Mass transfer and separation

Lecture 4

Recap motion of molecules in fluids

Objectives

- Diffusion
- Convection
- Mass transport coefficients

Diffusion

- Diffusion is a crucial process in the atmosphere and in solution. It is important to be able to predict the spread of a material through another when discussing reactions in solution and the spread of substances into the environment.
- The key idea is that particles tend to spread to achieve uniform distribution.
- You need to remember how to calculate flux and what is the chemical potential.

Diffusion

- The tendency of particles in gases, liquids and solids to spread can be discussed from 3 different viewpoints.
  - 2nd law of TD (tendency of *S* to↑ or for *G* to↓).
    - It appears that there is a force acting to disperse the solute. That force is illusory.
  - To set up a differential equation for the change in concentration in a region by considering *J*(material) through its boundaries.
    - The resultant 'diffusion equation' can in principle be solved for various configurations of the system, such as the shape of the vessel.
  - Mechanistic approach; imagine the diffusion is taking place in a series of random small steps.
    - Provides a model of what is taking place when matter diffuses.

The thermodynamic view

- At constant p and T, the max non-expansion work that can be done when a substance moves from a location of G to another of G+dG is dw=dG.
- As μ is the (partial) molar G, the max. non-expansive work per mole is dw=dμ.
- In a system where μ depends on position x; $dw = d\mu = \left(\frac{\partial\mu}{\partial x}\right)_{T,p} dx$.
- In general, work can always be expressed in terms of an opposing force; $dw = -Fdx$
- Comparing eq and eq, $F = -\left(\frac{\partial\mu}{\partial x}\right)_{T,p}$, thermodynamic force for mass transport.

The thermodynamic view

- There is not necessarily a real force pushing the particles down the slope of μ.
- The force may represent the spontaneous tendency of MQs to disperse as a consequence of the 2nd law of TD.
- In a solution, with solute activity of *a*; $\mu = \mu^{\emptyset} + RT\ln a$.
- If the solution is not uniform, *a* depends on the position (*x*) as: $F = -\left(\frac{\partial \mu}{\partial x}\right)_{T,p} = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{T,p}$
- If the solution is ideal a may be replaced by $c/c^{\emptyset}$ so $F = -RT\left(\frac{\partial \ln \frac{c}{c^{\emptyset}}}{\partial x}\right)_{T,p} = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$

TD force

- Suppose a linear concentration gradient is set up across a container at 25 °C, with points separated by 1.0 cm differing in concentration by 0.1 mol dm^{-3} around the mean value of 1.0 mol dm^{-3}.
- Calculate the thermodynamic force the solution experiences that ‘drives’ it to reach a uniform concentration.

- $F = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p}$

Answer

- $F = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{T,p} = \frac{(8.314\ J\ K^{-1}mol^{-1})\times(298\ K)}{1.0\ mol\ dm^{-3}} \times \frac{0.10\ mol\ dm^{-3}}{1.0\times10^{-2}\ m} = 2.5\times 10^{4}\ J\ m^{-1}mol^{-1}$

N

- So the thermodynamic force is a molar quantity.

Generalisation of diffusion

- Fick's 1st law of diffusion, $J(number) = -D\frac{d\mathcal{N}}{dx}$, as we've seen previously is deduced from the kinetic theory of gases.
- We can generalise this to apply for the diffusion of condensed phases as well.
- We assume *J* is a response to *F* arising from a concentration gradient.
- Diffusing particles reach a steady drift speed, *s*, when *F*=drag due to *η* of the medium.
- *s* α *F* and *F* α dc/dx, and as *J* α *s* → *J* α dc/dx, which is the content of Fick's law.

Generalisation of diffusion

- $J(number) = -D\frac{d\mathcal{N}}{dx}$ / *N_A^{-1}
- $J(amount) = -D\frac{dc}{dx}$; *D* – diffusion coefficient and d*c*/d*x* – slope of molar concentration.
- $J(amount) = sc$, as all particles within a distance of *sΔtA* can pass through an *A* window area in a Δ*t* interval; amount of substance that can pass through is *sΔtAc*, and *J*(amount)=(quantity)/Δ*tA*= *sΔtAc*/Δ*tA*=*sc*.
- Combining eq & eq: $sc = -D\frac{dc}{dx} = \frac{DcF}{RT}$ or $s = \frac{DF}{RT}$, once we know the effective force of *D*, we can calculate *s* of the particles regardless of the origin of *F*.

TD force & drift speed

- Laser measurements showed that a MQ with s=1.0 µm s^{-1} in water at 25 °C has D=5.0*10^{-9} m^2 s^{-1}.
- Calculate the corresponding TD force.

- $F=sRT/D$

Answer

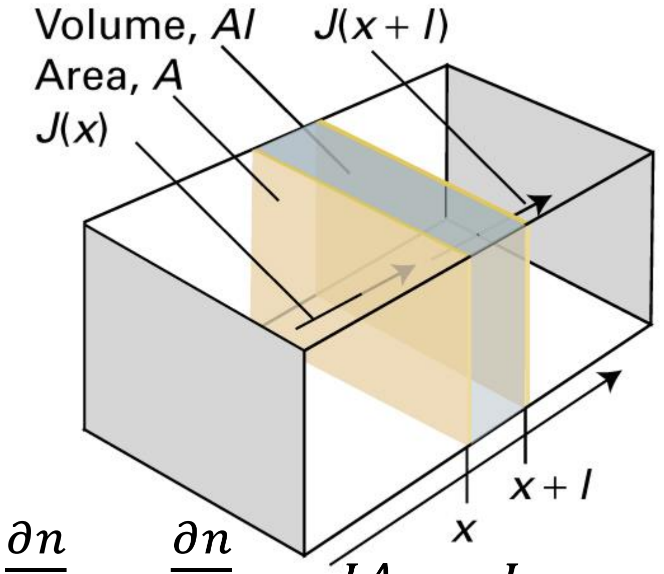
- $F=sRT/D=(1.0\text{-}10^{-6}\ \text{m s}^{-1})*(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})*(298\ \text{K})/(5.05*10^{-9}\ \text{m}^{2}\ \text{s}^{-1})$ $=5.0*10^{5}\ \text{J m}^{-1}\ \text{mol}^{-1}$

N

Diffusion equation

- Time-dependent diffusion processes, *i.e.* how to spread inhomogeneities in time.
- Consider the temperature of a metal bar that has been heated at one end: if the source of heat is removed, then the bar gradually settles down into a state of uniform T. When the source of heat is maintained and the bar can radiate, it settles down in a steady-state of non-uniform T.
- Or, consider the concentration distribution of a solute that has just been added in a solvent.
- We will focus on the diffusion of particles but similar arguments apply to the diffusion of physical properties, such as T.
- Our aim is to obtain an equation for the rate of change of the concentration of particles in an inhomogeneous region.

Simple diffusion



- Consider the above slab. Let the concentration be *c* at *x* at the time *t*. The rate with which the amount (in moles) of particles enters the slab is: $\frac{\partial c}{\partial t} = \frac{\partial \frac{n}{V}}{\partial t} = \frac{\frac{\partial n}{\partial t}}{V} = \frac{JA}{Al} = \frac{J}{l}$

Inflow; $\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} = \frac{J}{l}$

Outflow; $\frac{\partial c}{\partial t} = -\frac{J'Adt}{Aldt} = -\frac{J'}{l}$

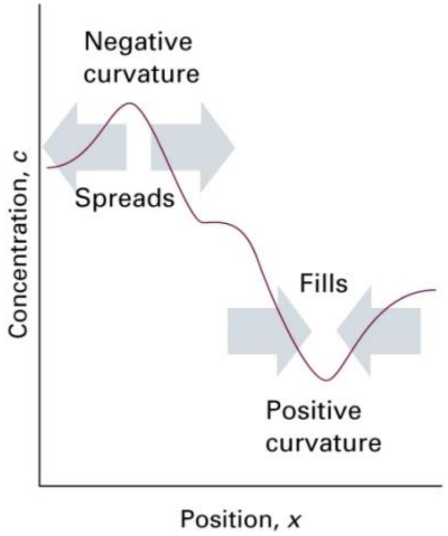
Net; $\frac{\partial c}{\partial t} = \frac{J - J'}{l}$

$$\boxed{c' = c\left(\frac{\partial c}{\partial x}\right) l}$$

$J - J' = -D\frac{\partial c}{\partial x} + D\frac{\partial c'}{\partial x} = -D\frac{\partial c}{\partial x} + D\frac{\partial}{\partial x}\left\{c + \left(\frac{\partial c}{\partial x}\right) l\right\} = Dl\frac{\partial^2 c}{\partial x^2}$, using Fick’s 1st law

Diffusion equation

- Updating the expression for the rate of change we get the diffusion equation, *aka* Fick's 2nd law of diffusion: $\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}$.
- The diffusion eq. shows that the rate of concentration change α the curvature (*i.e.* 2nd derivative) of the concentration wrt distance.
  - If *c* changes sharply from point to point (*i.e.* highly wrinkled) then *c* changes rapidly with time.
  - Where the curvature is +ve the dip tends to fill
  - Where the curvature if –ve the heap tends to spread.
  - Where the curvature is 0, *c* is constant in time
  - If *c* decreases linearly in with distance, c at any point is constant as inflow of particles balances the outflow.
- There is a natural tendency for wrinkles to disappear;



Nature abhors a wrinkle!!

Diffusion equation

- If c falls linearly across a small region of space, in the sense that $c=c_0-ax$, then $\partial^2 c/\partial x^2=0$ and, consequently, $\partial c/\partial t=0$.
- c in the region is constant as the inward flow through one window is matched by the outward flow through the other window.
- If c varies at $c=c^0-1/2ax^2$, what is the rate of concentration change?

- $\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2}$

Answer

- $c = c^0 - 1/2ax^2$
- $\partial^2 c/\partial x^2 = -a$
- $\partial c/\partial t = -Da$
- In this case the concentration decreases because there is a greater outward flow than inward flow.

Convection

- Transport of particles arising from the motion of a streaming fluid is called convection.
- If we ignore diffusion, the flux of particles through an *A* area in a Δ*t* interval when the fluid is flowing with a *v* velocity is calculated as $J_{conv} = \frac{\#\ MQs}{A\Delta t} = \frac{c \times V}{A\Delta t} = \frac{cAv\Delta t}{A\Delta t} = cv$, the convective flux.
- The rate of change of the concentration in a slab of thickness *l* and area *A* is $\frac{\partial c}{\partial t} = \frac{J_{conv} - J'_{conv}}{l} = \frac{cv}{l} - \left\{c + \left(\frac{\partial c}{\partial x}\right) l\right\} \frac{v}{l} = -\left(\frac{\partial c}{\partial x}\right) v$, provided the velocity does not depend on the position.

Diffusion with convection

- When both diffusion and convection occur, the generalised diffusion equation combining the two effects: $\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x}$.
- Further complication – and of the utmost importance in chemistry – arises from the change in the particles' concentration as a result of a reaction.

Convection

- Suppose there is a convective flow v. If c falls linearly across a small region of space, in the sense that $c=c_0-ax$, then $\partial c/\partial x=-a$ and the change of concentration in the region is $\partial c/\partial t=av$.
- If c varies at $c=c^0-1/2ax^2$, what is the rate of concentration change?
- If a=0.010 mol $\mathrm{dm^{-3}\ m^{-1}}$ and v=+1.0 mm $\mathrm{s^{-1}}$,

- $\frac{\partial c}{\partial t}$ =0.010 mol $\mathrm{dm^{-3}\ m^{-1}}$*(1.0 mm $\mathrm{s^{-1}}$)=1.0*10^{-5} mol $\mathrm{dm^{-3}\ s^{-1}}$.
- There is now an increase in the region because the inward convective flow outweighs the outward flow, and there is no diffusion.

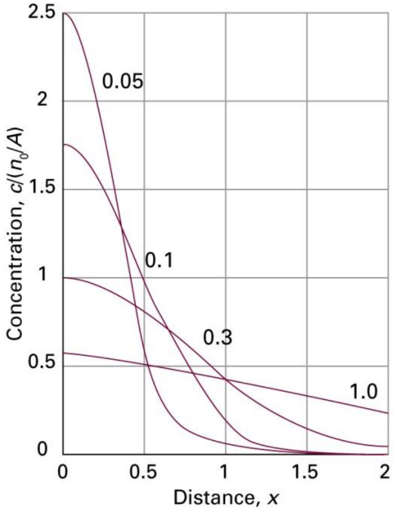
Solutions of the diffusion equation

- The diffusion equation is a 2nd order differential eq. wrt space and a 1st order differential eq. wrt time. So we must specify two boundary conditions for the spatial dependence and a single initial condition for the time dependence.
- Consider a solvent in which the solute is initially coated on one surface of the container (*cf.* layer of sugar on the bottom of a beaker of water). The single initial conditions is that at t=0 all N_0 particles are concentrated on the yz plane at x=0. The 2 boundary conditions are derived from the requirements
  - concentration must be finite everywhere
  - total amount of particles present is $n_0=(N_0/N_A)$ at all times.

Solutions of the diffusion equation

- These requirements imply that the flux of particles is 0 at the top and bottom surfaces of the system.

$$c(x,t) = \frac{n_0}{A(\pi D t)^{\frac{1}{2}}} e^{-x^2/4Dt}, \text{ 1D diffusion}$$



- Concentration tends to spread to uniformity

- In a 3D solvent (*cf.* sugar lump suspended), the *c* is spherically symmetrical and at a radius *r* is;

$$c(r,t) = \frac{n_0}{8(\pi D t)^{\frac{3}{2}}} e^{-r^2/4Dt}, \text{ 3D diffusion}$$

Capillary and diaphragm techniques

- Transport of substances across membranes, *etc.* may also be treated.
- The solutions of the diffusion eq. are useful for experimental determinations of *D*.
- In the capillary technique, a capillary tube open at one end and containing a solution, is immersed in a well-stirred larger quantity of solvent, and the concentration change is monitored in the tube. The solute diffuses from the open end at a rate that can be calculated by solving the diffusion eq. w the appropriate boundary conditions.
- In the diaphragm technique, the diffusion occurs through the capillary pores of a sintered glass diaphragm separating the well-stirred solution and the solvent. Concentrations are monitored and then related to the solutions of the diffusion eq. corresponding to this arrangement.
- *D* may also be measured other techniques, such as NMR.

Calculation of the average displacement

- Calculate the average displacement of particles in a time *t* in a 1D system if they have a *D* diffusion constant.
- First calculate the # of particles in a slab of d*x* thickness and *A* area at *x*, with *c* molar concentration.
- Then consider what the probability of a particle to be found at a certain distance from the origin is (*i.e.* what is their probability of being in the slab and how far did they travel from).
- Finally, calculate the average by weighting each distance by the probability.

- Use $c(x,t) = \frac{n_0}{A(\pi D t)^{\frac{1}{2}}} e^{-x^2/4Dt}$
- And remember the common integral, $\int_0^\infty x e^{-ax^2}\, dx = \frac{1}{2a}$

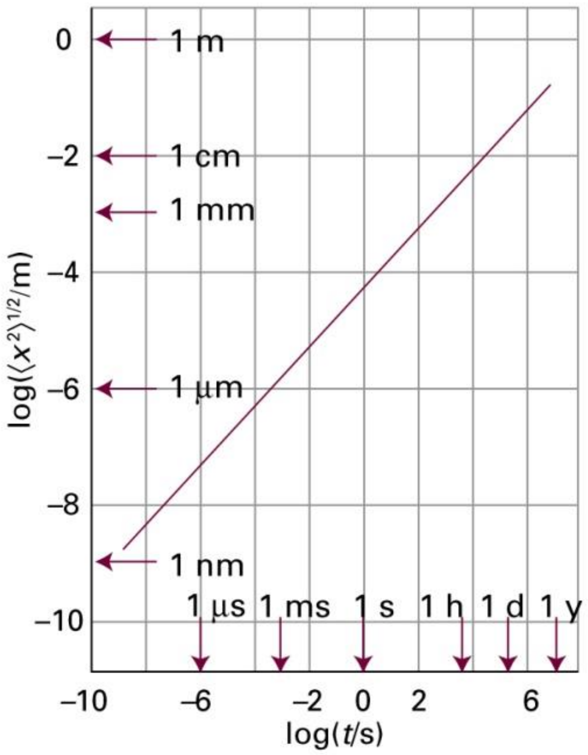
Answer

- # of particles in a slab of d*x* thickness and A area at x, with c molar concentration, is $cAN_A\mathrm{d}x$.
- The probability that any of the $N_0=n_0N_A$ particles in the slab is therefore $cAN_A\mathrm{d}x/N_0$. If the particle is in the slab, it has travelled a distance x from the origin.
- Therefore the average displacement of all the particles in the sum of each x weighted by the probability of its occurrence:
- $\langle x\rangle = \int_0^\infty x \frac{c(x,t)AN_A}{\underset{n_0N_A}{N_0}}dx = \frac{1}{(\pi Dt)^{1/2}}\int_0^\infty xe^{-x^2/4Dt}dx = 2\left(\frac{Dt}{\pi}\right)^{1/2}$

$$\int_0^\infty xe^{-ax^2}\,dx = \frac{1}{2a}$$

Average displacement of a diffusing particle

- As just seen, the average displacement of a diffusing particle is $\langle x \rangle = 2\left(\frac{Dt}{\pi}\right)^{1/2}$, in 1D.
- The root mean square of it is $\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}$, rms displacement in 1D.
- This is a valuable measure of the spread of particles when they can diffuse in both directions from the origin.



Diffusion is a very slow process!
And greatly accelerated by convection!!

Statistical view

- ~ an intuitive picture of diffusion as the particles moving in a series of small steps and gradually migrating from their original positions.
- Our model: particles may jump through a distance of λ in a time τ.
- The total distance travelled by a particle in a time t is thus $t\lambda/\tau$.
- However, the particle, will not necessarily be found at this distance from the origin as the direction of each step may be different.
- So for the net distance we need to consider changes of direction too.

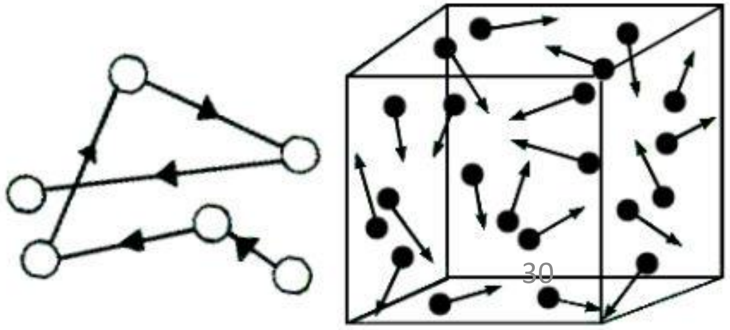
1D random walk

- Consider a 1D random walk of N steps, in which each step is of λ in either left or right in a τ time.
- The # of ways performing a walk with N_R steps to the right and N_L steps to the left is given by the binomial coefficient: $W = \frac{N!}{N_L! N_R!} = \frac{N!}{(N-N_R)! N_R!}$.
- The total possible # of paths is 2^N. The probability of the net distance walked being $n\lambda$ with $n=N_R-N_L=2N_R-N$ is $P(n\lambda) = \frac{\#\, paths\ with\ N_R\ steps\ to\ the\ right}{total\ \#\, paths} = \frac{W}{2^N} = \frac{N!}{(N-N_R)! N_R! 2^N}$.
- $\boldsymbol{P(n\lambda) = \frac{2^{N+1} e^{-2N\mu^2}}{2^N (2\pi N)^{1/2}} = \frac{2e^{-2N\mu^2}}{(2\pi N)^{1/2}}}$, **as** $\boldsymbol{N\mu^2 = \frac{(2N_R-N)^2}{4N} = \frac{(N_R-N_L)^2}{4N} = \frac{n^2}{4N}}$
- The net distance from the origin is $x=n\lambda$, and # of steps at t time is $N=t/\tau$ so $N\mu^2=\tau x^2/4t\lambda^2$.
- $P(x,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2\tau/2t\lambda^2}$, probability of a particle being at x distance from origin – 1D random walk.

Use Stirling's approximation;
$\ln x! \approx \ln(2\pi)^{1/2}+(x+1/2)\ln x - x$, when $x<<1$
And introduce parameter $\mu=(N_R/N)-1/2<<1$
So for the smallest μ the expansion may be used: $\ln(1/2\pm\mu)=-\ln 2\pm 2\mu-2\mu^2+\dots$

Statistical approach

- Differences between eqs $c(x,t) = \frac{n_0}{A(\pi D t)^{\frac{1}{2}}} e^{-x^2/4Dt}$ (1D diffusion) and $P(x,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2\tau/2t\lambda^2}$ (random walk) arise from the fact that in the present calculation the particles can migrate in either direction from the origin, and they can only be found at discrete points separated by λ.
- The fact that the 2 expressions are so similar suggests that diffusion may be understood in terms of small steps as the outcome of a large # of steps in random directions (Brownian motion).



Einstein-Smoluchowski equation

- To relate D and λ we compare the exponents in eqs $c(x,t) = \frac{n_0}{A(\pi D t)^{\frac{1}{2}}} e^{-x^2/4Dt}$ & $P(x,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} e^{-x^2\tau/2t\lambda^2}$.
- Einstein-Smochulowski eq.: $D = \frac{\lambda^2}{2\tau}$.
- For a 1D random walk, the above implies that the distance walked after *N*=*t*/*τ* steps of length *λ* is: $\langle x \rangle = \lambda \left(\frac{2N}{\pi}\right)^{1/2}$.
- 2D: $\langle r \rangle = \lambda N^{1/2}$ and 3D: $\langle r \rangle = \lambda \left(\frac{8N}{\pi}\right)^{1/2}$.
- The Einstein-Smochulowski eq. is the central connection of the microscopic details of particle motion with the macroscopic parameters relating to diffusion.

Random walk

- Suppose an SO_4^{2-} ion jumps through its own diameter each time it makes a move in an aqueous solution.
- Determine τ for D=1.1*10^{-9} m^2 s^{-1} and a=250 pm [pm]
- $\lambda=2a$
- $D=\lambda^2/2\tau$

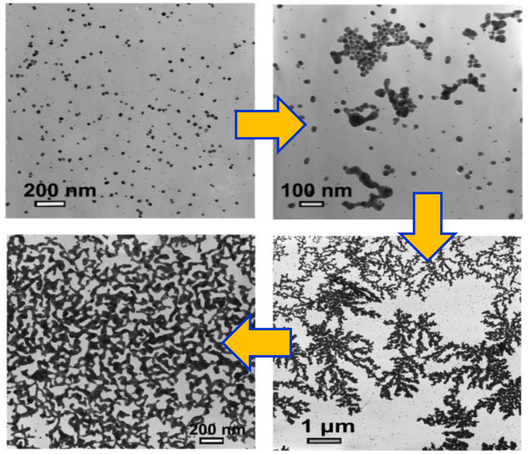
Answer

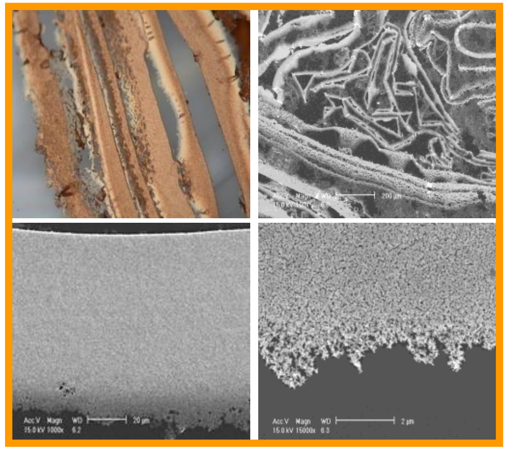
- $\tau=(2a)^2/2D=2a^2/D=2*(250*10^{-12}\text{ pm})^2/(1.1*10^{-9}\text{ m}^2\text{ s}^{-1})=1.1*, 10^{-10}\text{ s}$, i.e. 110 ps, or 10^{10} jumps per second.

Impact on nanotechnology

- Diffusion limited aggregation (DLA)

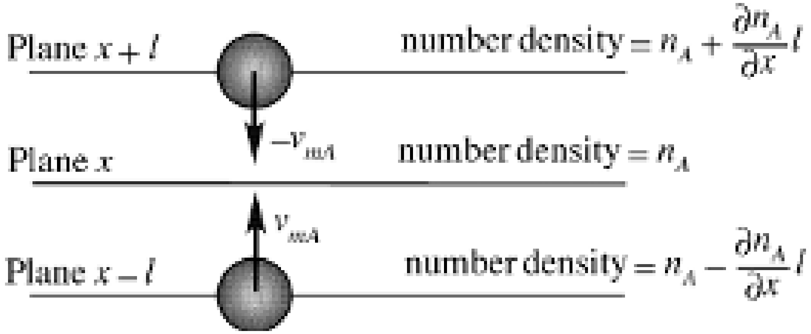
- Formation of nanoporous membranes through DLA process





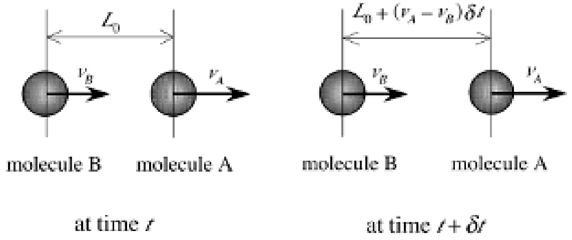
S. W. Han et al., *J. Mater. Chem.* **2008**, *18*, 2208.

Diffusion and mass transfer



- The phenomenon of diffusion is a result of motion of MQs in a fluid medium.
- On the MQlar scale, MQs seem to be moving randomly in various directions and at various velocities.
    - We assumes that motion of MQs is 1D and velocities of MQs of the same species are equal. Also, the # density of species *i* is a function of coordinate *x*.
- Consider effect of motion of MQs of species *A* in planes *x*+*l* and *x*-*l*.
- The diffusional flux of species *A*, J_A* may be related to the net # of *A* MQs passing through the plane *x* per unit area per unit time: $J_A^* \approx v_{mA} n_A|_{x-l} - v_{mA} n_A|_{x+l} = v_{mA}\left(n_A - \frac{\partial n_A}{\partial x} l\right) - v_{mA}\left(n_A + \frac{\partial n_A}{\partial x} l\right) = -2 v_{mA} l \left(\frac{\partial n_A}{\partial x}\right)$, similarly to the empirical Fick's law.

Diffusional flux and reference velocity of diffusion



- Assuming that motion of MQs is 1D and velocities of MQs of the same species are equal; $v_A=v_B=v_C=\ldots=v$
- As the distance btw MQs is unchanged in this case the concentration of each species will remain unchanged, *i.e.* diffusion phenomenon is not observe.
- If *v* of the MQs of species *i* are not equal, the distances btw the MQs will change in time → concentration of each component will change with time, *i.e.* diffusion phenomenon will be observed.
- Molar average velocity of a mixture of fluids: $v^* = \sum_{i=1}^{N} x_i * v_i$, reference velocity of diffusion. The MQs of species *i* are observed to move at a relative velocity of (v_i-v^*).
- Molar diffusional flux: $J_i^* = c_i(v_i - v^*) = cx_i(v_i - v^*)$, *c* – molar density of the fluid mixture, c_i – partial molar density of component *i*, x_i – molar fraction of component *i*.

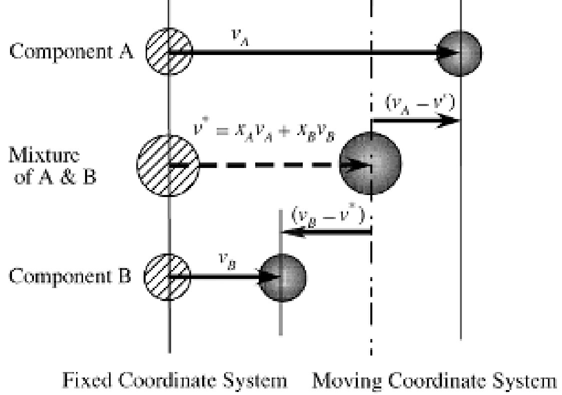
Summation theorem

- Summing all the diffusional fluxes of the system: $\sum_{i=1}^{N} J_i^* = c \sum_{i=1}^{N} x_i (v_i - v^*) = c\left(\sum_{i=1}^{N} x_i v_i - v^* \sum_{i=1}^{N} x_i\right) = c(v^* - v^*) = 0.$
- The sum of diffusional fluxes is always zero, $\sum_{i=1}^{N} J_i^* = 0.$
- Defining the mass average velocity, *baricentric velocity*, as $v = \sum_{i=1}^{N} \omega_i v_i$, ω_i – mass fraction component of *i*.
- The mass diffusional flux → $J_i = \rho_i (v_i - v) = \rho \omega_i (v_i - v)$, where ρ density of fluid and ρ_i – partial density of component *i*.
- For mass diffusional fluxes also: $\sum_{i=1}^{N} J_i = 0$

Binary diffusion flux

- For binary diffusion $J_A^* = cx_A(v_A - v^*) = -cD\left(\frac{\partial x_A}{\partial y}\right)$, where *D* – binary diffusion coefficient of component *A* through component *B* and *y* – distance in the direction of diffusion.
- As x_A+x_B=1, $J_A^* = cx_A(v_A - v^*) = cx_A x_B(v_A - v_B) = cx_B(v^* - v_B) = -J_B^*$. N.B. we should have known this from the summation theorem.
- Using $J_i = \rho\omega_i(v_i - v)$, we get $\omega_A + \omega_B = 1$.
- $J_A = \rho\omega_A(v_A - v) = \rho\omega_A\omega_B(v_A - v_B) = \rho\omega_B(v - v_B) = -J_B$
- Eliminating term and subsequent rearrangement we get $x_A = \frac{\omega_A/M_A}{\frac{\omega_A}{M_A}+\frac{\omega_B}{M_B}} = \frac{(M_B/M_A)\omega_A}{1+\{((M_B/M_A)-1\}\omega_A}$.

Binary diffusion flux



- $J_A = \frac{\rho \omega_A \omega_B}{c x_A x_B} J_A^* = \frac{M_A M_B}{\bar{M}}\left(-cD\frac{\partial x_A}{\partial y}\right) = -cD\frac{M_A M_B}{\bar{M}}\frac{\bar{M}^2}{M_A M_B}\frac{\partial \omega_A}{\partial y} = -\rho D\frac{\partial \omega_A}{\partial y}$, where $\bar{M} = x_A M_A + x_B M_B$. Indicates that the mass diffusional flux reduces to the empirical Fick's law.
- On rearrangement: $J_A = \frac{1}{1 + x_A\left(\frac{M_A}{M_B} - 1\right)}(M_A J_A^*)$, *i.e.* relationship between J_A & J_A^* is not only affected by difference in M but also in concentrations.
- Either of J_A & J_A^* is a good descriptor in a stationary fluid.
- However, in the case of transport phenomena in a flow system, the mass diffusional flux needs to be used as the eq. of motion & energy eq. are described in terms of the mass average velocity, *v*, and not in terms of the molar average velocity, *v**.
- The consequence of this is that by using the molar diffusional flux in a flow system, the difference btw the molar and mass average velocities *v**-*v* will cause a serious error in dealing with the diffusion eq. Therefore, the mass diffusional flux will be used.

Binary diffusion coefficient in the gas phase

- As we've seen, $J_A^* = cx_A(v_A - v^*) = -cD\left(\frac{\partial x_A}{\partial y}\right)$ and $J_A = \rho\omega_A(v_A -$

Multicomponent diffusion coefficients in the gas phase

- According to the kinetic theory of gases, the diffusional fluxes in a n *N*-component system may be expressed as:

$$\begin{gathered}
J_1^* = D_{11}\nabla x_1 + D_{12}\nabla x_2 + D_{13}\nabla x_3 + \cdots + D_{1N}\nabla x_N \\
J_2^* = D_{21}\nabla x_1 + D_{22}\nabla x_2 + D_{23}\nabla x_3 + \cdots + D_{2N}\nabla x_N \\
J_3^* = D_{31}\nabla x_1 + D_{32}\nabla x_2 + D_{33}\nabla x_3 + \cdots + D_{3N}\nabla x_N \\
\cdot \\
\cdot \\
\cdot \\
J_N^* = D_{N1}\nabla x_1 + D_{N2}\nabla x_2 + D_{N3}\nabla x_3 + \cdots + D_{NN}\nabla x_N
\end{gathered}$$

- J_i^* - molar diffusional flux of component i;
- ∇x_i - gradient of mole fraction of component I;
- Coefficients D_{11}, D_{12}, … D_{NN} – multicomponent diffusion coefficients
- Thought theoretically derived, no reliable method exists for estimating D_{ij}, nor is any observed value known, even for a ternary system.

Effective diffusion coefficient

- The effective diffusion coefficient addresses this by estimating rates of diffusion in multicomponent systems for the established binary diffusion coefficients;
- $J_A^* = cD_{m,A}\nabla x_A$ where $D_{m,A} = \frac{1-y_A}{\frac{y_B}{D_{AB}}+\frac{y_C}{D_{AC}}+\frac{y_D}{D_{AD}}\ldots}$, effective diffusion coefficient of component *A*, and D_{AB}, *etc.* are binary diffusion coefficients of *A* through *B*, *etc*.
- The diffusional flux may be estimated from the concentration gradient of a given component in a multicomponent system;

  (*Diffusion flux*)=(*Effective diffusion coefficient*)(*Concentration gradient*)
- NB, this is widely used to predict separation performance of a multicomponent distillation, *cf.* of crude oil.

Binary diffusion coefficient

- Calculate the binary diffusion coefficient of water vapour in are at 298 K and 1 atm.

Convective mass flux

- Transfer of a material through a fluid-fluid interface or a fluid-solid interface is called mass transfer. If the concentration near the interface is not uniform, mass transfer is closely related to diffusion.
- The rate of mass transfer of component *i* is usually expressed as the mass component *i* passing through unit area of the interface per unit time, *i.e.* the mass flux of component *i*; $N_i=\rho_s\omega_{is}v_{is}$, where ρ_s – density of fluid at the interface, ω_{is} – mass fraction of component *i* at the interface, and v_{is} – velocity of component *i* at the interface.
- Rearranging and using $J_i = \rho\omega_i(v_i - v)$, definition of mass diffusional flux: $N_i=\rho_s\omega_{is}(v_i-v_s)+\rho_s v_s\omega_{is}=J_{is}+\rho_s v_s\omega_{is}$; mass diffusional flux at the interface & transfer of component *i* by the accompanying flow due to diffusional flux to the interface, *i.e.* convective mass flux.

Rates of mass transfer

- The mass flux may be expressed as:

  (*Mass flux*)=(*Diffusional flux*)+(*Convective mass flux*)

- The fact that mass flux is always accompanied by convective mass flux is a phenomenon characteristic to mass transfer and has no parallels in momentum or heat transfer!
- Summation theorem: $\sum_{i=1}^{N} N_i = \sum_{i=1}^{N}(J_{is} + \rho_s v_s \omega_{is}) = \sum_{i=1}^{N} J_{is} + \rho_s v_s \sum_{i=1}^{N} \omega_{is} = \rho_s v_s.$
  - This is practically important to evaluate the diffusional flux from the observed mass transfer data for multicomponent distillation.
- The rate of mass transfer in terms of N_i^*, molar flux component: $N_i^*=N_i/M_i=c_s x_{is} v_{is}=c_s x_{is}(v_{is}-v_s^*)=J_{is}^*+c_s x_{is} v_s^*$
- Similarly, $\sum_{i=1}^{N} N_i^* = \sum_{i=1}^{N} J_{is}^* + c_s v_s^* \sum_{i=1}^{N} x_{is} = c_s v_s^*$, where c_s - molar density at the interface, x_{is} - mole fraction of component *i* at the interface, and v_s^* - molar average velocity of component *i* at the interface.

Unidirectional diffusion in binary mass transfer

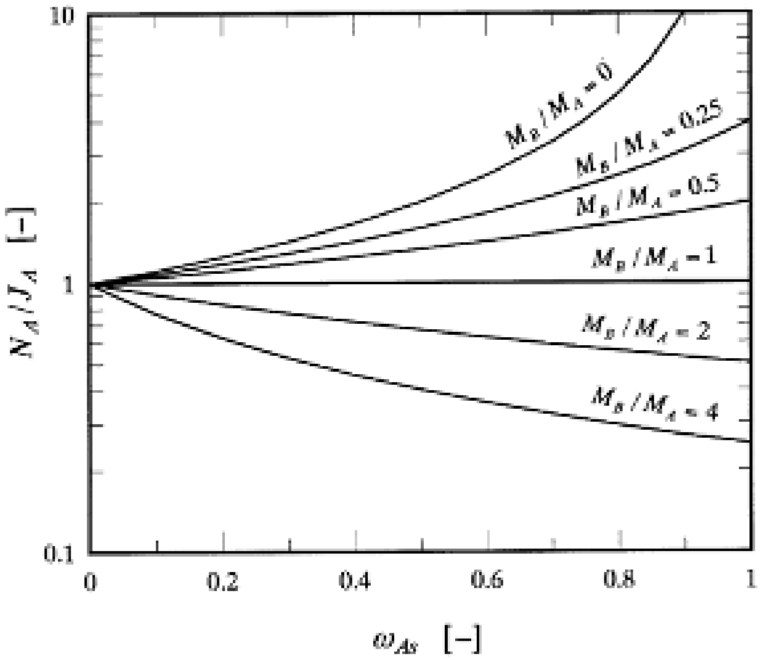
- Unidirectional diffusion - special case of mass transfer, in which component *A* transfers into a stationary fluid medium of component *B*, *cf.* absorption of pure gases by liquids or evaporation of pure liquids into gases.
- From the 0 mass flux condition for component *B*: $N_B = J_{Bs} + \rho_s v_s \omega_{Bs} = 0$.
- So the convective velocity at the interface: $v_s = \frac{-J_B}{\rho_s \omega_{Bs}} = \frac{1}{\rho_s (1-\omega_s)} J_{As}$.
- Substituting eq. into $N_i = J_{is} + \rho_s v_s \omega_{is}$; $N_A = J_{As} + \frac{\omega_{As}}{(1-x_{As})} J_{As} = \frac{1}{(1-\omega_{As})} J_{As}$, for the mass flux of A in unidirectional flow in a binary system
- Molar flux for unidirectional flow in a binary system: $N_A^* = \frac{1}{(1-x_{As})} J_{As}^*$.
- For the special case of multicomponent systems, in which only one component, *N*, is stagnant and the transfer of the remaining N-1 components takes place at the interface; $N_i = J_{is} + \frac{\omega_{is} \sum_{i \neq N} J_{is}}{1-\sum_{i \neq N} v}$.

Equimolal counterdiffusion

- Equimolal counterdiffusion – a special case of binary mass transfer, in which equal numbers of moles of each component are transferred in mutually opposite directions, *cf*. binary distillation.
- From the condition of equimolal counterdiffusion: $\frac{N_A}{M_A} + \frac{N_B}{M_B} = 0$.
- Rearranging eq. and using $N_i = J_{is} + \rho_s v_s \omega_{is}$, the convective flow is: $v_s = -\frac{(M_B/M_A - 1)}{1 + (M_B/M_A - 1)\omega_{As}}\left(\frac{J_{As}}{\rho_s}\right)$.
- Sub eq. into $N_i = J_{is} + \rho_s v_s \omega_{is}$; $N_A = \frac{J_{As}}{1 + (M_B/M_A - 1)\omega_{As}} \neq J_{As}$

Equimolal counterdiffusion

- The relationship btw mass flux & mass diffusional flux is not only affected by the difference in MQlar weights but also by the concentrations at the interface
- Though the above relationship is complicated, the corresponding eq. for the molar flux is simple: $N_A^* = N_A/M_A = J_A^*$ [kmol m^{-2}s^{-1}]
- As the molar average velocity at the interface, v_s*, is always 0 for equimolal counterdiffusion



Convective mass flux for mass transfer in a mixture of vapours

- In binary and multicomponent distillation, the condensation of mixed vapours and the evaporation of volatile solutions are always accompanied by an interfacial velocity, v_s, caused by the condensation of vapours or evaporation of liquids.
- Consider the energy balance at the interface for a partial condensation of binary vapours; $\lambda_A N_A+\lambda_B N_B+q_G+q_w=0$. λ_A – latent heat of vaporisation of *A* at the interface, q_G – vapour-phase sensible heat flux, and q_w – heat flux from the wall.
- Rearranging eq. and using $N_i=J_{is}+\rho_s v_s \omega_{is}$; $N_A=J_{As}+\rho_s v_s \omega_{As}$ & $N_B=J_{Bs}+\rho_s v_s \omega_{Bs}$
- Convective mass flux: $\rho_s \omega_s = \dfrac{(\lambda_B-\lambda_A)J_{As}-q_G-q_w}{\lambda_a \omega_{As}+\lambda_B \omega_{Bs}}$.

Convective mass flux for mass transfer in a mixture of vapours

- Similarly, for the convective mass flux in multicomponent distillation we get; $\rho_s v_s = \frac{\sum_{i=1}^{N}(\lambda_N - \lambda_i)J_{is} - q_G - q_w}{\sum_{i=1}^{N}(\lambda_i \omega_{is})}$.
- NB, it is eqs. $\rho_s \omega_s = \frac{(\lambda_B - \lambda_A)J_{As} - q_G - q_w}{\lambda_a \omega_{As} + \lambda_B \omega_{Bs}}$ & $\rho_s v_s = \frac{\sum_{i=1}^{N}(\lambda_N - \lambda_i)J_{is} - q_G - q_w}{\sum_{i=1}^{N}(\lambda_i \omega_{is})}$ that have permitted a new separation technology for stable isotopes.

Rate of evaporation

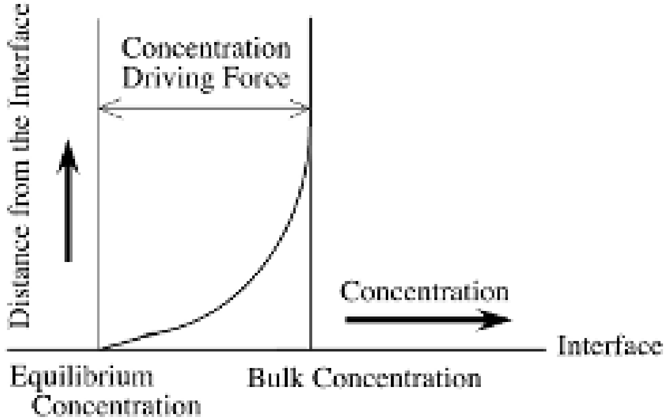
- Water is placed in a test tube and kept in air at 20 °C and 1 atm. Calculate the rate of evaporation of water, if the distance between the upper edge of the test tube and the surface of the water is 50 mm.

- Assume that the surface temperature is 20 °C.

Mass transfer coefficients

- We have seen that the rate of mass transfer is closely related to the diffusion at the interface, *i.e.* to concentration gradients at interface.
- In real-world problems however concentration gradients at the interface cannot be directly evaluated.
- By introducing mass transfer coefficient however the mass transfer rates can be calculated without using the concentration gradients in the interface, similarly to the heat transfer coefficients.

Concentration driving force



- Concentration distribution near an interface:
- Though concentration variation is very sharp near the interface it becomes more gradual in the region slightly further away and the concentration slowly approaches that of the bulk fluid.
- The concentration at the interface is in equilibrium (principles of local equilibrium: *A physical system should be in a local equilibrium if it cannot be distinguished from a global equilibrium by "infinitesimally localised measurements"*.)
- Therefore the rate of transfer can be taken to be proportional to the concentration difference between the interface & bulk fluid, the concentration driving force.

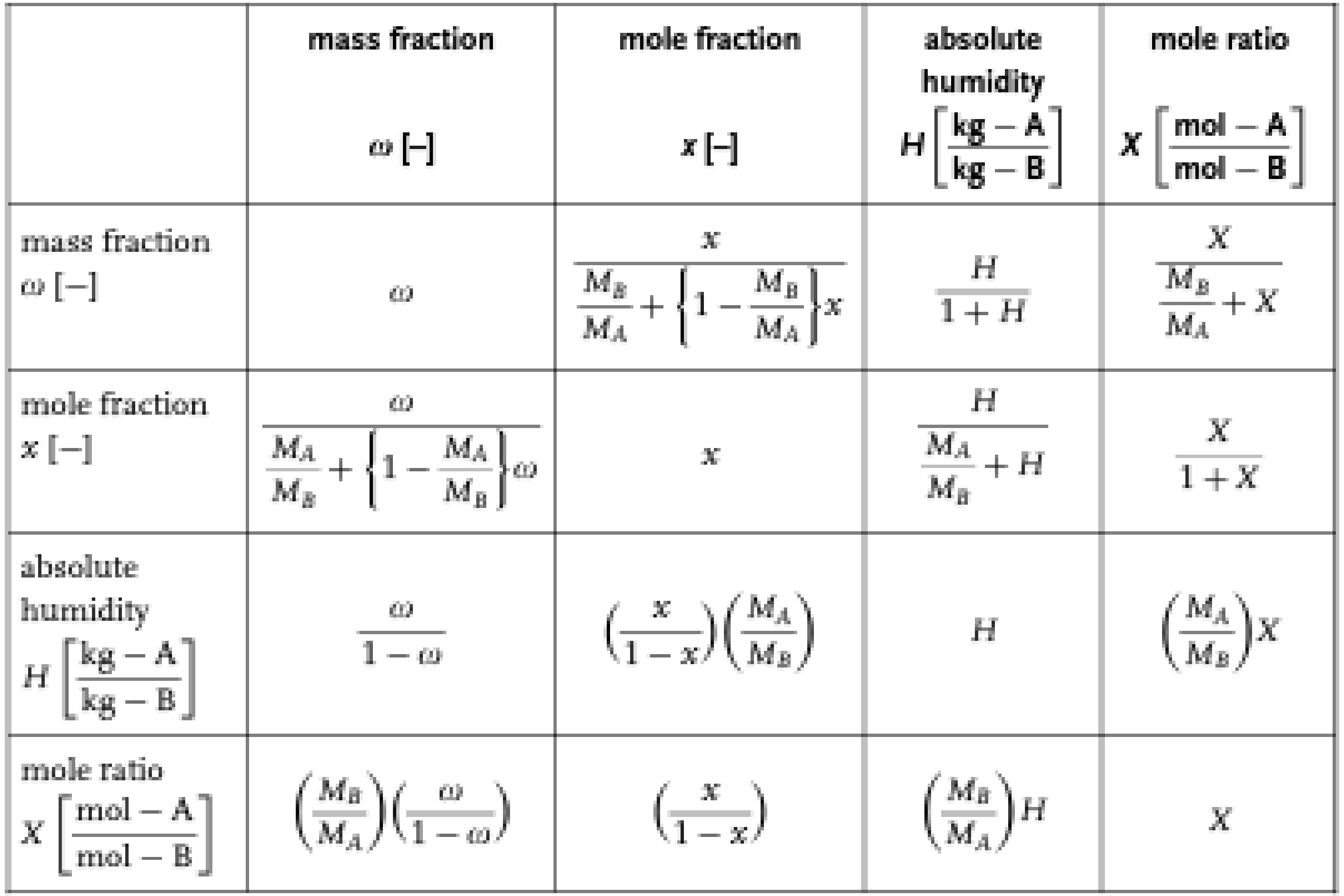
Mass transfer coefficients

- The proportionality constant is defines as the mass transfer coefficient

(*Rate of mass transfer*)=(*Mass transfer coefficient*)(*Concentration driving force*)

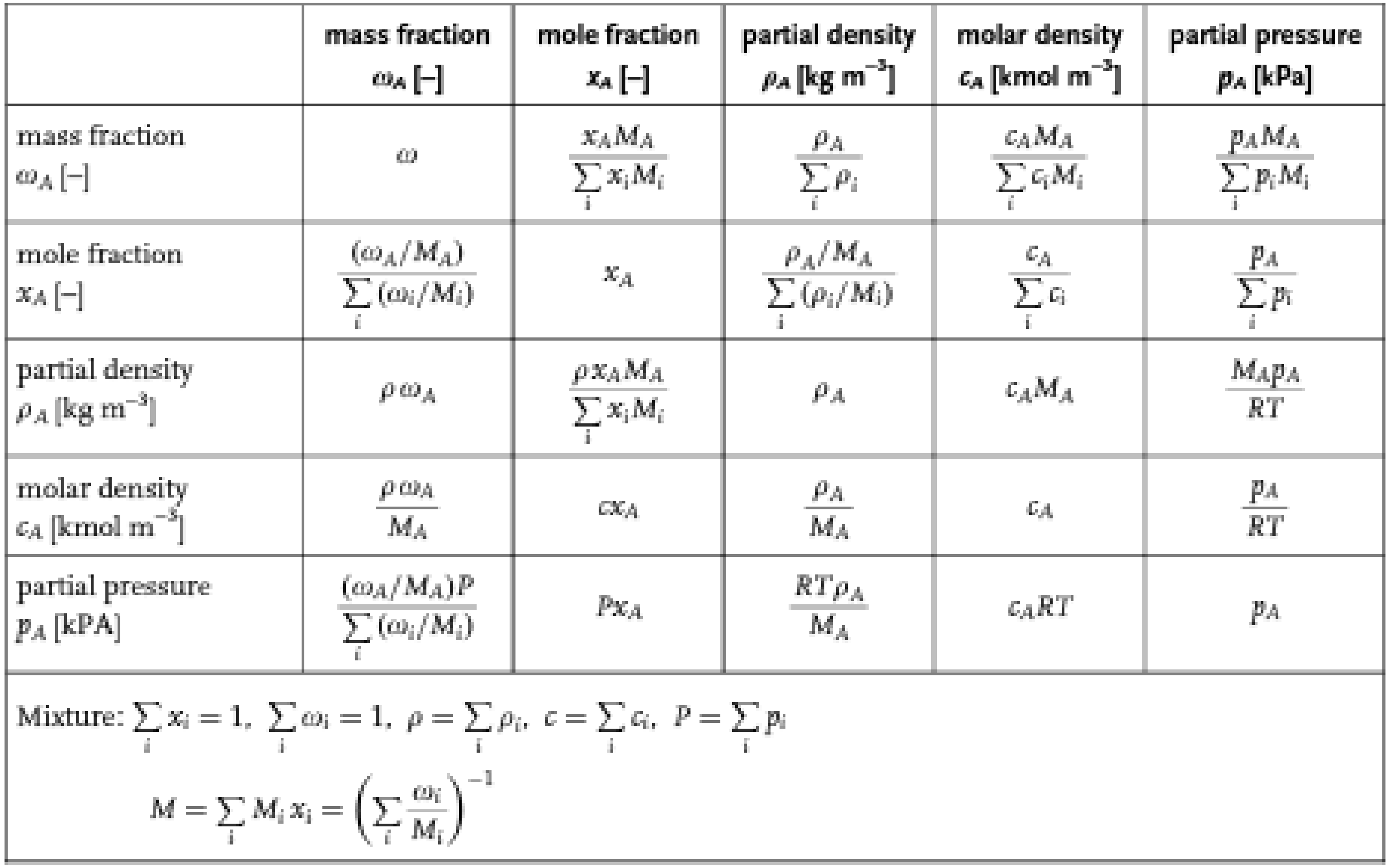
- Though the use of mass transfer coefficients allows us to estimate rates of mass transfer in real-life problems, we are faced with another problem;
- In contrast to heat transfer, various definitions of concentrations are being used, in a case-by-case way, which leads to various definitions of mass transfer coefficients

Relationships between concentrations in binary system



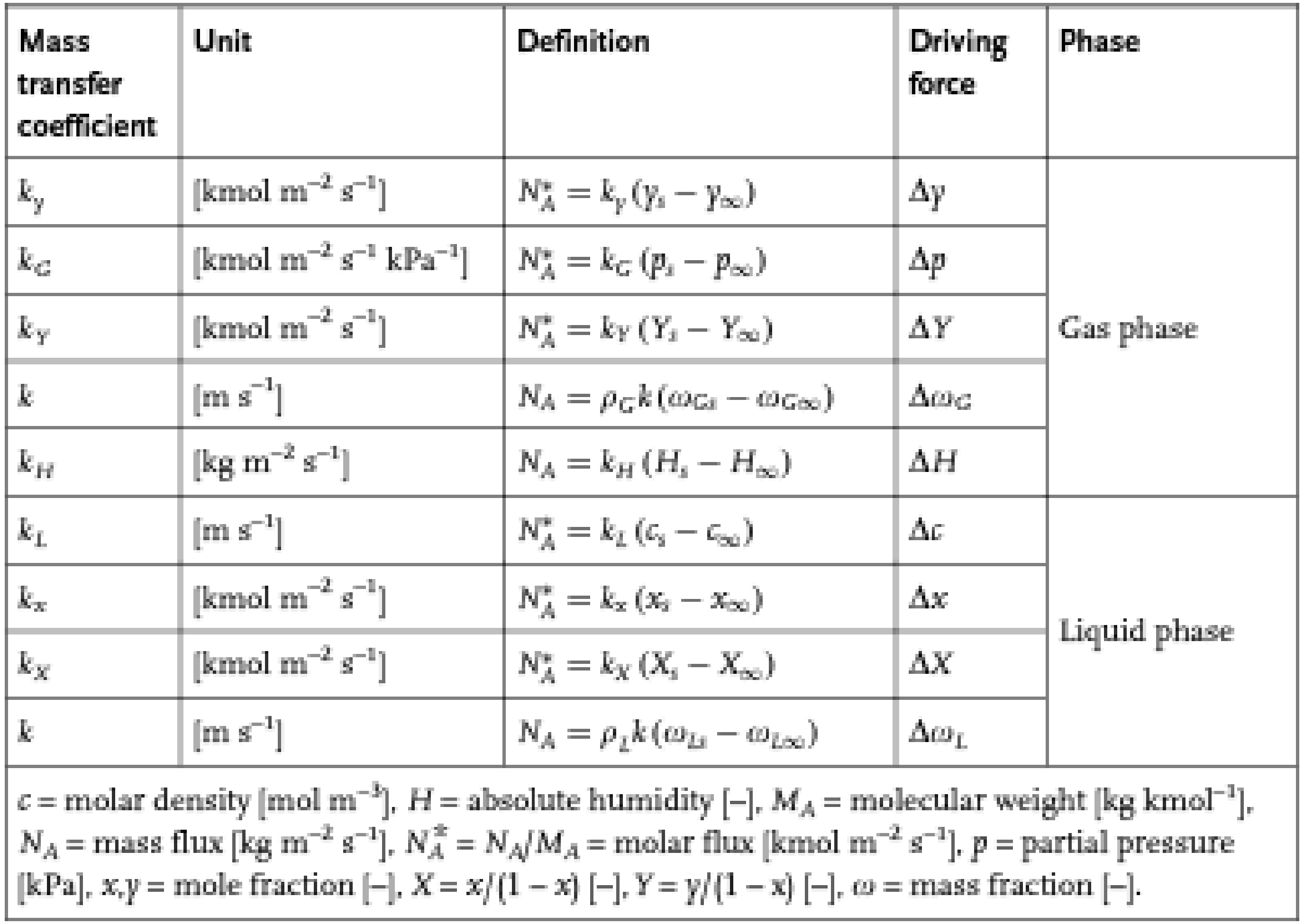
	mass fraction ω [–]	mole fraction x [–]	absolute humidity $H\left[\frac{\text{kg}-\text{A}}{\text{kg}-\text{B}}\right]$	mole ratio $X\left[\frac{\text{mol}-\text{A}}{\text{mol}-\text{B}}\right]$
mass fraction ω [–]	ω	$\frac{x}{\frac{M_B}{M_A}+\left\{1-\frac{M_B}{M_A}\right\}x}$	$\frac{H}{1+H}$	$\frac{X}{\frac{M_B}{M_A}+X}$
mole fraction x [–]	$\frac{\omega}{\frac{M_A}{M_B}+\left\{1-\frac{M_A}{M_B}\right\}\omega}$	x	$\frac{H}{\frac{M_A}{M_B}+H}$	$\frac{X}{1+X}$
absolute humidity $H\left[\frac{\text{kg}-\text{A}}{\text{kg}-\text{B}}\right]$	$\frac{\omega}{1-\omega}$	$\left(\frac{x}{1-x}\right)\left(\frac{M_A}{M_B}\right)$	H	$\left(\frac{M_A}{M_B}\right)X$
mole ratio $X\left[\frac{\text{mol}-\text{A}}{\text{mol}-\text{B}}\right]$	$\left(\frac{M_B}{M_A}\right)\left(\frac{\omega}{1-\omega}\right)$	$\left(\frac{x}{1-x}\right)$	$\left(\frac{M_B}{M_A}\right)H$	X

Relationships between various definitions of concentration in a multicomponent system



	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: $\sum_i x_i = 1,\ \sum_i \omega_i = 1,\ \rho = \sum_i \rho_i,\ c = \sum_i c_i,\ P = \sum_i p_i$ $M = \sum_i M_i x_i = \left(\sum_i \frac{\omega_i}{M_i}\right)^{-1}$					

Various definitions of mass transfer coefficients



Mass transfer coefficient	**Unit**	**Definition**	**Driving force**	**Phase**
k_y	[kmol m^{-2} s^{-1}]	$N_A^* = k_y\,(y_s - y_\infty)$	Δy	Gas phase
k_G	[kmol m^{-2} s^{-1} kPa^{-1}]	$N_A^* = k_G\,(p_s - p_\infty)$	Δp	
k_Y	[kmol m^{-2} s^{-1}]	$N_A^* = k_Y\,(Y_s - Y_\infty)$	ΔY	
k	[m s^{-1}]	$N_A = \rho_G k\,(\omega_{Gs} - \omega_{G\infty})$	$\Delta\omega_G$	
k_H	[kg m^{-2} s^{-1}]	$N_A = k_H\,(H_s - H_\infty)$	ΔH	
k_L	[m s^{-1}]	$N_A^* = k_L\,(c_s - c_\infty)$	Δc	Liquid phase
k_x	[kmol m^{-2} s^{-1}]	$N_A^* = k_x\,(x_s - x_\infty)$	Δx	
k_X	[kmol m^{-2} s^{-1}]	$N_A^* = k_X\,(X_s - X_\infty)$	ΔX	
k	[m s^{-1}]	$N_A = \rho_L k\,(\omega_{Ls} - \omega_{L\infty})$	$\Delta\omega_L$	

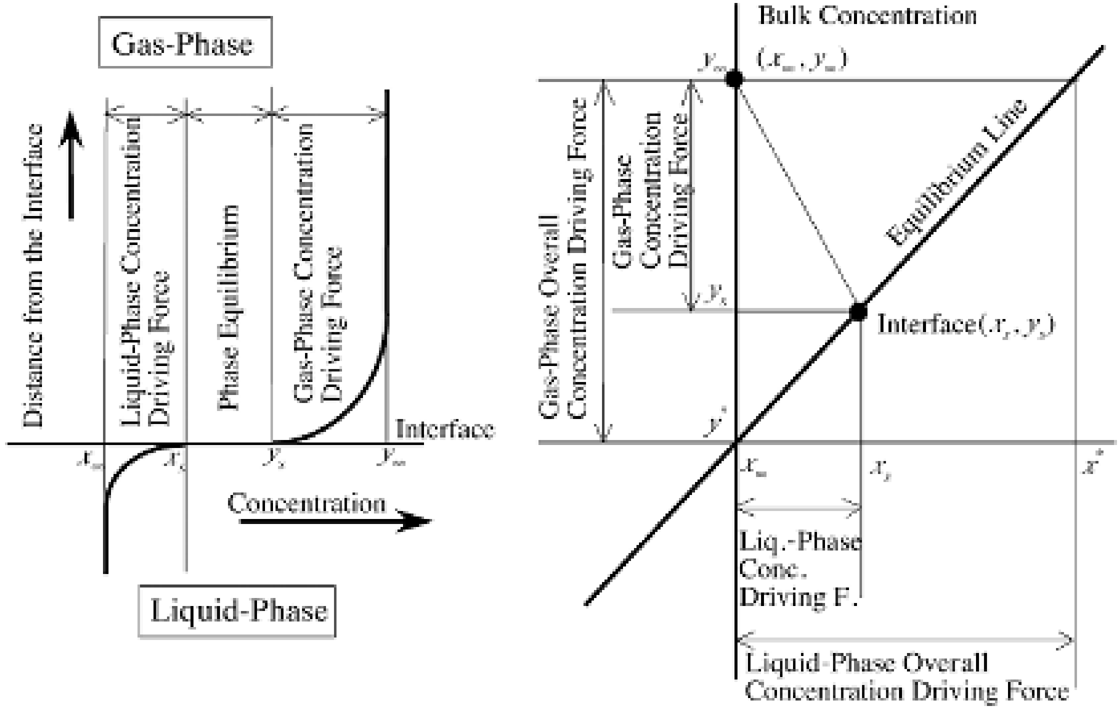
c = molar density [mol m^{-3}], H = absolute humidity [–], M_A = molecular weight [kg $kmol^{-1}$], N_A = mass flux [kg m^{-2} s^{-1}], $N_A^* = N_A/M_A$ = molar flux [kmol m^{-2} s^{-1}], p = partial pressure [kPa], x, y = mole fraction [–], $X = x/(1 - x)$ [–], $Y = y/(1 - x)$ [–], ω = mass fraction [–].

Relationship between mass transfer coefficients

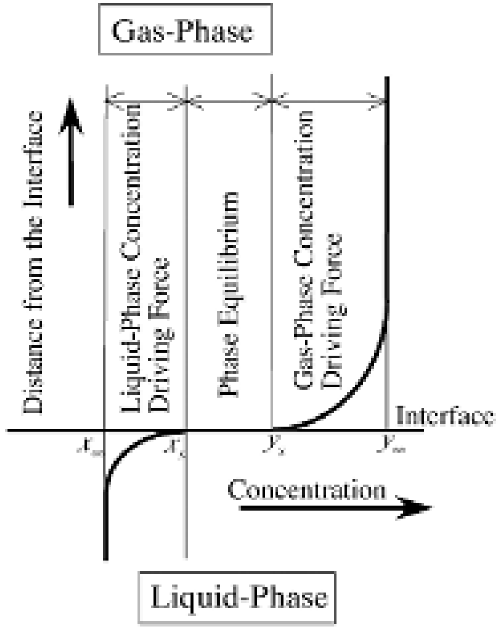
- Show the mutual relationship between mass transfer coefficients k, k_H, k_c, k_y, and k_G.

Overall mass transfer coefficients

- In industrial separation processes, there are usually concentration distributions on both sides of the interface, except in very rare case, *cf.* absorption of pure gases or the evaporation of pure liquids.
- As we cannot directly evaluate the concentration at the interface cannot calculate the rate of mass transfer by direct use of individual mass transfer coefficient.
- However, by defining the overall mass transfer coefficients, in analogy to the overall heat transfer coefficients, can calculate the rates of mass transfer as if the mass transfer resistance was inly one side of the interface.



Overall mass transfer coefficients



- Taking into account the concentration distribution, we get:
- $N_A{}^* = k_y(y_\infty - y_s) = k_x(x_s - x_\infty) = K_y(y_\infty - y^*) = K_x(x^* - x_\infty)$, where:
- k_y & k_x – liquid & gas-phase mass transfer coefficients
- K_y & K_x – liquid & gas-phase overall mass transfer coefficient
- $N_A{}^*$ - molar flux
- x_∞ - equilibrium mole fraction of bulk liquid
- x^* - mole fraction of the liquid in equilibrium with the bulk gas
- y_∞ - mole fraction of bulk gas
- y^* - mole fraction of the liquid in equilibrium with the bulk liquid

Overall mass transfer coefficients

- Assuming a linear equilibrium relationship between the gas and the liquid:
- Using $y^*=mx+b$ we obtain $(y_\infty-y^*)=(y_\infty-y_s)+m(x_s-x_\infty)$.
- Sub eq. into $N_A^*=k_y(y_\infty-y_s)=k_x(x_s-x_\infty)=K_y(y_\infty-y^*)=K_x(x^*-x_\infty)$ & rearrange to express the overall mass transfer coefficients: $\frac{1}{K_y}=\frac{m}{K_x}=\frac{1}{k_y}+\frac{m}{k_x}$.
- The significance of this is that we can estimate rates of mass transfer without evaluating the surface concentration if we have data of the individual mass transfer coefficients, k_x & k_y.
- We have seen mole fraction concentrations, similar results are obtained for mass fraction driving force or mole ratio driving force.

Questions?