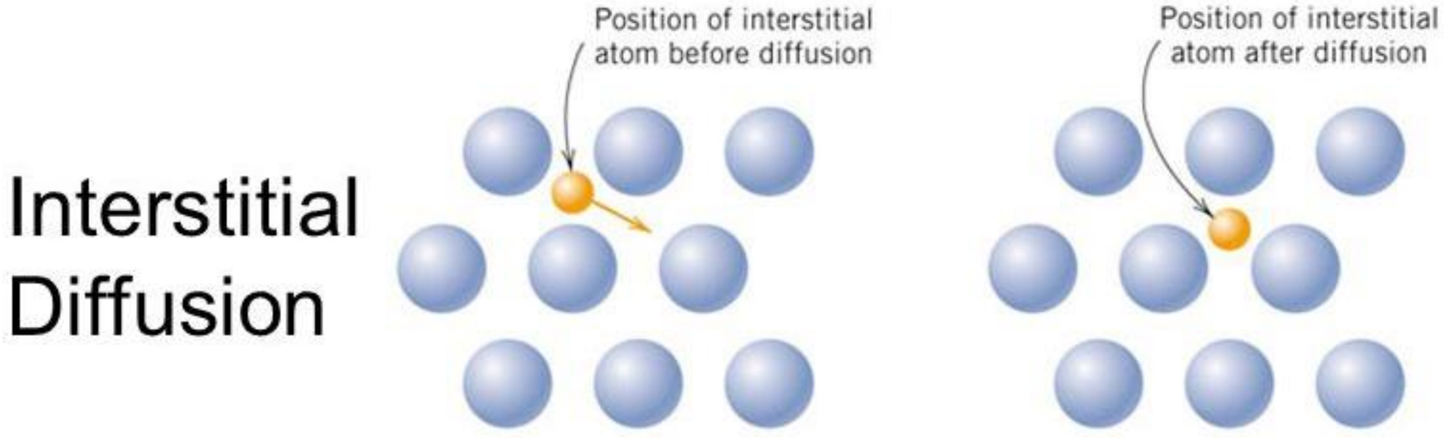


Si-O is around 1.5-1.7 Angstrom
Helium is a monoatomic gas and its size is 1.4 Angstrom
(i.e. nitrogen molecule, N_2, is around 3 Angstrom)

4.2. Diffusivity of gases and kinetic theory

What about solids?





4.1. Fick's law of molecular diffusion

Molecular diffusion in dilute systems

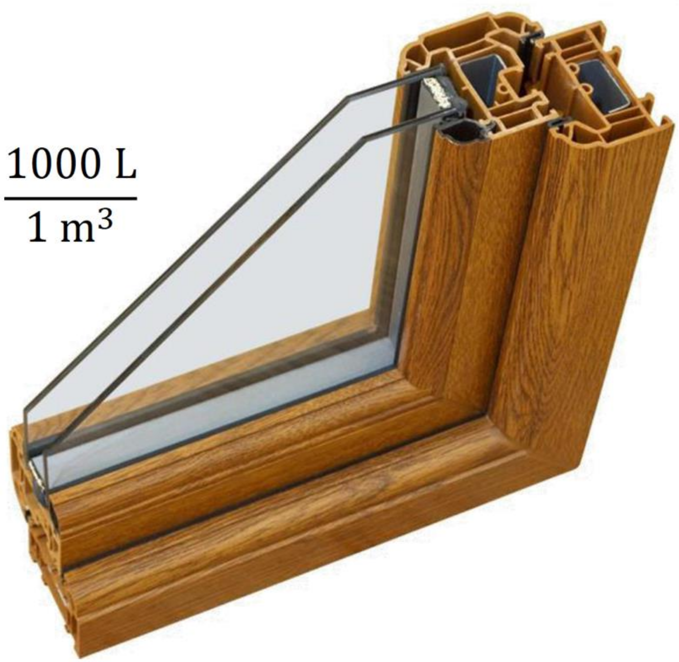
Example: Given their low thermal conductivity and reactivity, inert gases are often used as the gas between the panes of glass in a double-paned window assuming He is used at a pressure of 2 bar and 20°C, and the thickness of the glass is 2 mm, what is the rate of He transport through the slab?

The solubility of He in SiO_2 is 350 mM at 2 bar

$$\frac{J_A}{A} = \mathcal{D}_{AB}\frac{c_A}{Y}$$

$$\frac{J_A}{A} = \frac{4.5\ \times 10^{-11}\text{cm}^2}{\text{s}}\frac{350\ \text{mmol}}{\text{L}}\frac{1}{0.002\ \text{m}}\cdot\frac{1\ \text{m}^2}{10000\ \text{cm}^2}\frac{1000\ \text{L}}{1\ \text{m}^3}$$

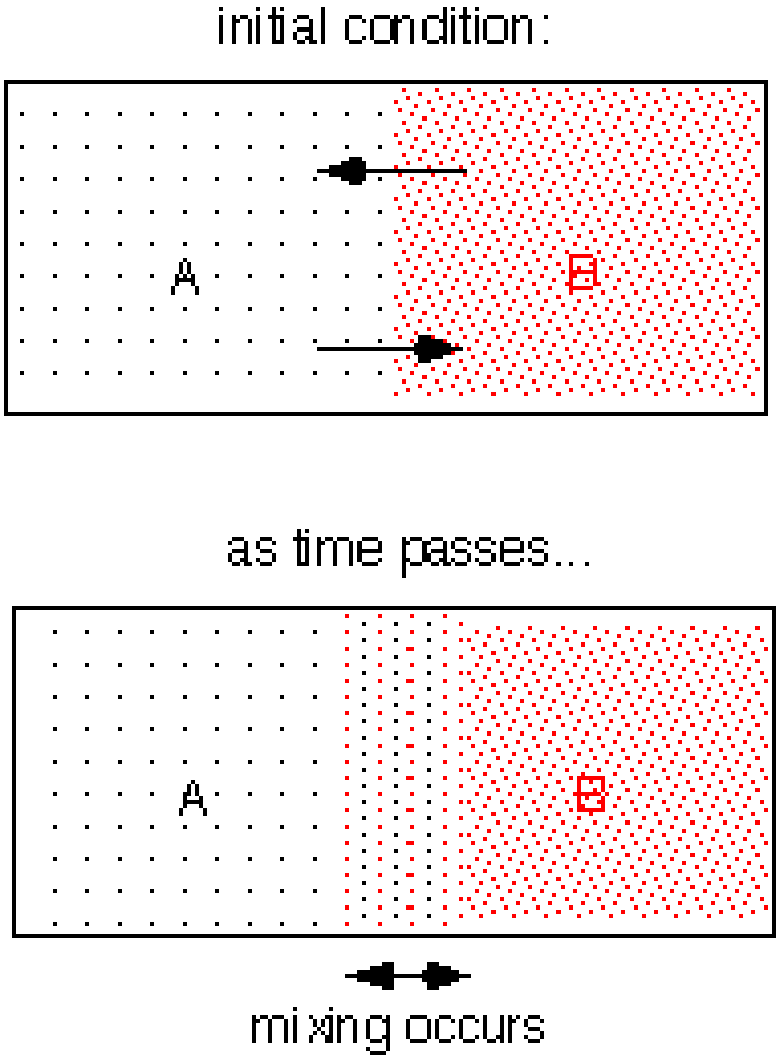
$$\frac{J_A}{A} = j_A = 7.875\ \times 10^{-17}\text{mmol s}^{-1}\ \text{m}^{-2}$$



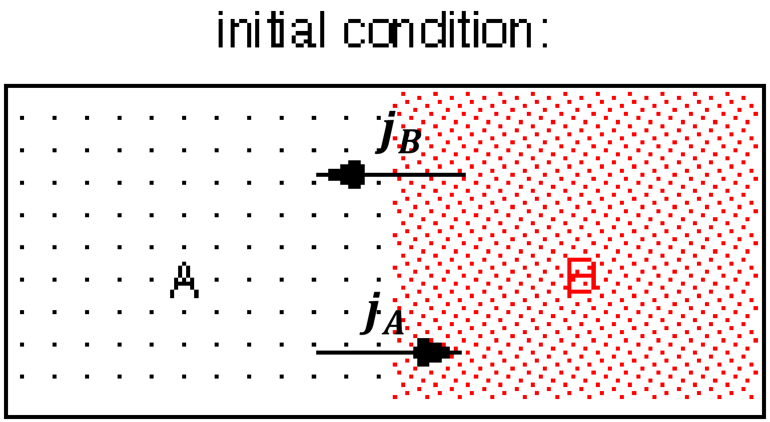
At that rate and assuming a inter-pane volume of 10 L (820 mmols) and a surface area of 2 m^2

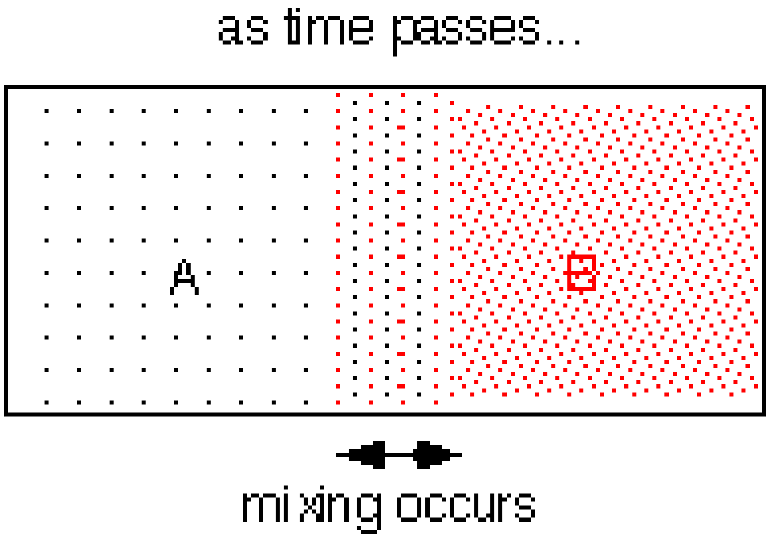
$5.2\ \times 10^{18}$ seconds

4.3. Fick’s law of molecular diffusion in binary systems



4.3. Fick’s law of molecular diffusion in binary systems





Some definitions:

c mixture molar concentration

j_A molar flux of A

v_A velocity of A

x_A mole fraction of A

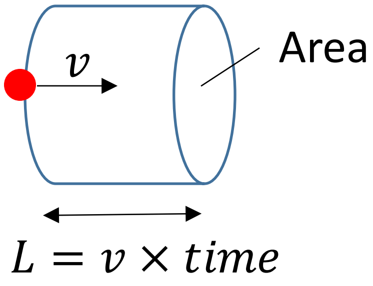
$(\chi_A+\chi_B = 1;\ c_A = c\chi_A)$

v_M mixture molar-averaged velocity

$v_M = x_A v_A + x_B v_B$

4.3. Fick's law of molecular diffusion in binary systems

Before proceeding we define the molar flux in terms of velocities. Because the molar flux is the number of moles per unit time per unit area, if v is the average velocity of specie A, in a similar way in which we have derived the mass flow rate $\dot{m}$ in Module 2, we can derive:



$$j = \frac{moles}{Area \times time} = \frac{concentration \times Volume}{Area \times time} = \frac{concentration \times Area \times v \times time}{Area \times time} =$$

$$= concentration \times v \quad \left[\frac{mol}{m^3} \times \frac{m}{s}\right] = \left[\frac{mol}{m^2\, s}\right]$$

4.3. Fick's law of molecular diffusion in binary systems

$$\boldsymbol{j_A = c x_A \overbrace{(v_A - v_M)}^{\text{velocity of A relative to the mixture (imagine to be an observer sitting on one particle A)}} = -c\, D_{AB} \frac{dx_A}{dy}}$$

Substituting $v_M = x_A v_A + x_B v_B$

$$j_A = c x_A (v_A - v_M) = c x_A (v_A - (x_A v_A + x_B v_B)) =$$

$$= c x_B x_B (v_A - v_B) = c x_B (v_M - v_B) = -j_B$$

$$\boxed{\boldsymbol{j_A = -j_B}}$$

Of course we can also write the same for B

$$\boldsymbol{j_B = c x_B (v_B - v_M) = -c\, D_{BA} \frac{dx_B}{dy}}$$

Some definitions:

c mixture molar concentration

j_A molar flux of A

v_A velocity of A

x_A mole fraction of A

$(\chi_A + \chi_B = 1;\ c_A = c\chi_A)$

v_M mixture molar-averaged velocity

$v_M = x_A v_A + x_B v_B$

4.3. Fick’s law of molecular diffusion in binary systems

IN MULTICOMPONENT SYSTEMS

$$\boldsymbol{J_i = -c \sum_j D_{ij} \frac{dx_i}{dy}}$$

No reliable method to estimate the diffusion coefficient in a multicomponent system is known

effective diffusion coefficient

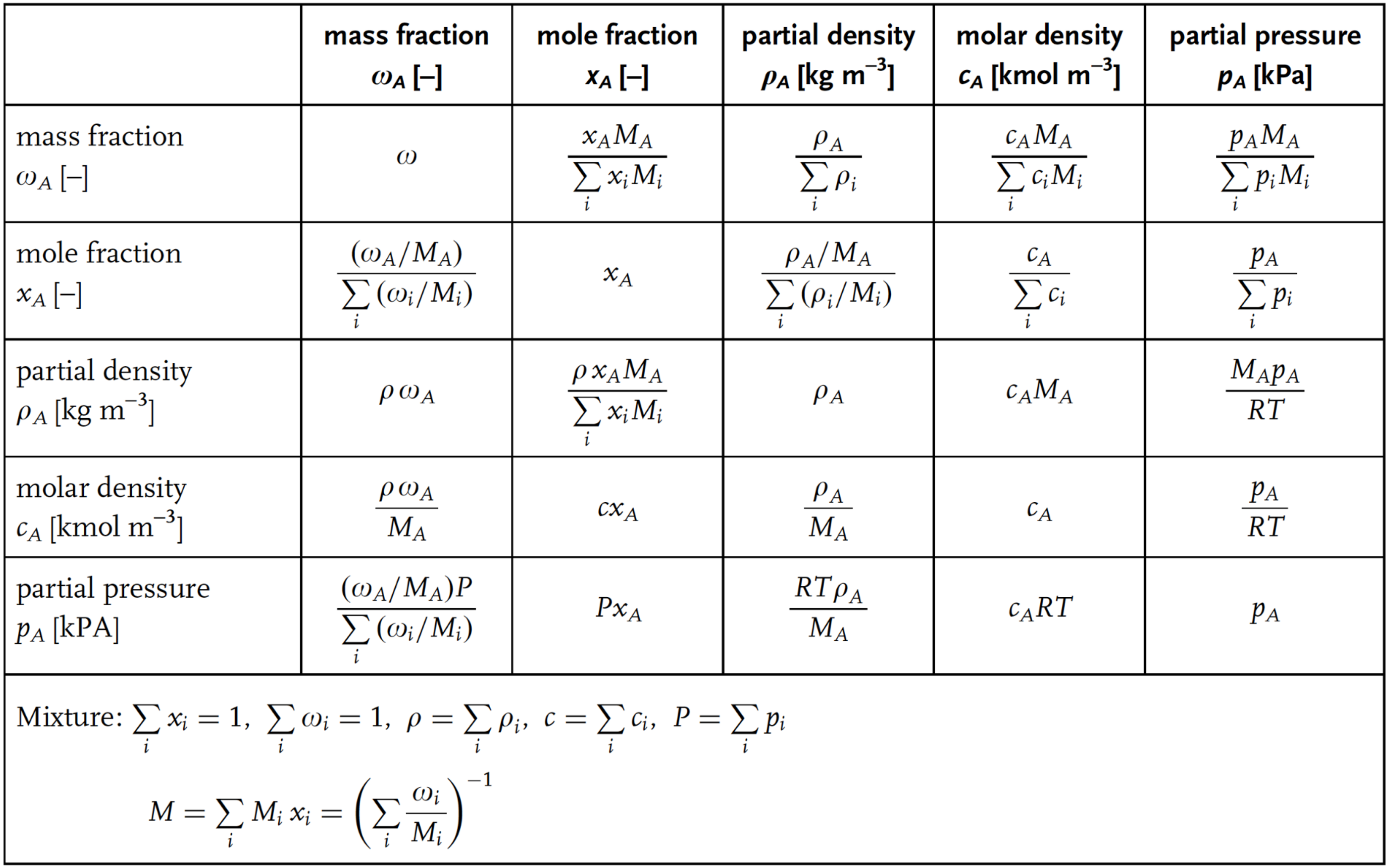
$$\boldsymbol{J_i = -c\, \overset{\downarrow}{D}_{m,i} \frac{dx_i}{dy}}$$

$$D_{m,A} = \frac{1 - x_A}{\frac{x_B}{D_{AB}} + \frac{x_C}{D_{AC}} + \frac{x_D}{D_{AD}} \dots \dots ..}$$

4.3. Fick’s law of molecular diffusion in binary systems

IN MULTICOMPONENT SYSTEMS

Relationships between various definitions of concentration in multicomponent systems



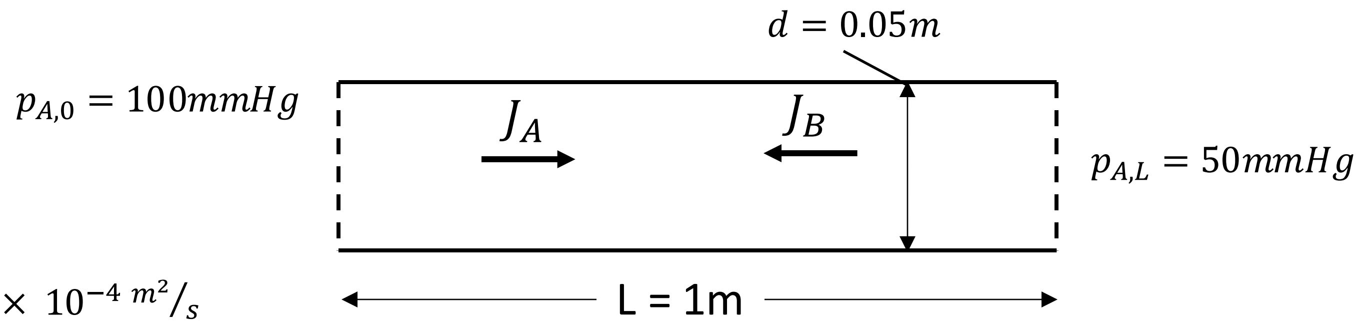
	mass fraction ω_A **[–]**	**mole fraction** x_A **[–]**	**partial density** ρ_A **[kg m^{-3}]**	**molar density** c_A **[kmol m^{-3}]**	**partial pressure** p_A **[kPa]**
mass fraction ω_A [–]	ω	$\frac{x_A M_A}{\sum_i x_i M_i}$	$\frac{\rho_A}{\sum_i \rho_i}$	$\frac{c_A M_A}{\sum_i c_i M_i}$	$\frac{p_A M_A}{\sum_i p_i M_i}$
mole fraction x_A [–]	$\frac{(\omega_A/M_A)}{\sum_i (\omega_i/M_i)}$	x_A	$\frac{\rho_A/M_A}{\sum_i (\rho_i/M_i)}$	$\frac{c_A}{\sum_i c_i}$	$\frac{p_A}{\sum_i p_i}$
partial density ρ_A [kg m^{-3}]	$\rho\,\omega_A$	$\frac{\rho\, x_A M_A}{\sum_i x_i M_i}$	ρ_A	$c_A M_A$	$\frac{M_A p_A}{RT}$
molar density c_A [kmol m^{-3}]	$\frac{\rho\,\omega_A}{M_A}$	$c x_A$	$\frac{\rho_A}{M_A}$	c_A	$\frac{p_A}{RT}$
partial pressure p_A [kPA]	$\frac{(\omega_A/M_A)P}{\sum_i (\omega_i/M_i)}$	$P x_A$	$\frac{RT\rho_A}{M_A}$	$c_A RT$	p_A

Mixture: $\sum_i x_i = 1,\ \sum_i \omega_i = 1,\ \rho = \sum_i \rho_i,\ c = \sum_i c_i,\ P = \sum_i p_i$

$$M = \sum_i M_i\, x_i = \left(\sum_i \frac{\omega_i}{M_i}\right)^{-1}$$

4.3. Fick's law of molecular diffusion in binary systems

Example 1 Calculate the **mass flow rate** of CO_2 and nitrogen through the tube.



$d = 0.05m$

$p_{A,0} = 100mmHg$

J_A

J_B

$p_{A,L} = 50mmHg$

L = 1m

A = CO_2
B = N_2
$D_{AB} = 0.16 \times 10^{-4}\, m^2/s$

$$J_A = -\left(\frac{\pi d^2}{4}\right) D_{AB} \frac{(C_{A,L} - C_{A,0})}{L}$$

$$PV = nRT \qquad n = \frac{PV}{RT} \qquad C = \frac{n}{V} = \frac{P}{RT}$$

$$J_A = -\left(\frac{\pi d^2}{4}\right) \frac{D_{AB}}{RTL} (P_{A,L} - P_{A,0}) = 8.45 \times 10^{-11} \frac{kmol}{s}$$

$$J_B = -J_A$$

$$\dot{m}_A = J_A \cdot M_A = 3.72 \times 10^{-9} \frac{kg}{s}$$

$$M_{CO_2} = 44 \frac{kg}{mol}$$

$$\dot{m}_B = J_A \cdot M_B = 2.37 \times 10^{-9} \frac{kg}{s}$$

$$M_{N_2} = 28 \frac{kg}{mol}$$

4.3. Fick's law of molecular diffusion in binary systems

Example 2

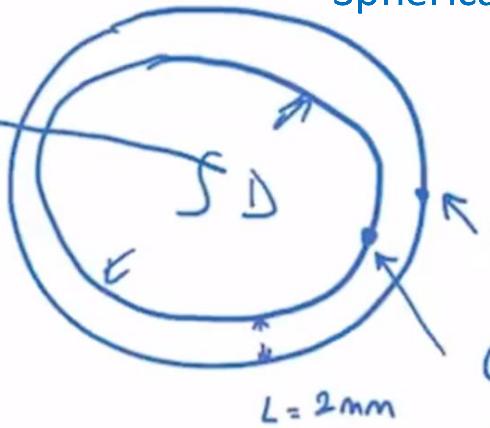
Hydrogen (A)

$P = 10$ bar

$T = 300\ K$

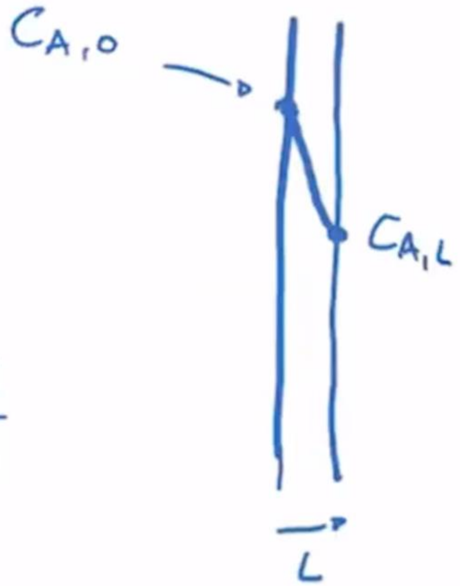
$M_A = 2\ \frac{kg}{kmol}$

Spherical tank



$\underline{\underline{C_{A,L}}} = 0$

$\underline{\underline{C_{A,0}}} = 1.5\ \frac{kmol}{m^3}$



Diameter = 100 mm

steel = B $\qquad D_{AB} = 0.3 \times 10^{-12}\ \frac{m^2}{s}$

FIND: ① INITIAL RATE OF HYDROGEN MASS LOSS FROM THE TANK

② INITIAL RATE OF PRESSURE DROP IN THE TANK

1

$$\dot{m}_A = J_A \cdot M$$

$$J_A = \frac{A\, D_{AB}\, C_{A,0}}{L} \simeq 7.07\ 10^{-12}\ \frac{kmol}{s}$$

$$\text{Area} = \pi D^2$$

$$\dot{m}_A = 14.14 \times 10^{-12}\ \frac{kg}{s}$$

2

$$\dot{m}_A = \frac{d(\rho_A V)}{dt} = \frac{\pi D^3}{6} \cdot \frac{d\rho_A}{dt}$$

ρ_A = density of A inside the tank

$$P_A V = \underset{\substack{\uparrow \\ \text{moles}}}{n} RT \qquad P_A = \frac{n}{V} RT = C_A RT$$

$$n = \frac{m}{M_A} \qquad P_A = \frac{m}{V}\frac{RT}{M_A} = \rho \frac{RT}{M_A} \qquad \rho = P_A \frac{M_A}{RT}$$

$$\triangleright \quad \dot{m}_A = \frac{\pi D^3}{6}\frac{M_A}{RT}\frac{dP_A}{dt}$$

$$\frac{dP_A}{dt} = \dot{m}_A \frac{6}{\pi D^3}\frac{RT}{M_A} = -3.5\times 10^{-7}\ \frac{\text{bar}}{\text{s}}$$

4.3. Fick's law of molecular diffusion in binary systems

Example 3

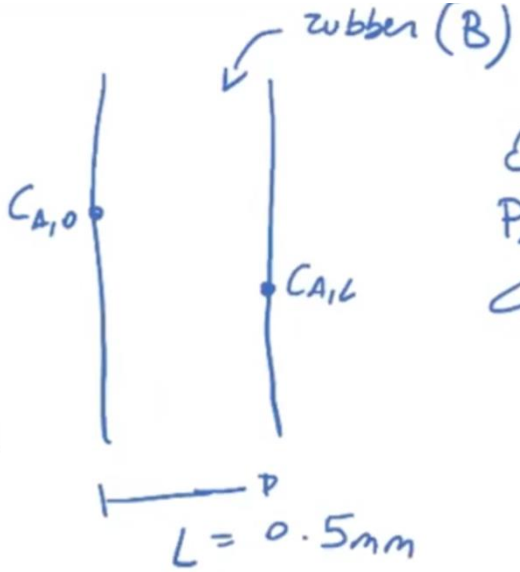
①

Oxygen (A)

$P_{A,1} = 2$ bars

$C_{A,1}$

$C_{A,0} \neq C_{A,1}$



②

Oxygen (A)

$P_{A,2} = 1$ bar

$C_{A,2}$

$C_{A,L} \neq C_{A,2}$

QUESTIONS:

① DETERMINE THE MOLAR FLUX

② $C_{A,2}$?

$$D_{AB} = 0.21 \times 10^{-9} \ m^2/s$$

$$S_{AB} = 3.12 \times 10^{-3} \ \frac{kmol}{m^3 \cdot bar}$$

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① $J_A = -\dfrac{D_{AB}}{L}\left(C_{A,L} - C_{A,0}\right)$

$$\boxed{\begin{aligned} \rightarrow\ C_{A,0} &= S \cdot P_{A,1} \\ \rightarrow\ C_{A,L} &= S \cdot P_{A,2} \end{aligned}}$$

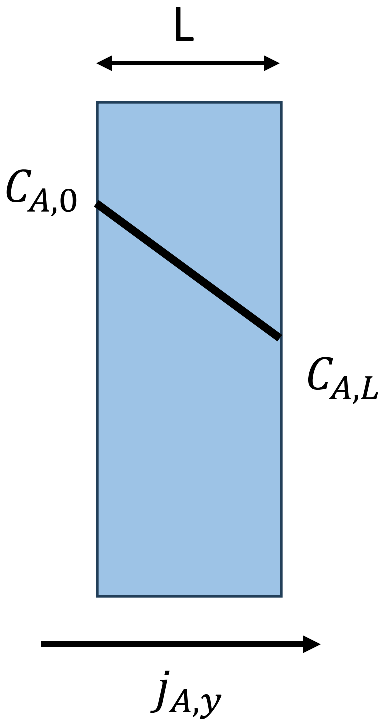
$$J_A = 1.31 \times 10^{-9} \ \frac{kmol}{m^2 \cdot s}$$

$$C_{A,1} = \frac{P_{A,1}}{RT} = 0.0807 \ \frac{kmol}{m^3}$$

$$C_{A,2} = \frac{P_{A,2}}{RT} = 0.0607 \ \frac{kmol}{m^3}$$

$$C_{A,1} \neq C_{A,0} \qquad C_{A,2} \neq C_{A,L}$$

RECAP



Fick's Law: describes molecular diffusion

$$j_{A,y} = \frac{J_A}{Area} = -D_{AB}\frac{\partial C}{\partial y} = -D_{AB}\frac{(C_{A,L} - C_{A,0})}{Y}$$

Molar flux

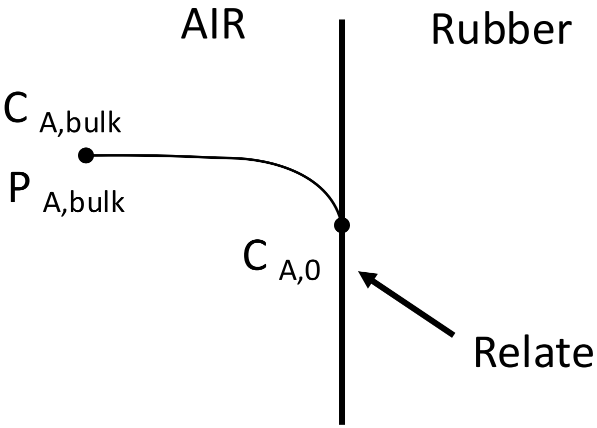
In diluite binary systems

$$\boxed{\boldsymbol{j_A = -j_B}}$$

$$\dot{m}_{A} = M_A \cdot J_A$$

Mass flow rate = molecular weight x molar flow rate

Solubility



Related to the solubility of A in the rubber

TODAY

4.4. Equilibrium at interfaces: the Henry’s Law

4.5. Convective-diffusion equation in binary systems

(example relative to evaporation of a liquid in a non diffusing gas)

4.6. Mass transfer coefficient for molecular transport between two phases

(across interfaces)

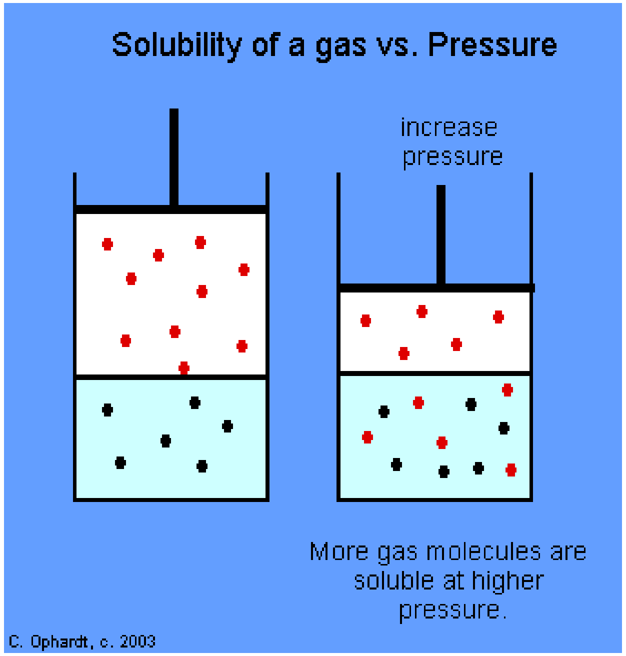
4.4. Equilibrium at interfaces: the Henry's Law

The Henry's law is only valid for dilute solutions i.e. when component A is a solute and correlate the concentration of the solute between two phases at equilibrium. If we are looking at gas/liquid interface, the Henry's law states that "At a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with the liquid"

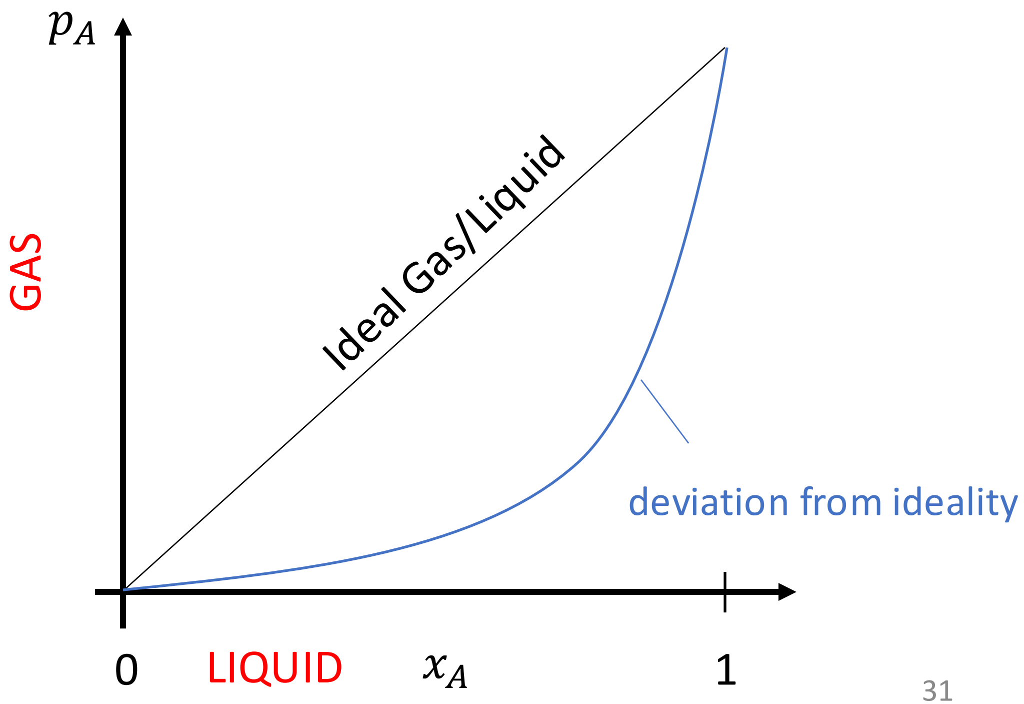
$$p_A = K_H x_A$$

partial pressure of A in the gas phase

Molar fraction of A in the liquid phase



C. Ophardt, c. 2003



4.4. Equilibrium at interfaces: the Henry's Law

K_H can be expressed in different dimensions depending on how we express concentration

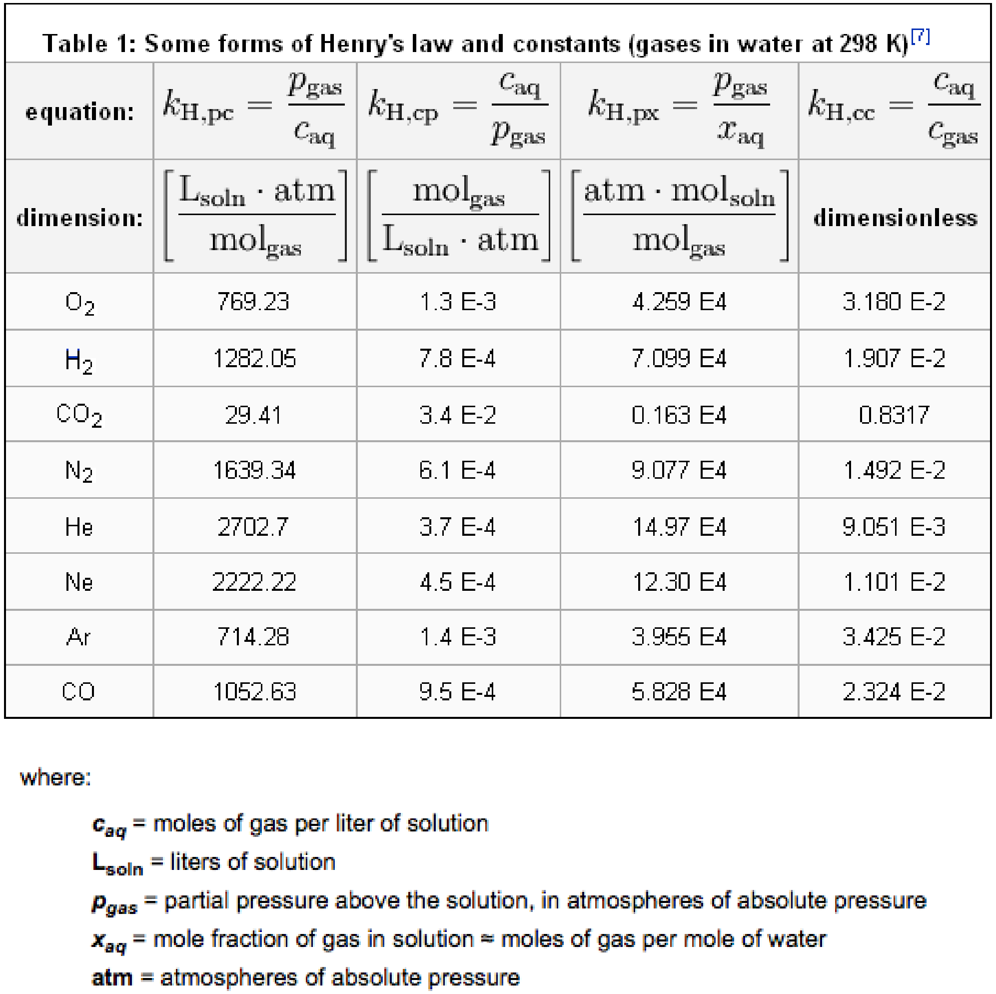


Table 1: Some forms of Henry's law and constants (gases in water at 298 K)[7]

equation:	$k_{H,pc} = \frac{p_{gas}}{c_{aq}}$	$k_{H,cp} = \frac{c_{aq}}{p_{gas}}$	$k_{H,px} = \frac{p_{gas}}{x_{aq}}$	$k_{H,cc} = \frac{c_{aq}}{c_{gas}}$
dimension:	$\left[\frac{L_{soln} \cdot atm}{mol_{gas}}\right]$	$\left[\frac{mol_{gas}}{L_{soln} \cdot atm}\right]$	$\left[\frac{atm \cdot mol_{soln}}{mol_{gas}}\right]$	**dimensionless**
O_2	769.23	1.3 E-3	4.259 E4	3.180 E-2
H_2	1282.05	7.8 E-4	7.099 E4	1.907 E-2
CO_2	29.41	3.4 E-2	0.163 E4	0.8317
N_2	1639.34	6.1 E-4	9.077 E4	1.492 E-2
He	2702.7	3.7 E-4	14.97 E4	9.051 E-3
Ne	2222.22	4.5 E-4	12.30 E4	1.101 E-2
Ar	714.28	1.4 E-3	3.955 E4	3.425 E-2
CO	1052.63	9.5 E-4	5.828 E4	2.324 E-2

where:

c_{aq} = moles of gas per liter of solution

L_{soln} = liters of solution

p_{gas} = partial pressure above the solution, in atmospheres of absolute pressure

x_{aq} = mole fraction of gas in solution ≈ moles of gas per mole of water

atm = atmospheres of absolute pressure

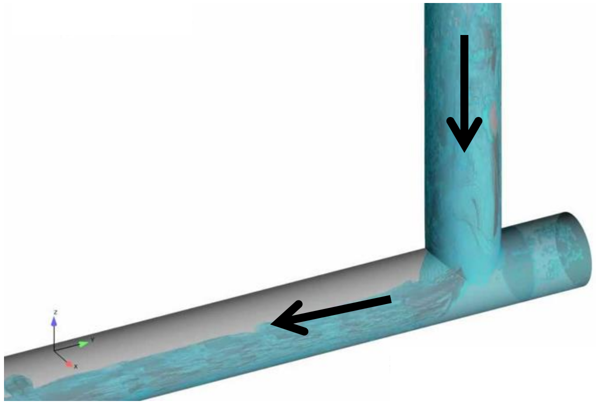
4.5. Convective-diffusion equation for a binary system

- Molecular diffusion (from high to low concentration)

+

- Advective mass transport (transport by bulk motion of the fluid)

?



e.g. convection (which applies to the movement of fluid driven by density gradients created by temperature difference)

Note: in most cases these two transport mores are combined in convective mass transport

4.5. Convective-diffusion equation for a binary system

DIFFERENT WAYS TO EXPRESS FLOW RATE and FLUX IN MASS TRANSPORT:

$$\dot{\boldsymbol{m}} = \frac{mass}{time} \qquad \left[\frac{Kg}{s}\right]$$

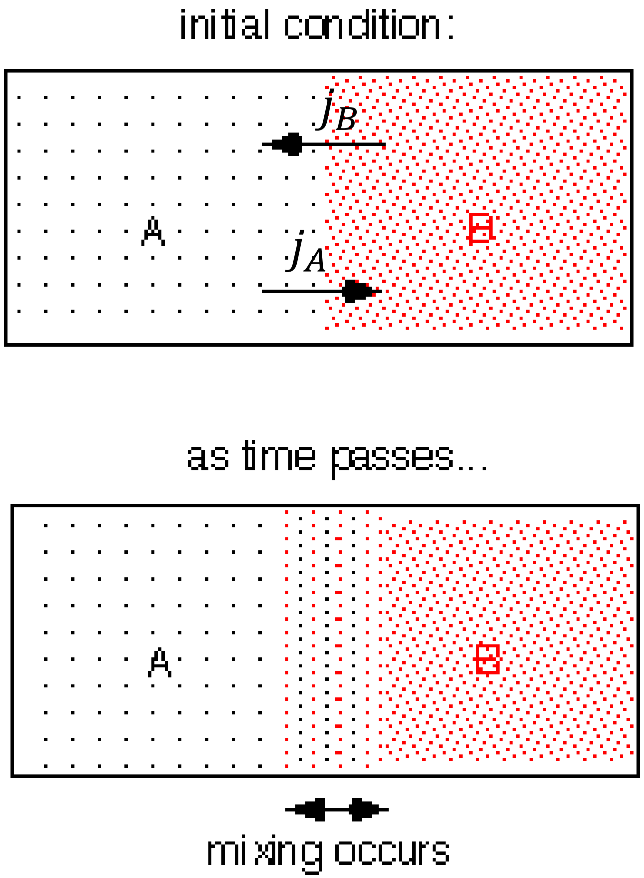
$$\boldsymbol{J} = \frac{moles}{time} \qquad \left[\frac{mol}{s}\right] \qquad\qquad \boldsymbol{j} = \frac{J}{A} = \frac{moles}{Area \times time} \quad \left[\frac{mol}{m^2 s}\right]$$

$$\dot{m} = J \times \mathrm{M} (\text{where M is } the\ molecular\ weight)$$

In some cases you may find also $\boldsymbol{n\ and\ N}$ to indicate the molar flux and flow rate, respectively.

Often $n\ and\ N$ are referred to as the absolute flux and flow, which include diffusive and convective components; instead $j\ and\ J$ are referred to as the diffusive components of the flux and flow.

4.5. Convective-diffusion equation for a binary system



What we have seen already: **DIFFUSION ONLY!**

$$j_A = c x_A (v_A - v_M) = -c\, D_{AB} \frac{dx_A}{dy}$$

$$j_B = c x_B (v_B - v_M) = -c\, D_{BA} \frac{dx_B}{dy}$$

$$j_A = -j_B$$

j_A molar flux of A
v_A velocity of A
x_A mole fraction of A
c mixture molar concentration
v_M mixture molar-averaged velocity

4.5. Convective-diffusion equation for a binary system

CONVECTION + DIFFUSION

$$\boldsymbol{n_A = c x_A v_M - c\, D_{AB} \frac{dx_A}{dy}}$$

molar convective flux of A
(carried by v_M)

molar diffusive flux of A
(relative to v_M)

considering that $v_M = x_A v_A + x_B v_B$

but also $v_M = \frac{n}{c} = \frac{n_A + n_B}{c}$

$$\boxed{\boldsymbol{n_A = x_A (n_A + n_B) - c\, D_{AB} \frac{dx_A}{dy}}}$$

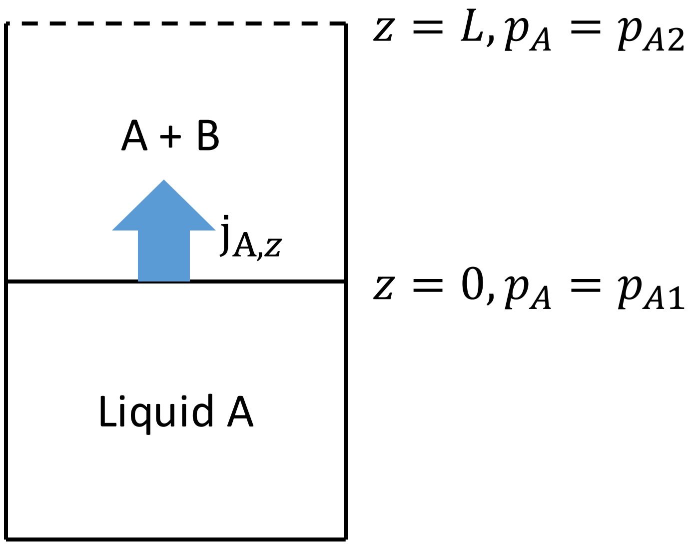
Note: you may find also $\boldsymbol{n_A = x_A (n_A + n_B) + j_A}$ in books where $\boldsymbol{j_A}$ is used to indicate the diffusive flux

4.5. Convective-diffusion equation for a binary system

Example: Evaporation of A through a stationary non-diffusing gas B

Consider the system show in the figure where liquid A is evaporating into a non-diffusing gas B. At steady state, the partial pressure of species A at gas-liquid interface is given as p_{A1} while the partial pressure of species A at the top of vessel is given as p_{A2}. The liquid level in the vessel is maintained at z=0. D_{AB} is known. Derive the diffusive flux $j_{A,z}$.

STEADY STATE
open container=
no accumulation =
no increased pressure



4.5. Convective-diffusion equation for a binary system

Example: Evaporation of A through a stationary non-diffusing gas B

$$\boldsymbol{j_{A,z} = -c\, D_{AB} \frac{dx_A}{dz} = -\frac{D_{AB}}{RT}\frac{dP_A}{dz}}$$

If we integrate between $z = 0\ and\ z = L$ and the text says: "The liquid level in the vessel is maintained at z=0"

$$j_{A,z} = -\frac{D_{AB}}{RT}\frac{(p_{A2} - p_{A1})}{L}$$

Please note that the diffusion is from the interface (z=0$^+$) to the gas.

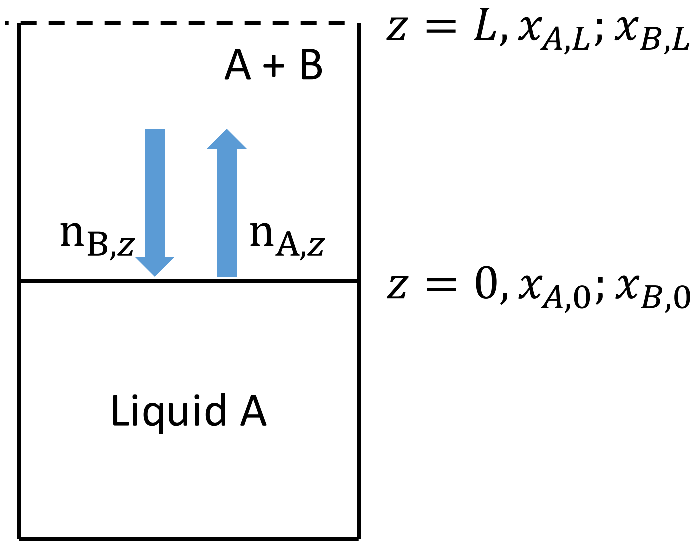
$$x_{A1} = \frac{p_A^{sat}}{p_{tot}} \qquad x_{A2} = \frac{p_{A2}}{P_{tot}}$$

$p_{A1} = p_A^{sat}$ is the vapour pressure of A into gas B, which is going to be in equilibrium with the liquid phase

4.5. Convective-diffusion equation for a binary system

Example: Evaporation of A through a stationary non-diffusing gas B

Derive the total molar flux $\mathrm{n}_{\mathrm{A},z}$



Remember c is the concentration of the mixture

$$\mathrm{n}_{\mathrm{A,z}} = -c\mathcal{D}_{\mathrm{A}B}\frac{dx_{\mathrm{A}}}{dz} + \mathrm{x}_A\left(\mathrm{n}_{\mathrm{A,z}} + \mathrm{n}_{\mathrm{B,z}}\right)$$

Because $\mathrm{n}_{\mathrm{B},z} = 0$

$$\mathrm{n}_{\mathrm{A,z}} = -c\mathcal{D}_{\mathrm{A}B}\frac{dx_{\mathrm{A}}}{dz} + \mathrm{x}_A\, n_{A,z}$$

If B is non diffusing in A, $\mathrm{n}_{\mathrm{B},z} = 0$ at steady state

It can be re-written like

$$\mathrm{n}_{\mathrm{A,z}} = -\frac{c\mathcal{D}_{\mathrm{A}B}}{1 - \mathrm{x}_A}\frac{dx_A}{dz}$$

4.5. Convective-diffusion equation for a binary system

Example: Evaporation of A through a stationary non-diffusing gas B

$$\boxed{\mathrm{n}_{\mathrm{A,z}} = -\frac{c\mathcal{D}_{\mathrm{AB}}}{1-\mathrm{x}_A}\frac{dx_A}{dz}}$$

Because we are at steady state:

$$\frac{dn_{A,z}}{dz} = 0$$

$$\frac{d}{dz}\left(\frac{1}{1-\mathrm{x}_A}\frac{dx_A}{dz}\right) = 0$$

$$-\ln(1-x_A) = C_1 x + C_2$$

Integrating between $x_{A,0}$ and $x_{A,L}$, we find the constants C_1 and C_2

$$\frac{1-x_A}{1-x_{A,0}} = \left(\frac{1-x_{A,L}}{1-x_{A,0}}\right)^{\frac{z}{L}}$$

$$x_A = 1 - \left[(1-x_{A,0})\left(\frac{1-x_{A,L}}{1-x_{A,0}}\right)\right]^{\frac{z}{L}}$$

We derive and find $\frac{dx_A}{dz}$,
then we integrate between $x_{A,0}$ and $x_{A,L}$

$$\boxed{\mathrm{n}_{\mathrm{A,z}} = \frac{c\mathcal{D}_{\mathrm{AB}}}{L}\,ln\left(\frac{1-x_{A,L}}{1-x_{A,0}}\right)}$$

Note: IF there is a flowing gas (e.g. air) on top of the open container $x_{A,L}$=0

4.0. Modes of mass transport

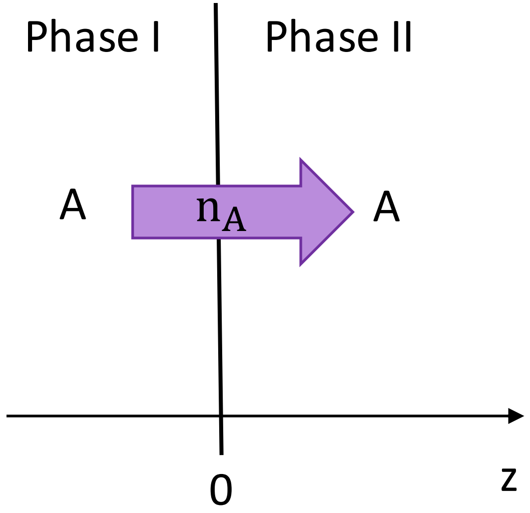
- Molecular diffusion (from high to low concentration)

Diffusion is the process by which molecules, ions, or other small particles spontaneously mix, moving from regions of relatively high concentration into regions of lower concentration.

This process can be described in two ways:
1. Fick’s Law and diffusion coefficient, which is a more fundamental description
2. In terms of mass transfer coefficient, which is an approximate engineering idea that often gives a simpler description.

4.6. Mass transfer coefficient for molecular transport between two phases

Until this point we have look at diffusion and convection when species A and B are dissolved in the same phase (i.e. both in gas or in solid).
The question we would like to answer now is: How do we describe diffusion across boundaries between two phases? (e.g.evaporation of A from liquid to gas phase)



Boundary conditions:

1) The concentration at the interphase are governed by equilibrium laws

$$C_A^{phaseI}\Big|_{z=0_-},\ C_A^{phaseII}\Big|_{z=0_+}$$

1) The fluxes are equal at the interphase:

$$n_A^{Phase\ I} = n_A^{Phase\ II}$$

Note: The concentrations in the two phases might not be equal, the chemical potentials are:

$$\mu_A^{phaseI}\Big|_{z=0_-} = \mu_A^{phaseII}\Big|_{z=0_+}$$

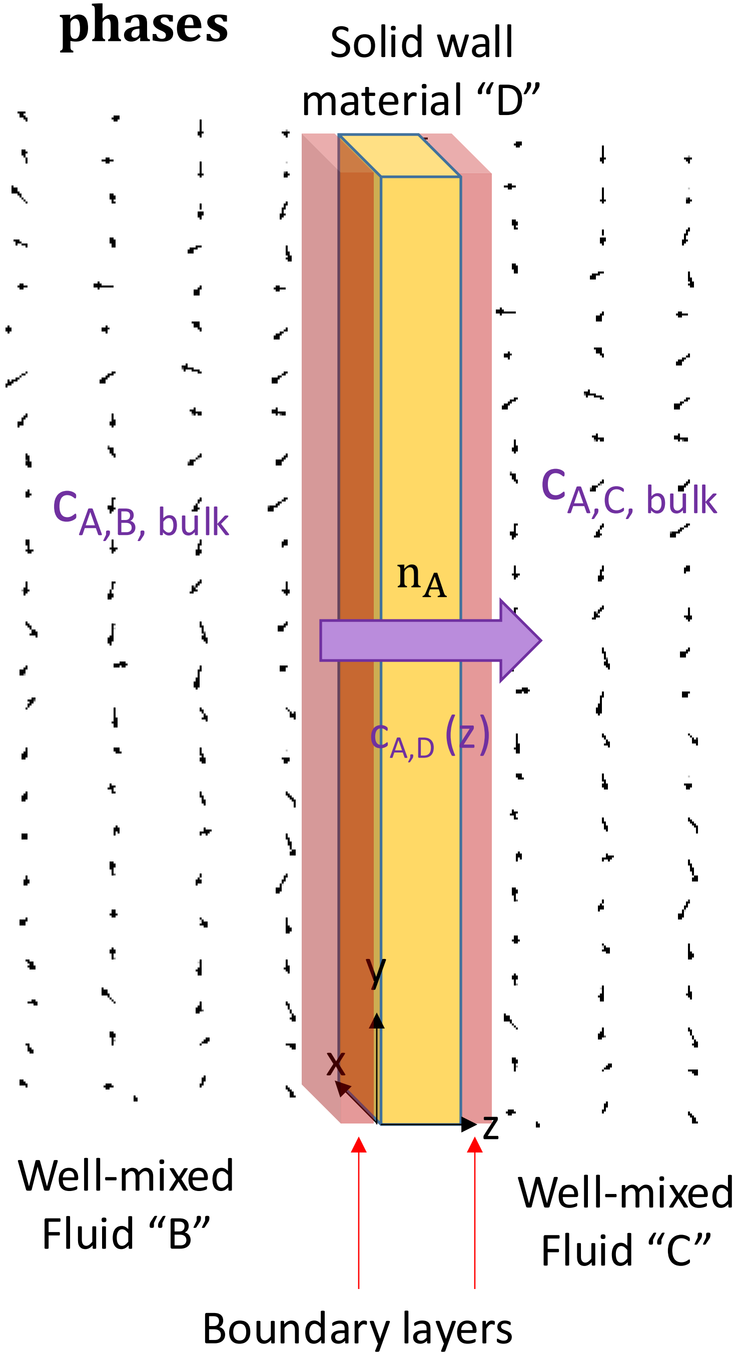
4.6. Mass transfer coefficient for molecular transport between two phases

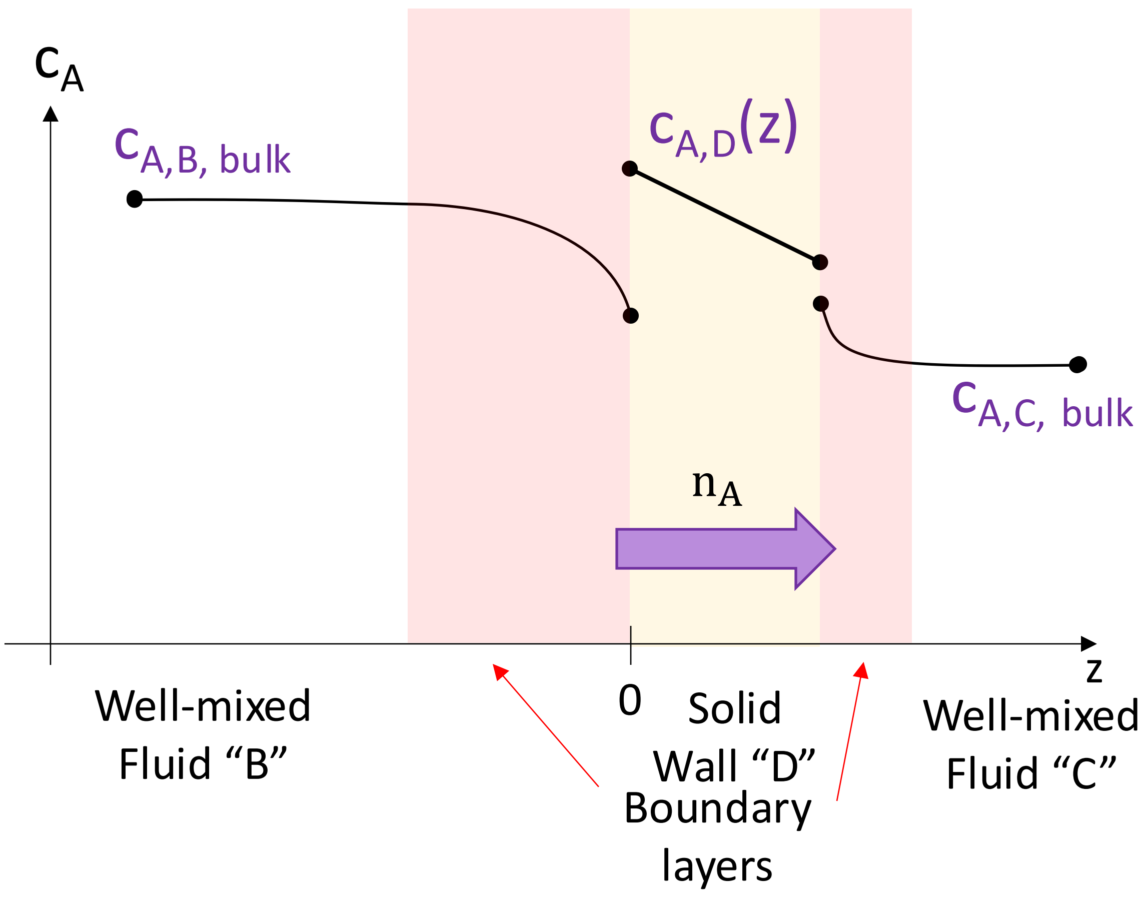
Consider the transfer of molecules

If the fluid flow is sufficiently turbulent we can consider there to be two regions:

-Well mixed fluid all of the same concentration

-Boundary layer near the interface





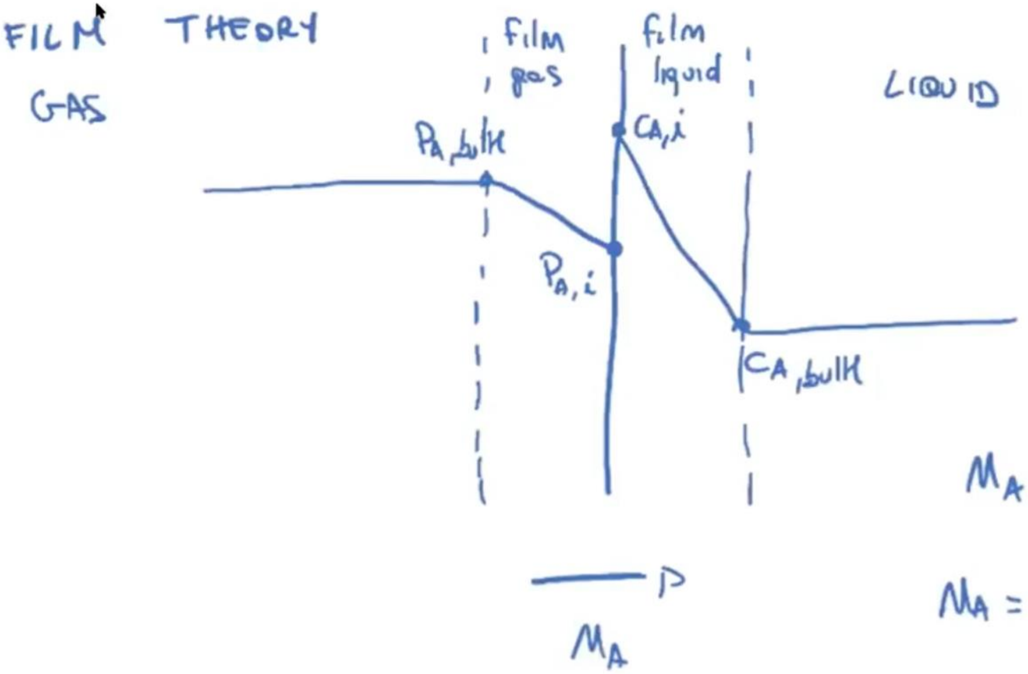
(at steady state)

THE MASS TRANSFER COEFFICIENT

K= mass transfer coefficient

$$\underline{M_A} = -\underline{K}\,\underline{\Delta C}$$

Which ΔC are we going to use?



$$P_{A,i} = H_H C_{A,i}$$

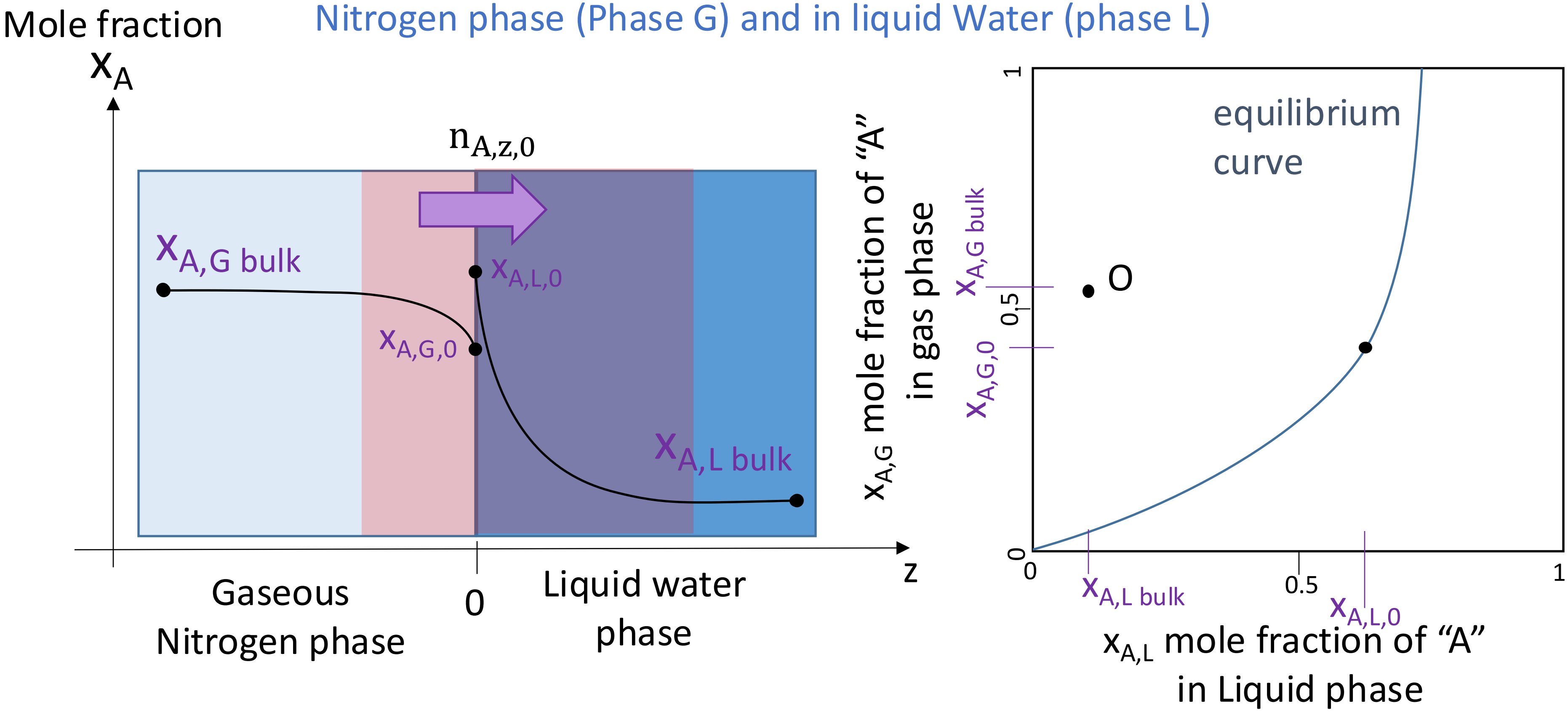
$$M_A = K_G (P_{A,bulk} - P_{A,i})$$

$$M_A = K_L (C_{A,i} - C_{A,bulk})$$

$$M_A = K_G (P_{A,bulk} - P_{A,i}) = K_L (C_{A,i} - C_{A,bulk})$$

4.6. Mass transfer coefficient for molecular transport between two phases

Consider a simple case: dissolved gas (component “A”) in a Gaseous Nitrogen phase (Phase G) and in liquid Water (phase L)



$$n_{A,z,0} = k_{x,G,loc}(x_{A,G,bulk} - x_{A,G,0}) = k_{x,L,loc}(x_{A,L,0} - x_{A,L,bulk})$$

At steady state, the flux of A in one phase must equal the flux of A in the other phase (otherwise there will be accumulation of A on one side or the other), therefore the two fluxes equate.

4.6. Mass transfer coefficient for molecular transport between two phases

Consider a simple case: dissolved gas (component “A”) in a Gaseous Nitrogen phase (Phase G) and in liquid Water (phase L)

$$\mathrm{n}_{\mathrm{A,z,0}} = k^{app}_{\mathrm{x},G,loc}(\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}}) = k^{app}_{\mathrm{x},L,loc}(\mathrm{x}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,bulk}})$$

Apparent local mass transfer coefficient, based on mole fraction in phase “G” (gas phase)

Apparent local mass transfer coefficient, based on mole fraction in phase “L” (liquid phase)

Why *apparent*? Because we are ignoring the possible mass transfer at the interface, which is ok when working in diluited systems

Why *local*? Because the concentrations at the interface are considered

4.6. Mass transfer coefficient for molecular transport between two phases

$$\mathrm{n}_{\mathrm{A,z,0}} = k^{app}_{\mathrm{x,G,}loc}(\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}}) = k^{app}_{\mathrm{x,L,}loc}(\mathrm{x}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,bulk}}) \tag{9.1}$$

For a binary system:

$$\mathrm{n}_{\mathrm{A,z}} = \underbrace{-c\mathcal{D}_{AB}\frac{dx_{\mathrm{A}}}{dz}}_{\text{Diffusive flux}} + \underbrace{\mathrm{x}_{A}\left(\mathrm{n}_{\mathrm{A,z}} + \mathrm{n}_{\mathrm{B,z}}\right)}_{\text{Advective flux}}$$

At interface (z=0)

$$\begin{aligned} -c\mathcal{D}_{AB}\frac{dx_{\mathrm{A}}}{dz}\bigg|_{z=0^-} &= \mathrm{n}_{\mathrm{A,G,0}} - \mathrm{x}_{\mathrm{A,G,0}}\left(\mathrm{n}_{\mathrm{A,G,0}} + \mathrm{n}_{\mathrm{B,G,0}}\right) = k_{\mathrm{x},G,loc}(\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}}) \\ -c\mathcal{D}_{AB}\frac{dx_{\mathrm{A}}}{dz}\bigg|_{z=0^+} &= \mathrm{n}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,0}}\left(\mathrm{n}_{\mathrm{A,L,0}} + \mathrm{n}_{\mathrm{B,L,0}}\right) = k_{\mathrm{x},L,loc}(\mathrm{x}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,bulk}}) \end{aligned} \tag{9.2}$$

Then some algebra gives:

$$k^{app}_{\mathrm{x,G,}loc} = \frac{k_{\mathrm{x,G,}loc}}{\left(1 - \mathrm{x}_{\mathrm{A,G,0}}\left(1 + \frac{\mathrm{n}_{\mathrm{B,G,0}}}{\mathrm{n}_{\mathrm{A,G,0}}}\right)\right)} \qquad k^{app}_{\mathrm{x,L,loc}} = \frac{k_{\mathrm{x,L,}loc}}{\left(1 - \mathrm{x}_{\mathrm{A,L,0}}\left(1 + \frac{\mathrm{n}_{\mathrm{B,L,0}}}{\mathrm{n}_{\mathrm{A,L,0}}}\right)\right)} \tag{9.3}$$

*Of course, $k^{app}_{\mathrm{x,G,}loc} \approx k_{\mathrm{x,G,}loc}$ or $k^{app}_{\mathrm{x,L,loc}} \approx k_{\mathrm{x,L,}loc}$ when $\mathrm{x}_{\mathrm{A,G,0}}$ or $\mathrm{x}_{\mathrm{A,L,0}}$ is small (dilute)

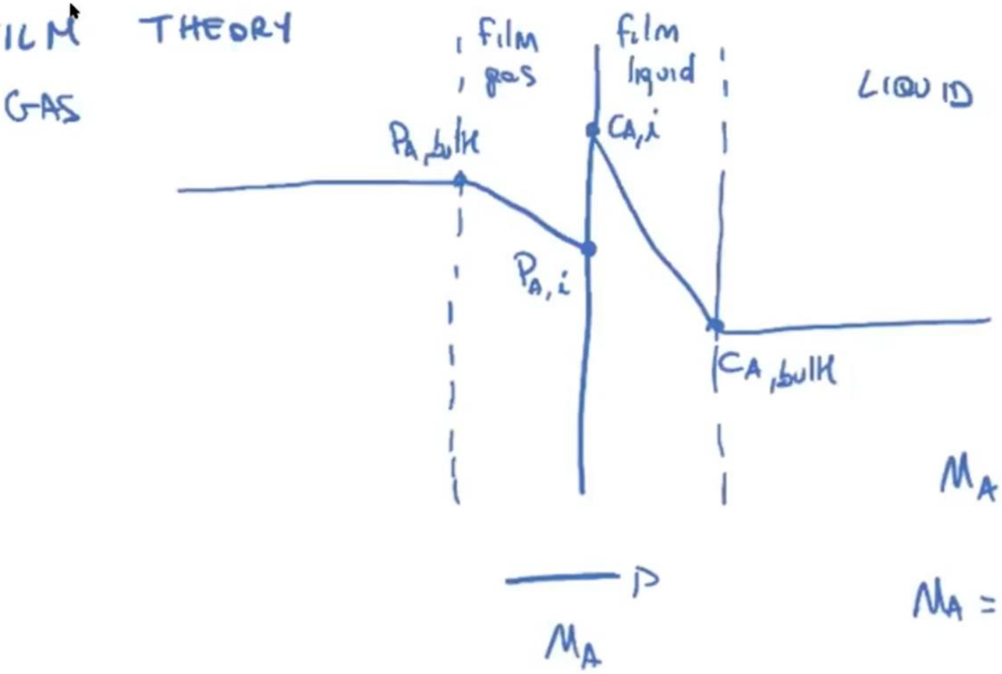
THE MASS TRANSFER COEFFICIENT

K= mass transfer coefficient

$$\underline{N_A} = -\underline{K}\,\underline{\Delta C}$$

Which ΔC are we going to use?

FILM THEORY



$$P_{A,i} = H_H C_{A,i}$$

$$N_A = K_G (P_{A,bulk} - P_{A,i})$$

$$\updownarrow$$

$$N_A = K_L (C_{A,i} - C_{A,bulk})$$

$$N_A = K_G (P_{A,bulk} - P_{A,i}) = K_L (C_{A,i} - C_{A,bulk})$$

NEXT STEP = ELIMINATE $C_{A,i}$ and $P_{A,i}$

From the local k to the overall K

We introduce ”equilibrium” values wherein:

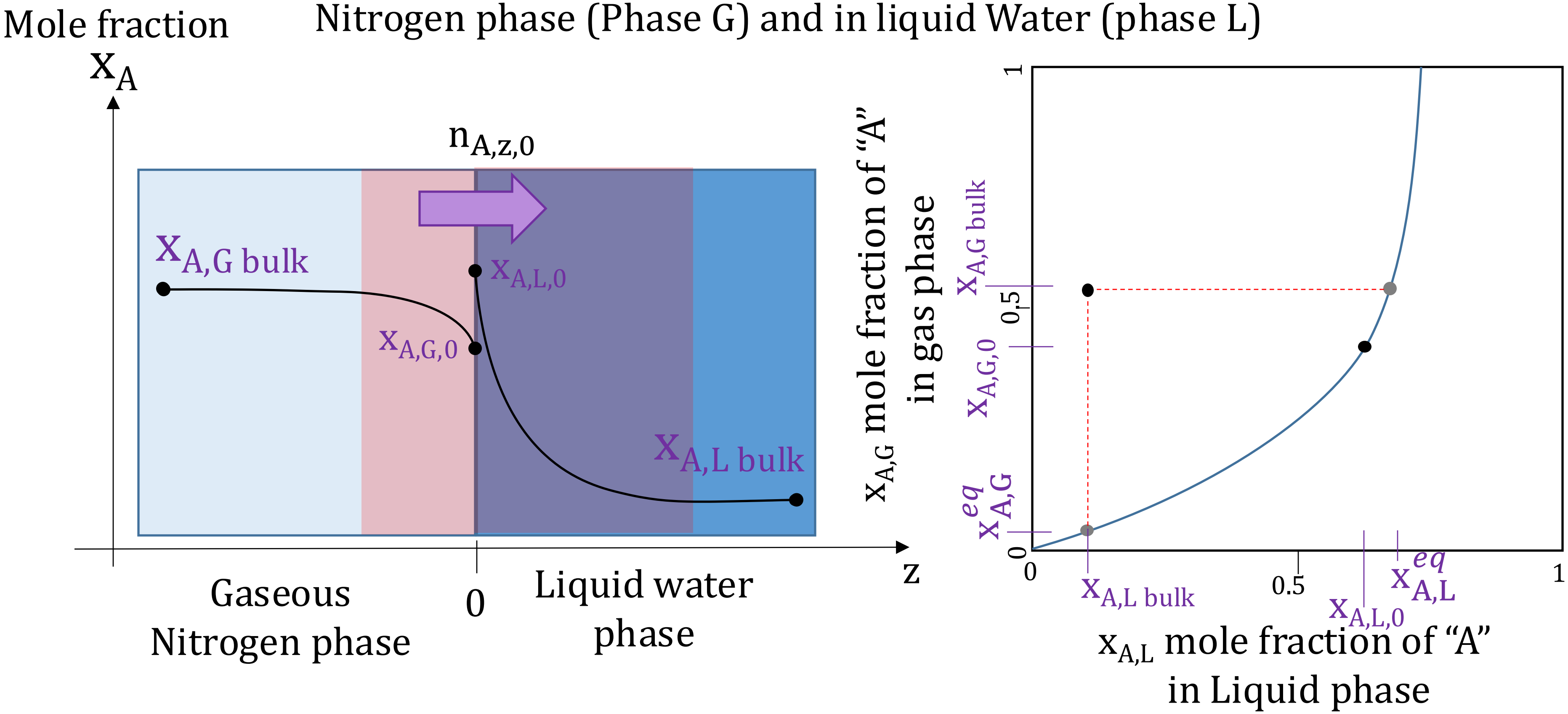
In the gas phase $P_A^{eq} = K_H C_{A,bulk}$

In the liquid phase $P_{A,bulk} = K_H C_A^{eq}$

Along with an overall mass transport coefficient in place of the local mass transport coefficient

4.6. Mass transfer coefficient for molecular transport between two phases

Consider a simple case: dissolved gas (component "A") in a Gaseous Nitrogen phase (Phase G) and in liquid Water (phase L)



$$n_{A,z,0} = k^{app}_{x,G,loc}(x_{A,G,bulk} - x_{A,G,0}) = k^{app}_{x,L,loc}(x_{A,L,0} - x_{A,L,bulk}) \quad (9.1)$$

Because it is not possible to measure the concentration at interfaces, we define the transfer using **overall transfer coefficients**:

$$n_{A,z,0} = K^{app}_{x,G}(x_{A,G,bulk} - x^{eq}_{A,G}) = K^{app}_{x,L}(x^{eq}_{A,L} - x_{A,L,bulk}) \quad (9.4)$$

4.6. Mass transfer coefficient for molecular transport between two phases

Then

$$K_{\mathrm{x},G}^{app}(\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}}^{eq}) = k_{\mathrm{x},G}^{app}(\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}})$$

and

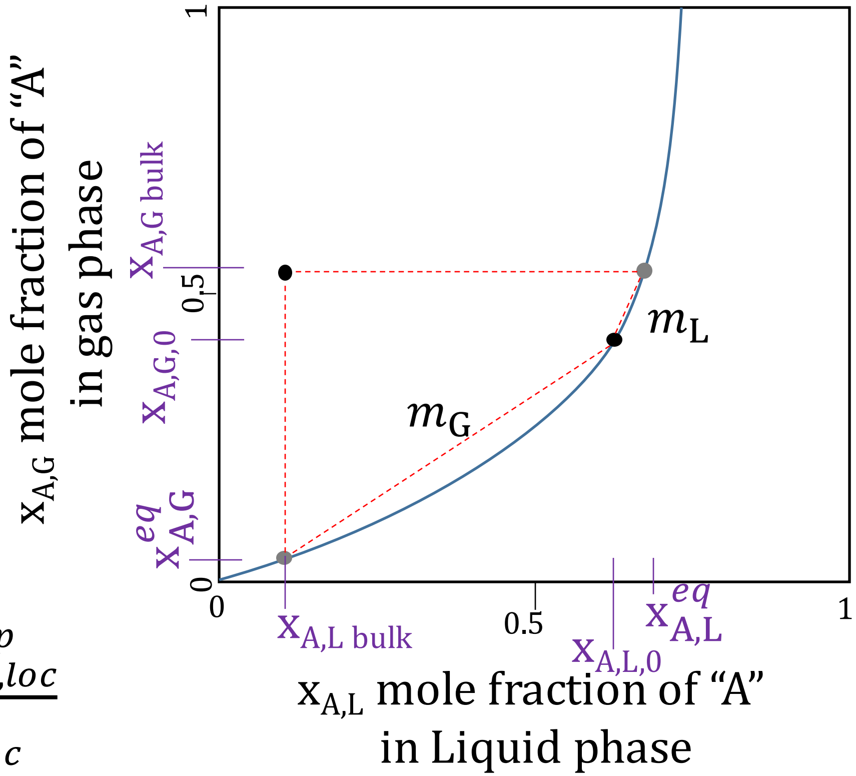
$$K_{\mathrm{x},L}^{app}(\mathrm{x}_{\mathrm{A,L,0}}^{eq} - \mathrm{x}_{\mathrm{A,L,bulk}}) = k_{\mathrm{x},L}^{app}(\mathrm{x}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,bulk}})$$

We can then derive the **partition coefficient**

$$m_{\mathrm{G}} = \frac{\mathrm{x}_{\mathrm{A,G,0}} - \mathrm{x}_{\mathrm{A,G}}^{eq}}{\mathrm{x}_{\mathrm{A,L,0}} - \mathrm{x}_{\mathrm{A,L,bulk}}} \qquad m_{\mathrm{L}} = \frac{\mathrm{x}_{\mathrm{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G,0}}}{\mathrm{x}_{\mathrm{A,L}}^{eq} - \mathrm{x}_{\mathrm{A,L,0}}}$$

Some algebra:

$$\frac{k_{\mathrm{x},L,loc}^{app}}{K_{\mathrm{x},L}^{app}} = 1 + \frac{k_{\mathrm{x},L,loc}^{app}}{m_{\mathrm{L}} k_{\mathrm{x},G,loc}^{app}} \qquad \frac{k_{\mathrm{x},G,loc}^{app}}{K_{\mathrm{x},G}^{app}} = 1 + \frac{m_{\mathrm{G}} k_{\mathrm{x},G,loc}^{app}}{k_{\mathrm{x},L,loc}^{app}}$$



In diluited systems,
since $m_{\mathrm{G}} \approx m_{\mathrm{L}}$ an average can be defined

$$m_{avg} = \tfrac{1}{2}(m_{\mathrm{G}} + m_{\mathrm{L}})$$

$$\frac{k_{\mathrm{x},L,loc}^{app}}{m_{avg} k_{\mathrm{x},G,loc}^{app}} \ll 1$$

Little gas phase resistance
Liquid phase controlled

$$\frac{k_{\mathrm{x},L,loc}^{app}}{m_{avg} k_{\mathrm{x},G,loc}^{app}} \gg 1$$

Little liquid phase resistance
Gas phase controlled

Exercise 4.4

(Application of mass transfer coefficient)

Mass transfer of Formaldehyde: Water containing a small amount of formaldehyde ($c_{A,L,bulk} = 3.3mM$) is produced by a waste stream of a chemical plant. A pool of the waster water is released outside and the overall flux of formaldehyde into the air ($c_{A,G,bulk} = 0mM$)is estimated to be $n_{A,0} = 2.01 * 10^{-7} \frac{mol}{m^2 s}$. The equilibrium relation between the concentration of formaldehyde in the liquid and the gas is $H = \frac{c_{A,G}}{c_{A,L}}$ where $H = 2.0 * 10^{-5}$ at 25°C. The local mass transfer coefficient on the gas side is known to be $17.9 \frac{m}{hr}$. Can you estimate the mass transfer coefficient on the liquid side, $k_{A,L}^{app}$ and the overall mass transfer coefficients for both the liquid and gas phases $K_{A,G}^{app}$, $K_{A,L}^{app}$. Is mass transfer on one side limiting?

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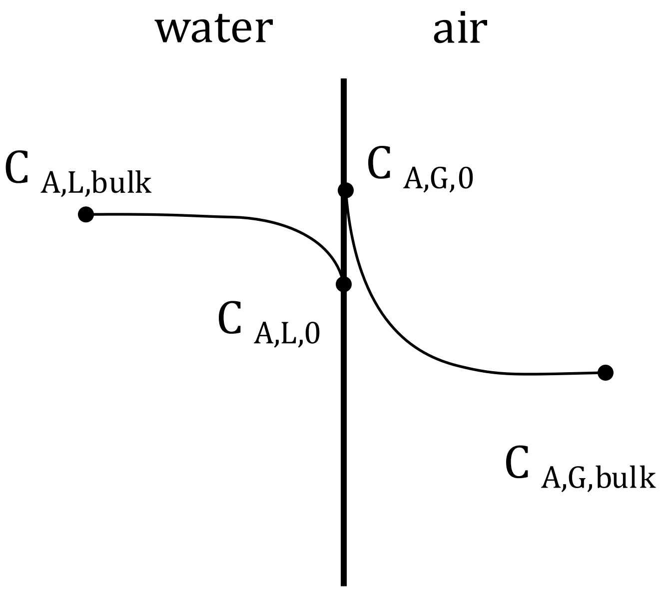
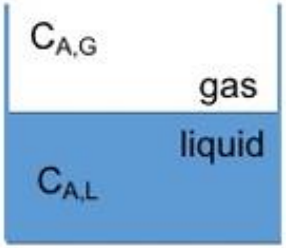




$C_{A,L,bulk}$ = 3.3mM = 3.3mol/m^3

$C_{A,G,bulk} = 0$

$n_{A,0} = 2.01 * 10^{-7} \frac{mol}{m^2 s}$.

$C_{A,G} = C_{A,L} H$

$H = 2.0 * 10^{-5}$

$k_{C,G,loc}^{app} = 17.9 \frac{m}{hr}$

$k_{C,L,loc}^{app} = ?$

$K_{C,L}^{app} = ?$

$K_{C,L}^{app} = ?$

$$\mathrm{n_{A,0}} = k^{app}_{\mathrm{c},G,loc}\left(\mathrm{c_{A,G,0}} - \mathrm{c_{A,G,bulk}}\right) = k^{app}_{\mathrm{c},L,loc}\left(\mathrm{c_{A,L,bulk}} - \mathrm{c_{A,L,0}}\right)$$

Because $\mathrm{c_{A,G,bulk}} = 0$ $\quad \mathrm{c_{A,G,0}} = \frac{\mathrm{n_{A,0}}}{k^{app}_{\mathrm{c},G,loc}} = 2.01 \times 10^{-7} \frac{mol}{m^2 s} \times \frac{1hr}{17.9m} \times \frac{3600s}{1hr} = 4.04 \times 10^{-5} \frac{mol}{m^3}$

$$\mathrm{c_{A,L,0}} = \frac{\mathrm{c_{A,G,0}}}{H} = 2.01 \frac{mol}{m^3}$$

$$\boldsymbol{k^{app}_{\mathrm{c},L,loc}} = \frac{\mathbf{n_{A,0}}}{\mathbf{c_{A,L,bulk}} - \mathbf{c_{A,L,0}}} = \frac{\mathbf{2.01 \times 10^{-7}} \boldsymbol{mol.m^3}}{\mathbf{(3.3 - 2.01)}\boldsymbol{m^2.s.mol}} = \mathbf{1.55 \times 10^{-7}} \frac{\boldsymbol{m}}{\boldsymbol{s}} = \mathbf{5.58 \times 10^{-4}} \frac{\boldsymbol{m}}{\boldsymbol{hr}}$$

What about the overall mass transfer coefficients?

$$\mathrm{n_{A,0}} = K^{app}_{\mathrm{c},G}\left(\mathrm{c_{A,G,eq}} - \mathrm{c_{A,G,bulk}}\right)$$

$$\mathrm{c^{eq}_{A,G}} = \mathrm{c_{A,L,bulk}} \times H = 3.3 \times 2 \times 10^{-5} = 6.6 \times 10^{-5} \frac{mol}{m^3}$$

$$\boldsymbol{K^{app}_{\mathrm{c},G,loc}} = \frac{\mathbf{n_{A,0}}}{\mathbf{c_{A,G,eq}} - \mathbf{c_{A,G,bulk}}} = \frac{\mathbf{2.01 \times 10^{-7}} \boldsymbol{mol.m^3}}{\mathbf{(6.6 \times 10^{-5} - 0)}\boldsymbol{m^2.s.mol}} = \mathbf{3.03 \times 10^{-3}} \frac{\boldsymbol{m}}{\boldsymbol{s}} = \mathbf{10.9} \frac{\boldsymbol{m}}{\boldsymbol{hr}}$$

$$\mathrm{n_{A,0}} = K^{app}_{\mathrm{c},L,loc}\left(\mathrm{c_{A,L,bulk}} - \mathrm{c_{A,L,eq}}\right)$$

$$\mathrm{c^{eq}_{A,L}} = \frac{\mathrm{c_{A,G,bulk}}}{H} = 0$$

$$\boldsymbol{K^{app}_{\mathrm{c},L,loc}} = \frac{\mathbf{n_{A,0}}}{\mathbf{c_{A,L,bulk}}} = \frac{\mathbf{2.01 \times 10^{-7}} \boldsymbol{mol.m^3}}{\mathbf{3.3}\ \boldsymbol{m^2.s.mol}} = \mathbf{6.06 \times 10^{-8}} \frac{\boldsymbol{m}}{\boldsymbol{s}} = \mathbf{2.18 \times 10^{-4}} \frac{\boldsymbol{m}}{\boldsymbol{hr}}$$

To determine if mass transfer is limited on one side, we have to calculate m_{G}, m_{L} and m_{avg}

$$m_{\mathrm{G}} = \frac{\mathrm{c}_{\mathrm{A,G,0}} - \mathrm{c}^{eq}_{\mathrm{A,G,bulk}}}{\mathrm{c}_{\mathrm{A,L,0}} - \mathrm{c}_{\mathrm{A,L,bulk}}} = \frac{4.04 \times 10^{-5} - 6.6 \times 10^{-5}}{2.01 - 3.3} = 1.97 \times 10^{-5}$$

$$m_{\mathrm{L}} = \frac{\mathrm{c}_{\mathrm{A,G,bulk}} - \mathrm{c}_{\mathrm{A,G,0}}}{\mathrm{c}^{eq}_{\mathrm{A,L}} - \mathrm{c}_{\mathrm{A,L,0}}} = \frac{0 - 4.04 \times 10^{-5}}{0 - 2.01} = 2.02 \times 10^{-5}$$

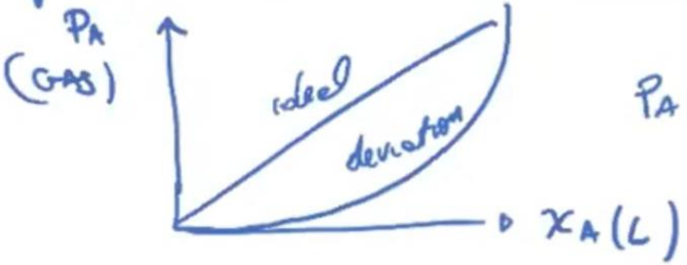
$$m_{avg} = \frac{1}{2}(m_{\mathrm{G}} + m_{\mathrm{L}}) = \frac{1}{2}(1.97 \times 10^{-5} + 2.02 \times 10^{-5}) = 1.99 \times 10^{-5}$$

$$\frac{\boldsymbol{k^{app}_{\mathrm{c},L,loc}}}{\boldsymbol{m_{avg} k^{app}_{\mathrm{c},G,loc}}} = \frac{\mathbf{5.58 \times 10^{-4}} \, \boldsymbol{\frac{m}{hr}}}{\mathbf{1.99 \times 10^{-5} \times 17.9} \, \boldsymbol{\frac{m}{hr}}} = \mathbf{1.53}$$

This means that the transport in none of the two phases is dominating.

RECAP

HENRY'S LAW → dilute solutions and correlates the concentration of a solute between two phases



$$P_A = K_H x_A$$

→ COMBINATION OF ADVECTION AND DIFFUSION

$$N_A = x_A (N_A + N_B) - C D_{AB} \frac{dx_A}{dy}$$

evaporation of A through non-diffusing gas B

$$N_{A,z} = \frac{c D_{AB}}{L} \ln\left(\frac{1 - x_{A,L}}{1 - x_{A,0}}\right)$$

$z = 0$

$x_{A,L} = 0$

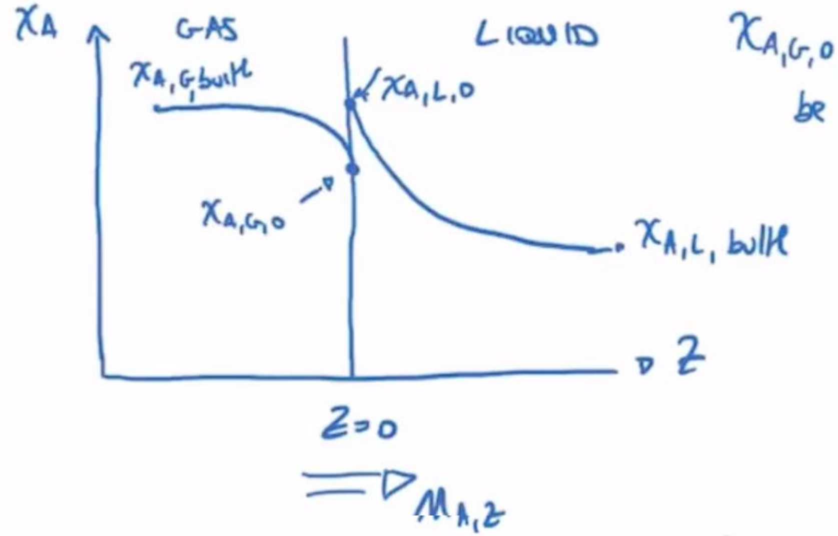
if B is flowing on top

→ TRANSPORT ACROSS TWO PHASES

the flux within each phase is driven by a concentration gradient.

RECAP

CONCENTRATION DIAGRAM



$x_{A,G,0}$ and $x_{A,L,0}$ will be linked via an equilibrium law

$$N_{A,z} = K_{x,G,loc}\left(x_{A,G,bulk} - x_{A,G,0}\right) = K_{x,L,loc}\left(x_{A,L,0} - x_{A,L,bulk}\right)$$

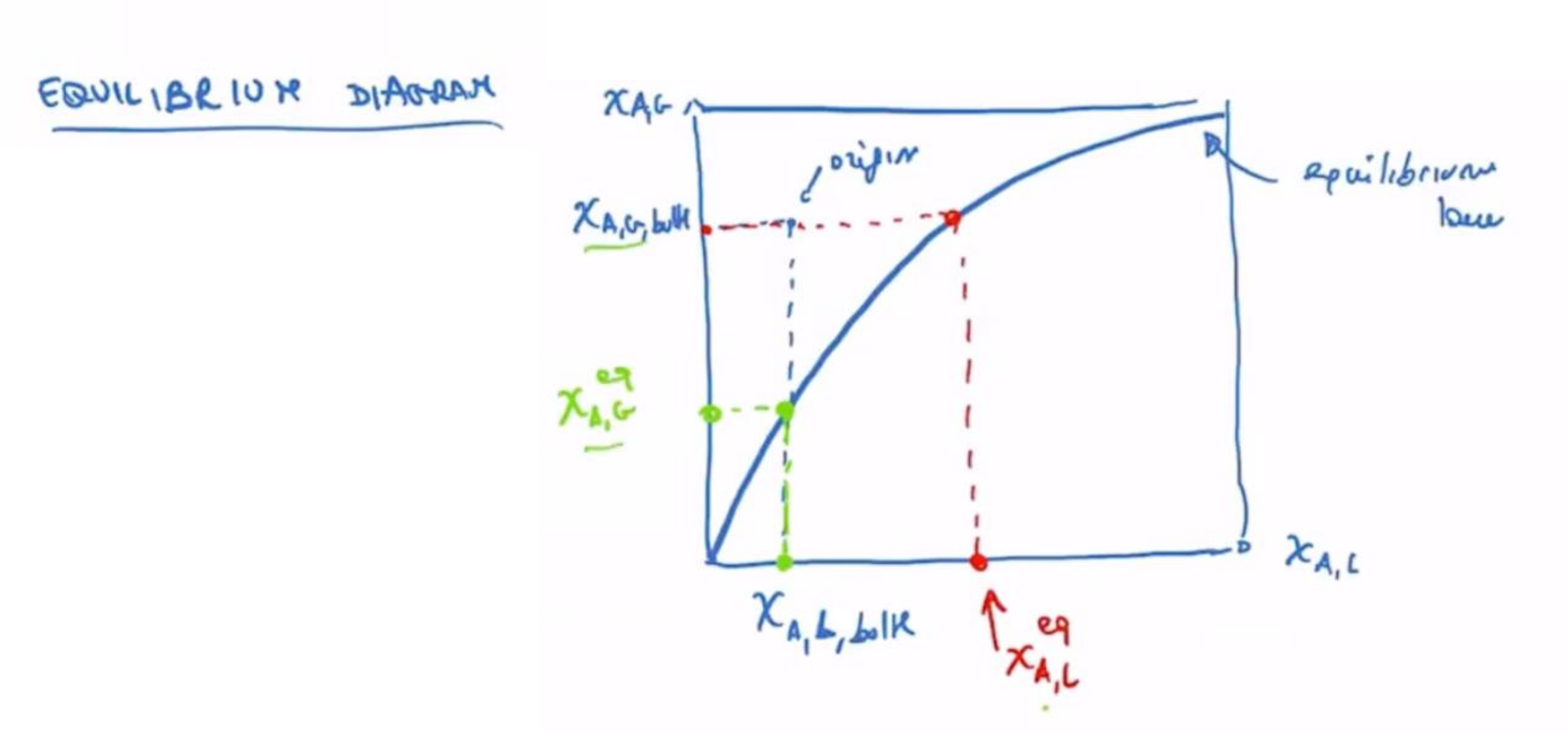
$x_{A,G,0}$ and $x_{A,L,0}$ are connected via an equilibrium law

$$N_{A,z} = K_{x,G,overall}\left(x_{A,G,bulk} - x_{A,G}^{eq}\right) = K_{x,L,overall}\left(x_{A,L}^{eq} - x_{A,L,bulk}\right)$$

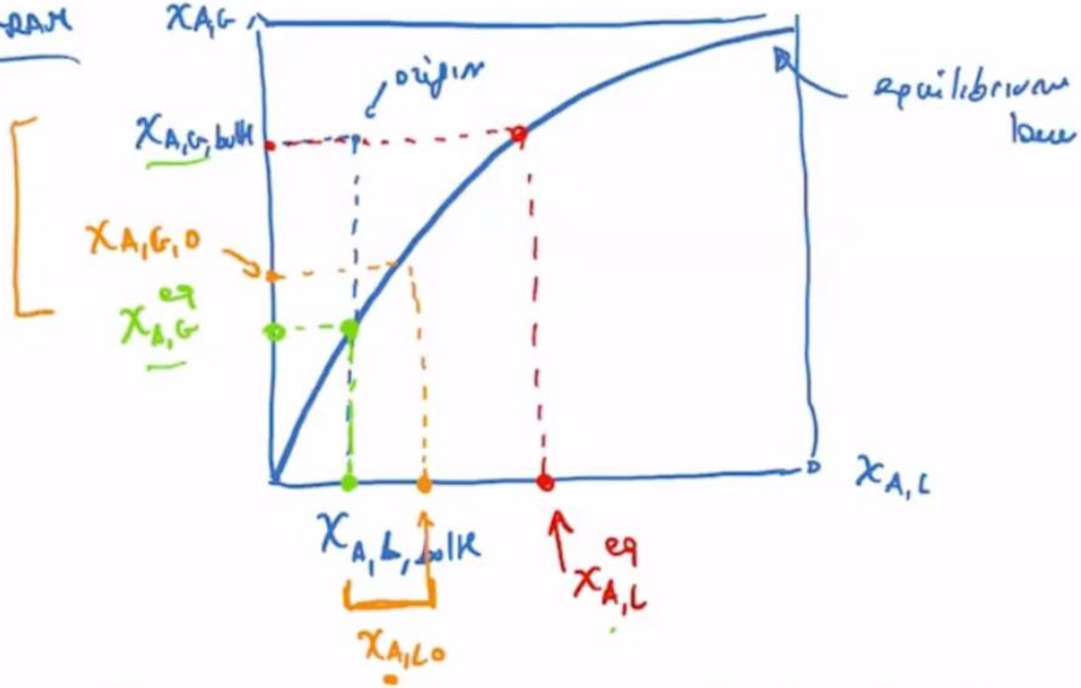
$x_{A,G}^{eq}$ = "hypothetical" concentration in equilibrium with the bulk liquid

$x_{A,L}^{eq}$ = " " " with the bulk gas

RECAP


EQUILIBRIUM DIAGRAM
$x_{A,G}$
origin
$x_{A,G,bulk}$
equilibrium line
$x_{A,G}^{eq}$
$x_{A,L}$
$x_{A,L,bulk}$
$x_{A,L}^{eq}$

EQUILIBRIUM DIAGRAM



the phase limiting the mass transport is the liquid phase

$\Downarrow$

ΔC in the liquid phase $<$ ΔC in the gas phase

$$\left(x_{A,L,0} - x_{A,L,bulk}\right) < \left(x_{A,G,bulk} - x_{A,G,0}\right)$$

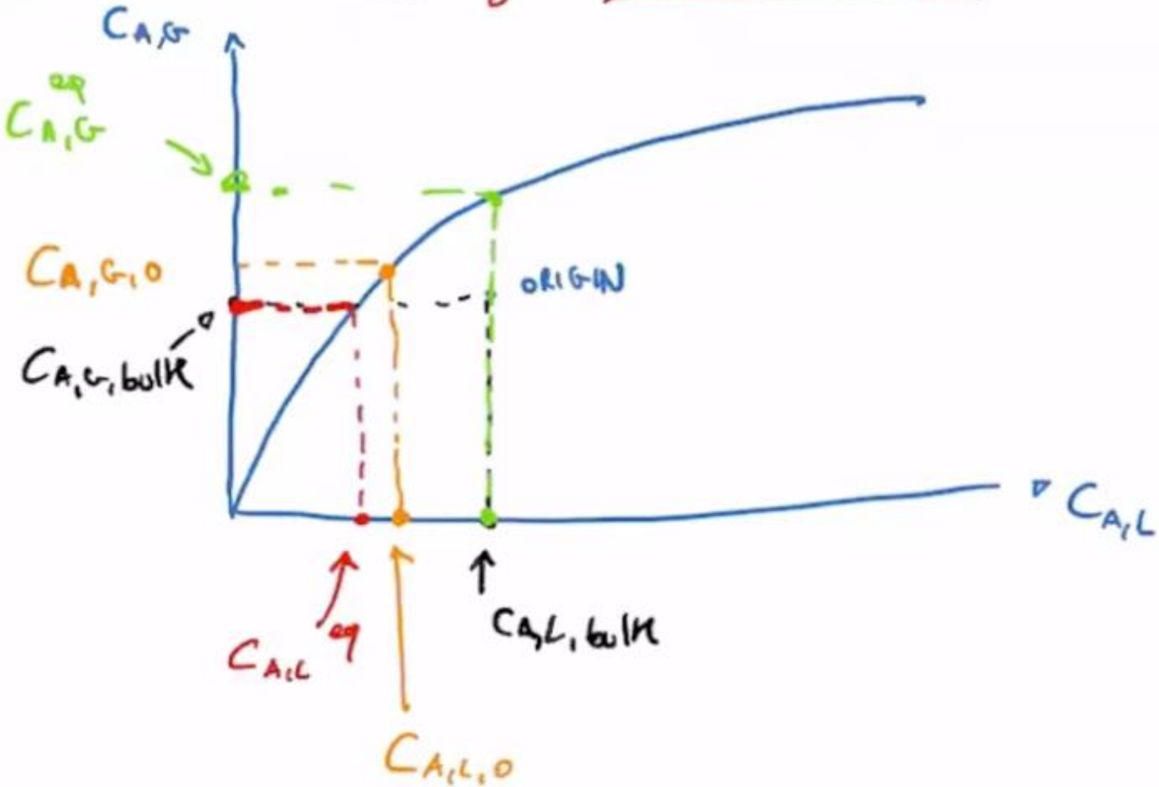
Given the equilibrium diagram and the origin identify knowing that the gas phase is controlling the mass transport

$C_{A,G,bulk}$ $C_{A,L,bulk}$

$C_{A,G,0}$ $C_{A,G}^{eq}$

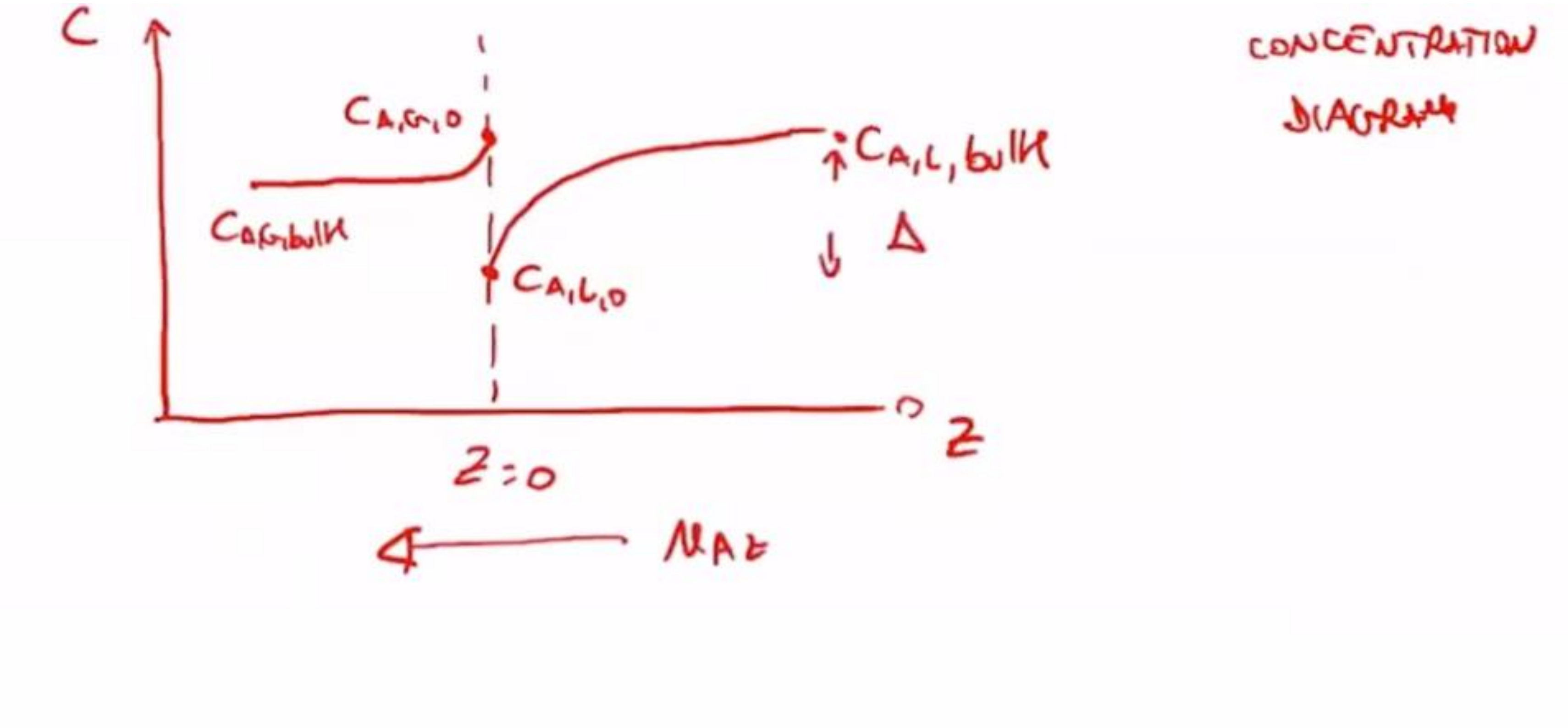
$C_{A,L,0}$ $C_{A,L}^{eq}$

EQUILIBRIUM DIAGRAM



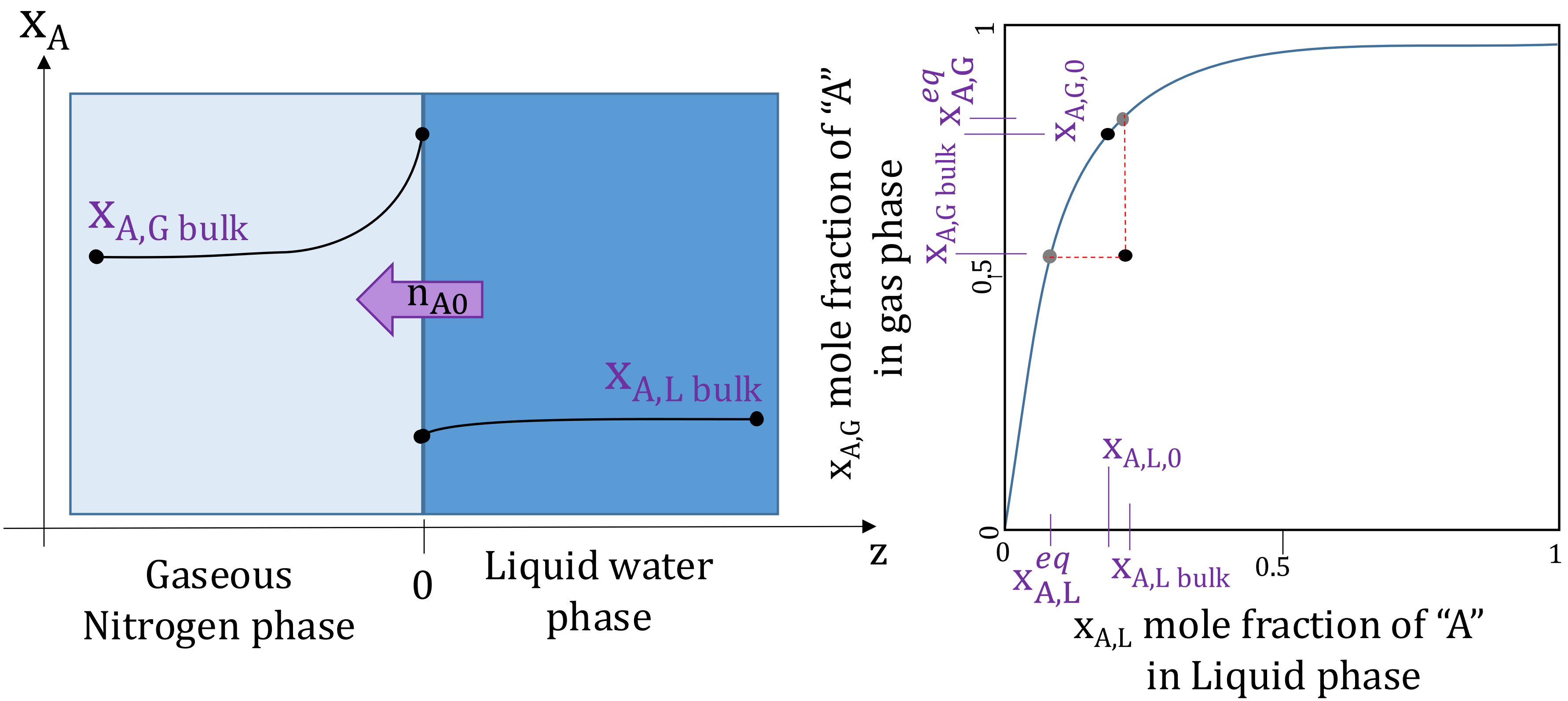
$\Delta C_G < \Delta C_L$

If you were asked to draw the direction of the flux:



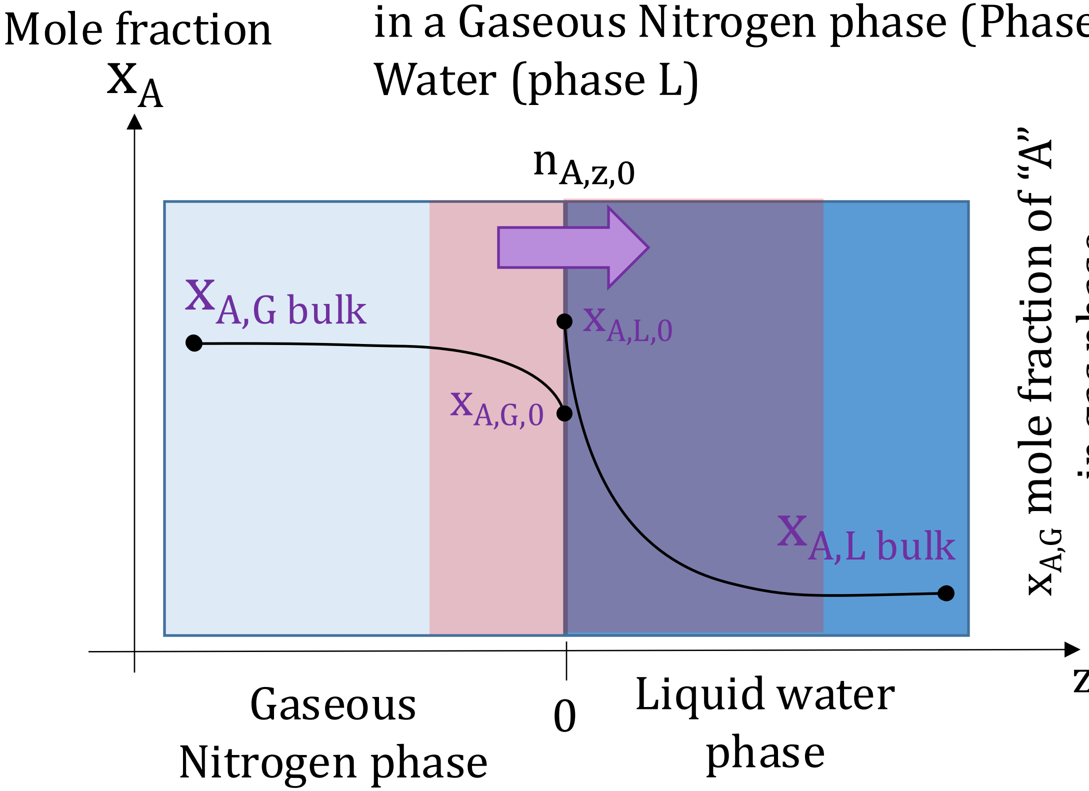
4.6. Mass transfer coefficient for molecular transport between two phases

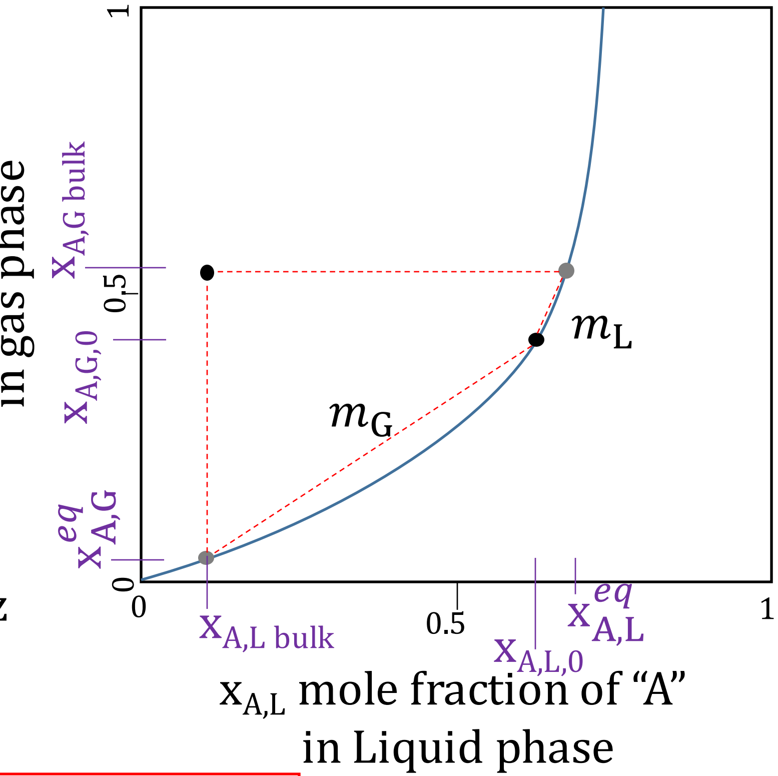
Example: given the equilibrium diagram draw the flux direction and the value of the mole fraction with respect to z for the case of a *liquid phase controlled* mass transfer



4.6. Mass transfer coefficient for molecular transport between two phases

Consider a simple case: dissolved gas (component “A”) in a Gaseous Nitrogen phase (Phase G) and in liquid Water (phase L)





$$\frac{k_{x,L,loc}^{app}}{m_{avg}k_{x,G,loc}^{app}} \ll 1$$ Little gas phase resistance *Liquid phase controlled*

$$\boxed{k_{x,L,loc}^{app} = K_{x,L}^{app}}$$

$$\frac{k_{x,L,loc}^{app}}{m_{avg}k_{x,G,loc}^{app}} \gg 1$$ Little liquid phase resistance *Gas phase controlled*

$$k_{x,G,loc}^{app} > k_{x,L,loc}^{app}$$

$$n_{A,z,0} = k_{x,G,loc}^{app}(x_{A,G,bulk} - x_{A,G,0}) = k_{x,L,loc}^{app}(x_{A,L,0} - x_{A,L,bulk}) \quad (9.1)$$

4.5. Mass transfer coefficient for molecular transport between two phases

Types of mass transfer coefficients units and values (assuming transfer from gas phase to liquid phase):

Based on a gas phase G with respect to mole fraction

$$\mathrm{n_{A,0}} = k_{\mathrm{x},G,loc}^{app}(\mathrm{x_{A,G,bulk}} - \mathrm{x_{A,G,0}}) = K_{\mathrm{x},G}^{app}(\mathrm{x_{A,G,bulk}} - \mathrm{x}_{\mathrm{A,G}}^{eq})$$

$$[\mathrm{k_x}] = [\mathrm{K_x}] = [\mathrm{mol\ \ s^{-1}\ m^{-2}}]$$

Based on a gas phase G with respect to concentration

$$\mathrm{n_{A,0}} = k_{\mathrm{c},G,loc}^{app}(\mathrm{c_{A,G,bulk}} - \mathrm{c_{A,G,0}}) = K_{\mathrm{c},G}^{app}(\mathrm{c_{A,G,bulk}} - \mathrm{c}_{\mathrm{A,G}}^{eq})$$

$$[\mathrm{k_c}] = [\mathrm{K_c}] = [\mathrm{m\ \ s^{-1}}]$$

Based on a gas phase G with respect to partial pressure

$$\mathrm{n_{A,0}} = k_{\mathrm{p},G,loc}^{app}(p_{\mathrm{A,G,bulk}} - p_{\mathrm{A,G,0}}) = K_{\mathrm{p},G}^{app}(p_{\mathrm{A,G,bulk}} - p_{\mathrm{A,G}}^{eq})$$

$$[\mathrm{k_p}] = [\mathrm{K_p}] = [\mathrm{mol\ \ s^{-1}\ m^{-2}\ bar^{-1}}]$$

Based on a Liquid phase L with respect to mole fraction

$$\mathrm{n_{A,0}} = k_{\mathrm{x},L,loc}^{app}(\mathrm{x_{A,L,0}} - \mathrm{x_{A,L,bulk}}) = K_{\mathrm{x},L}^{app}(\mathrm{x}_{\mathrm{A,L}}^{eq} - \mathrm{x_{A,L,bulk}})$$

$$[\mathrm{k_x}] = [\mathrm{K_x}] = [\mathrm{mol\ \ s^{-1}\ m^{-2}}]$$

Based on a Liquid phase L with respect to concentration

$$\mathrm{n_{A,0}} = k_{\mathrm{c},L,loc}^{app}(\mathrm{c_{A,L,0}} - \mathrm{x_{A,L,bulk}}) = K_{\mathrm{c},L}^{app}(\mathrm{c}_{\mathrm{A,L}}^{eq} - \mathrm{c_{A,L,bulk}})$$

$$[\mathrm{k_c}] = [\mathrm{K_c}] = [\mathrm{m\ \ s^{-1}}]$$

Jasmone exercize

Jasmone ($C_{11}H_{16}O$) is a valuable material in the perfume industry, used in many soap and cosmetics. Suppose we are recovering this material from a **water** suspension (concentration of jasmone in water is 5mM) by an extraction with **benzene**. The local mass transfer coefficient in water is $3.0 \cdot 10^{-4}\,\frac{cm}{s}$ and the local mass transfer coefficient in benzene is $2.4 \cdot 10^{-3}\,\frac{cm}{s}$. The interfacial concentrations are in equilibrium according to the following equation $C_{j,benzene} = 170\ C_{j,water}$.

a) Calculate the interfacial concentration of jasmone in water and in benzene

b) Calculate the molar flux

c) Determine if one side is limiting the mass transport using the partition coefficients

d) Draw the qualitative liquid/liquid **concentration diagram**, which means identify the concentration values, in bulk and at the interface, along with the direction of the molar flux (in the exam sheets, not here).

e) Qualitatively identify bulk, equilibrium and interface concentrations in the **equilibrium diagram** (in the exam sheets, not here).

f) Can you briefly explain in which cases we introduce the overall mass transfer coefficient? Do the equilibrium concentration have any physical meaning?

$C_{j,\text{water},\text{bulk}} = 5\,\text{mM}$ $\quad$ $C_{j,\text{benzene},\text{bulk}} = 0\,\text{mM}$

$K_{c,\text{water},\text{local}} = 3 \times 10^{-4}\ \frac{\text{cm}}{\text{s}}$ $\quad$ $C_{j,\text{benzene}} = 170\ C_{j,\text{water}}$

$K_{c,\text{benzene},\text{local}} = 2.4 \times 10^{-3}\ \frac{\text{cm}}{\text{s}}$

---

a) If we equate the local fluxes of jasmone:

$$n_j = k_W^{loc}\left(C_{j,W,b} - C_{j,W,o}\right) = k_B^{loc}\left(C_{j,B,o} - C_{j,B,b}\right)(\boldsymbol{Eq.1})$$

Also, it is given that the interface concentration are in equilibrium as per the following relation:

$$C_{j,B,o} = 170 * C_{j,W,o}\ (\boldsymbol{Eq.2})$$

In order to solve for $C_{j,W,o}$:

$$k_W^{loc}\left(C_{j,W,b} - C_{j,W,o}\right) = k_B^{loc}(170 * C_{j,W,o} - C_{j,B,b})$$

$$C_{j,W,o} = \frac{\left(k_W^{loc} C_{j,w,b} + k_B^{loc} C_{j,B,b}\right)}{\left(170 k_B^{loc} + k_W^{loc}\right)}(\boldsymbol{Eq.3})$$

If we put the values from the question,

$$C_{j,W,o} = \frac{(3 \times 10^{-6} \times 0.005 + 2.4 \times 10^{-5} \times 0)}{(170 \times 2.4 \times 10^{-5} + 3 \times 10^{-6})}$$

$$C_{j,W,o} = 3.6 \times 10^{-6} M$$

$$C_{j,B,o} = 170 * C_{j,W,o} = 0.612 \times 10^{-3} M$$

b) In order to solve for the molar flux, we can use the $(\boldsymbol{Eq.1})$

$$n_j = k_W^{loc}\left(C_{j,W,b} - C_{j,W,o}\right)$$

$$n_j = 3 \times 10^{-6} m/s \times (0.005 - 0.0000036) \times 10^3 mol/m^3$$

$$n_j = 0.015 \times 10^{-3} mol/m^2 s$$

c) To determine if mass transfer is limited on one side, we have to calculate m_{B}, m_{W} and m_{avg}

$$m_{\mathrm{B}} = \frac{\mathrm{c_{j,B,0}} - \mathrm{c}_{\mathrm{j,B,b}}^{eq}}{\mathrm{c_{j,W,0}} - \mathrm{c_{j,W,b}}} = \frac{0.612 \times 10^{-3} - 170 \times 0.005}{3.6 \times 10^{-6} - 0.005} = 170$$

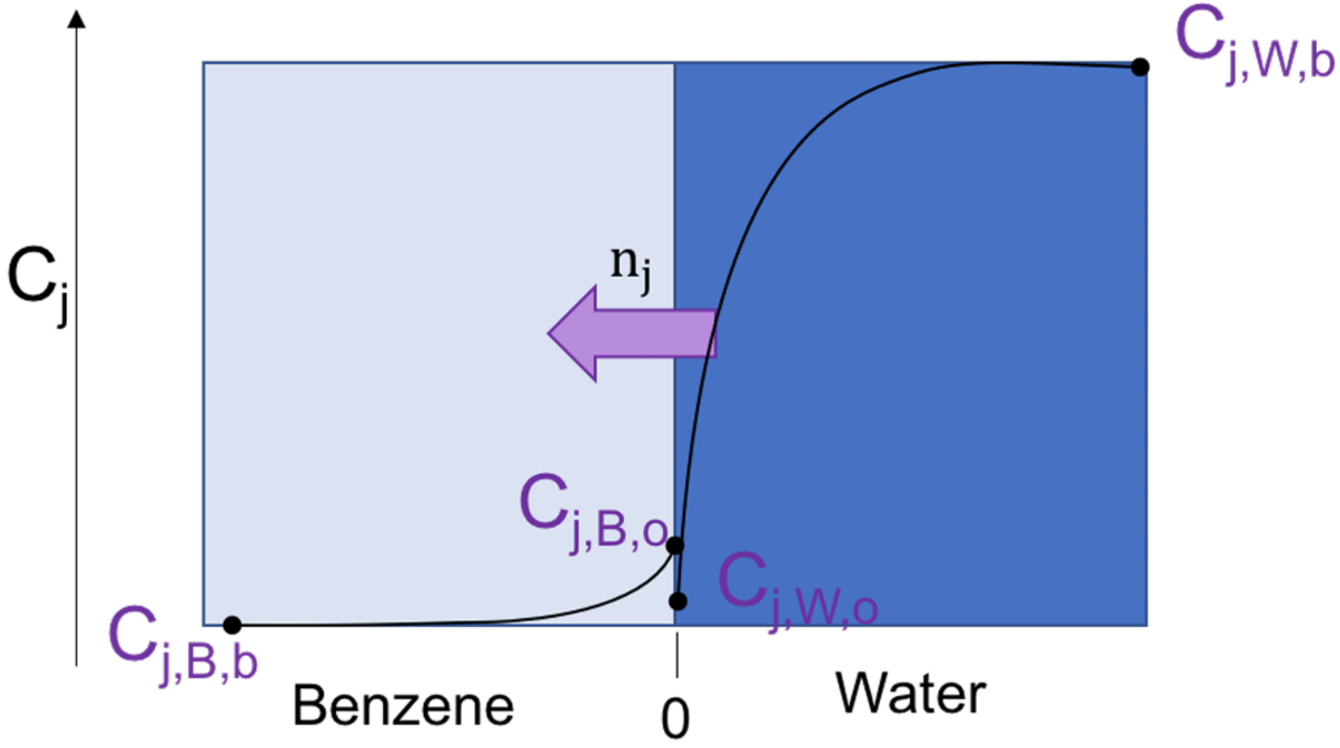
$$m_{\mathrm{W}} = \frac{\mathrm{c_{j,B,b}} - \mathrm{c_{j,B,0}}}{\mathrm{c}_{\mathrm{j,W}}^{eq} - \mathrm{c_{j,W,0}}} = \frac{0 - 0.612 \times 10^{-3}}{0 - 3.6 \times 10^{-6}} = 170$$

$$m_{avg} = \frac{1}{2}(m_{\mathrm{B}} + m_{\mathrm{W}}) = \frac{1}{2}(170 + 170) = 170$$

$$\boldsymbol{\frac{k_W^{loc}}{m_{avg} k_{\mathrm{B}}^{loc}} = \frac{3 \times 10^{-6}\,\frac{m}{s}}{170 \times 2.4 \times 10^{-5}\,\frac{m}{s}} = 0.0007}$$

Since $\boldsymbol{\frac{k_W^{loc}}{m_{avg} k_{\mathrm{B}}^{loc}} \ll 1,}$ the mass transfer is controlled by the water phase.

d)



where

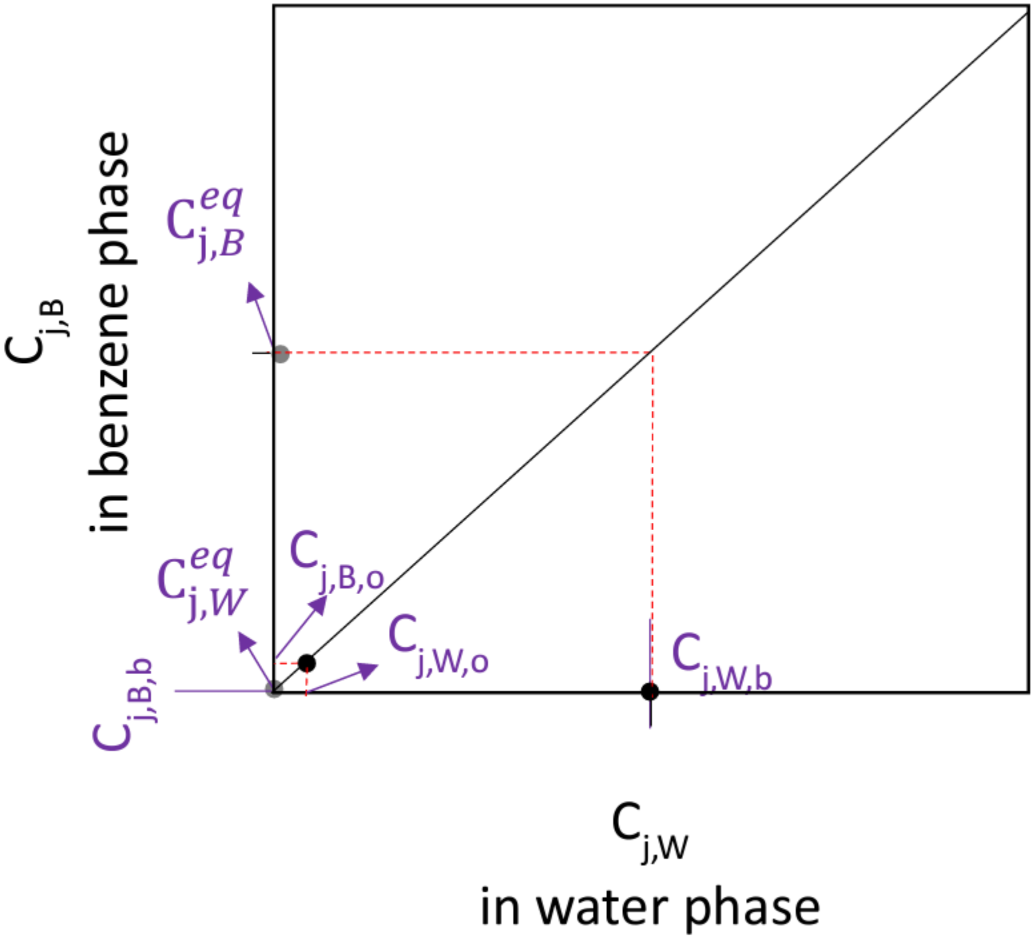
$$C_{j,W,b} = 0.005M$$

$$C_{j,W,o} = 0.0000036M$$

$$C_{j,B,b} = 0$$

$$C_{j,B,o} = 0.0006M$$

e) The graph below is quantitative, a qualitative version is also accepted considering the challenge in positioning $C_{j,B,b}$ and $C_{j,w,eq}$ at the origin.



$$C^{eq}_{j,W} = \frac{C_{j,B,b}}{170} = 0$$

$$C^{eq}_{j,B} = 170 \times C_{j,W,b} = 0.85M$$

The aswer to point f provides additional information on the equilibrium values, do read it for the sake of your knowledge