Mass Transfer Summary

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- $1\ atm = 1.013 \cdot 10^5\ \text{Pa} = 760\ \text{mmHg}$
- $M_{air} = 28.97\ \frac{\text{g}}{\text{mol}}$
- $1\ ft = 30.48\ \text{cm} = 12\ \text{in}$
- $1\ gal = 3.7854\ \text{l}$
- $1\ lb = 453.59\ \text{g}$

- $c = \frac{\rho}{MM} = \frac{n}{V} = \frac{p}{RT}\left[\frac{mol}{cm^3}\right]$
- $\bar{MM} = \frac{\sum c_i MM_i}{c}$
- $j_{vol} = \frac{\dot{V}}{A} = j_1 \frac{MM}{\rho}\left[\frac{m}{s}\right]$
- $\nu = \frac{\mu}{\rho}\left[\frac{cm^2}{s}\right],\quad Sc = \frac{\nu}{D}$

Diffusion in dilute solutions

First and second Fick's law:

> **Theorem: Fick's laws**
>
> 1. In one dimension, the fist law can be written as: $\boxed{j = -D\frac{\partial c}{\partial k}}$
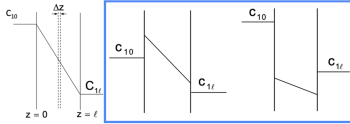>   where $k = z$ for Cartesian Coordinate and $k = r$ for both Spherical and Cylindric coordiante. $[D = m^2/s]$
> 2. The second law can be written as: $\boxed{\frac{\partial c}{\partial t} = D \cdot \nabla^2 c}$
>
>   - $\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}$
>   - $\frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial c}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2 c}{\partial \phi^2} + \frac{\partial^2 c}{\partial z^2}$
>   - $\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial c}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 c}{\partial \phi^2}$

> **Theorem: Henry's law**
>
> $H = \frac{p}{c} = \frac{\text{conc. in membrane}}{\text{conc. in solution}}$ (Ex: 25% Humidity: $p_{sat} \to 0.25 \cdot p_{sat}$)

$$Fo = \frac{Dt}{l^2} \Rightarrow \begin{cases} Fo \gg 1, & \text{for steady state} \\ Fo \ll 1, & \text{for semi infinite Stab.} \end{cases}$$

Diffusion across a thin film (s. 2.5):

Fick's 2nd law $\to 0 = \frac{\partial^2 c_1}{\partial z^2}$ with B.C.: $\begin{cases} z = 0, & c_1 = Hc_{10} \\ z = l, & c_1 = Hc_{1l} \end{cases}$

$$\boxed{c_1 = Hc_{10} + H\left(c_{1l} - c_{10}\frac{z}{l}\right)} \quad \text{and} \quad j_1 = \frac{HD}{l}(-\Delta c_1) = \frac{HD}{l}(c_{10} - c_{1l})$$

Note: In the (second/third) graph the solute is (more/less) soluble in the membrane than in the adjacent solution.
If c_{1l} not constant, from MB: $A_{membrane} \cdot j_1(c_{1l}(t)) = \frac{\partial c_{1l}}{\partial t} \cdot V_{chamber}$
Note: If not constant Area (sk. 16): $J_1 = A \cdot j_1 = -A \cdot D \cdot \frac{\partial c_1}{\partial z} \Rightarrow \frac{\partial c_1}{\partial t} = D \cdot \left(\frac{\partial^2 c_1}{\partial z^2} + \frac{1}{A}\frac{\partial A}{\partial z}\frac{\partial c_1}{\partial z}\right)$
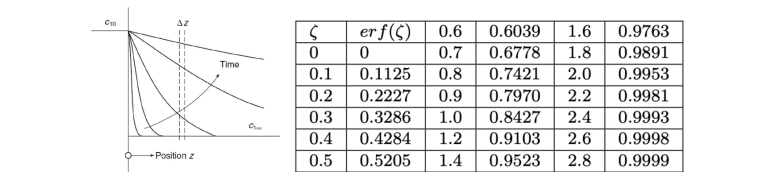
Concentration-dependent diffusion (s. 2.10-11):

Unsteady diffusion in a semi-infinite stab (s. 2.19):

Fick's 2nd law $\to \frac{\partial c_1}{\partial t} = \frac{\partial^2 c_1}{\partial z^2}$ with B.C.: $\begin{cases} t = 0, & \forall z, c_1 = c_{1\infty} \\ t > 0, & z = 0 : c_1 = c_{10} \\ & z = \infty : c_1 = c_{1\infty} \end{cases}$

$j_1 = \sqrt{\frac{D}{\pi t}}\exp\left(-\frac{z^2}{4Dt}\right)(c_{10} - c_{1\infty}) \Rightarrow \#$ **diffused moles:** $n_1 = \int_0^t j_1 \cdot A dt$

$\boxed{\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = erf\left(\frac{z}{\sqrt{4Dt}}\right)} \Rightarrow W_{eff} = W_1 + (W_2 - W_1)\cdot \frac{erf(W_{eff}) - erf(W_1)}{erf(W_2) - erf(W_1)}$

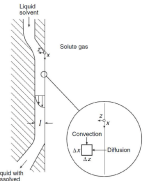| ζ	$erf(\zeta)$	0.6	0.6039	1.6	0.9763
0	0	0.7	0.6778	1.8	0.9891
0.1	0.1125	0.8	0.7421	2.0	0.9953
0.2	0.2227	0.9	0.7970	2.2	0.9981
0.3	0.3286	1.0	0.8427	2.4	0.9993
0.4	0.4284	1.2	0.9103	2.6	0.9998
0.5	0.5205	1.4	0.9523	2.8	0.9999

Steady dissolution of a sphere (s. 2.25):

Diffusion into a falling film (s. 2.33):

Note: If steady $\to$ flow has no effect if solution is dilute! (s. 2.31)

From Mass balance ($v = v_{max}$): $\frac{\partial c_1}{\partial x/v_{max}} = \frac{\partial^2 c_1}{\partial z^2}$ with $t = x/v_{max}$

B.C.: $\begin{cases} x = 0, & \forall z, c_1 = 0 \\ x > 0, & z = 0 : c_1 = c_{1,sat} \\ & z = l : c_1 = 0 \\ & z = \infty : c_1 = 0 \end{cases}$ $\quad \frac{c_1}{c_{1,sat}} = 1 - erf(\zeta),$

$\zeta = \frac{z}{\sqrt{4Dx/v_{max}}}$

$j_1|_{z=0} = \sqrt{\frac{Dv_{max}}{\pi x}}c_{1,sat}$

Diaphragm-cell diffusion (s. 3.3):

Combination of a steady-state (inside diaphragm) and a transient problem (in liquid reservoirs).

Upper compartment $\to$ almost pure solvent: $V_{upper} \cdot \frac{\partial c_{1,upper}}{\partial t} = +A \cdot j_1$
Lower compartment $\to$ solution: $V_{lower} \cdot \frac{\partial c_{1,lower}}{\partial t} = -A \cdot j_1$
With $j_1 = \frac{D \cdot H}{l}(c_{1,low} - c_{1,up})$ and B.C.: $t = 0 : c_{1,low} - c_{1,up} = c_{1,low}^0 - c_{1,up}^0$:

$$\boxed{D = \frac{1}{\beta t}\ln\left(\frac{c_{1,low}^0 - c_{1,up}^0}{c_{1,low} - c_{1,up}}\right)} \quad \text{and} \quad \beta = \frac{A \cdot H}{\lambda}\left(\frac{1}{V_{low}} + \frac{1}{V_{up}}\right)$$

Note: Pseudo steady state approximation holds iff $1 \gg \frac{t_D}{t_C}$, where $t_D = \frac{l^2}{D}$ and $t_C = \frac{1}{\beta D}$. (s. 3.9)

Diffusion in concentrated solutions

Different forms of diffusion equation (s. 3.12):

The total average solute velocity can be split into a part due to diffusion and a part due to convection through the so called reference velocity v^a:
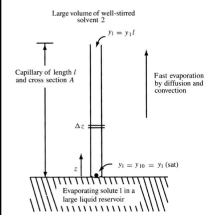
$$n_1 = c_1 v_1 = c_1(v_1 - v^a) + c_1 v^a = \underbrace{j_1^a}_{\text{diff. flux}} + \underbrace{c_1 v^a}_{\text{convection}}$$

Note: For gases use as reference velocity v^a the volume-average v^0 or molar-average v^*, while for liquids use the volume-average v^0 or the mass-average $\mathbf{v}$. We also denote:

- ω_i = mass fractions
- $y_i = \frac{c_i}{c} = \frac{n_i}{n} = \frac{p_i}{p} = \frac{c_i \bar{MM}}{\rho MM_i} = c_i \bar{V}_i$ = mole fractions (last Vol fraction)

Choice	Total flux (diffusion + convection)	Diffusion equation	Reference velocity	Where best used
Mass	$\boldsymbol{n}_1 = \boldsymbol{j}_1^m + \rho_1 \boldsymbol{v}$	$\boldsymbol{j}_1^m = \rho_1(\boldsymbol{v}_1 - \boldsymbol{v})$ $= -D\rho\nabla\omega_1$	$\boldsymbol{v} = \omega_1\boldsymbol{v}_1 + \omega_2\boldsymbol{v}_2$ $\rho\boldsymbol{v} = \boldsymbol{n}_1 + \boldsymbol{n}_2$	Constant-density liquids; coupled mass and momentum transport
Molar	$\boldsymbol{n}_1 = \boldsymbol{j}_1^* + c_1\boldsymbol{v}^*$	$\boldsymbol{j}_1^* = c_1(\boldsymbol{v}_1 - \boldsymbol{v}^*)$ $= -Dc\nabla y_1$	$\boldsymbol{v}^* = y_1\boldsymbol{v}_1 + y_2\boldsymbol{v}_2$ $c\boldsymbol{v}^* = \boldsymbol{n}_1 + \boldsymbol{n}_2$	Ideal gases where the total molar concentration c is constant
Volume	$\boldsymbol{n}_1 = \boldsymbol{j}_1 + c_1\boldsymbol{v}^0$	$\boldsymbol{j}_1 = c_1(\boldsymbol{v}_1 - \boldsymbol{v}^0)$ $= -D\nabla c_1$	$\boldsymbol{v}^0 = c_1\bar{V}_1\boldsymbol{v}_1 + c_2\bar{V}_2\boldsymbol{v}_2$ $= \bar{V}_1\boldsymbol{n}_1 + \bar{V}_2\boldsymbol{n}_2$	Best overall; good for constant-density liquids and for ideal gases; may use either mass or mole concentration
Solvent	$\boldsymbol{n}_1 = \boldsymbol{j}_1^{(2)} + c_1\boldsymbol{v}_2$	$\boldsymbol{j}_1^{(2)} = c_1(\boldsymbol{v}_1 - \boldsymbol{v}_2)$ $= -D_1\nabla c_1$	$\boldsymbol{v}_2$	Rare except for membranes; note that $D_1 \neq D_2 \neq D$
Maxwell–Stefan		$\nabla y_1 = \frac{y_1 y_2}{D'}(\boldsymbol{v}_2 - \boldsymbol{v}_1)$	None	Written for ideal gases; difficult to use in practice

Fast diffusion through a stagnant film (s. 3.19):

Mass balance (MB): $0 = \frac{\partial n_1}{\partial z} \to n_1 = \frac{N_1}{A(z)} = -Dc\frac{\partial y_1}{\partial z} + c_1\bar{V}_1 n_1$
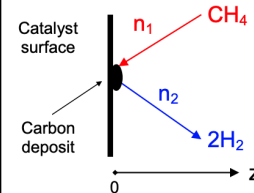
With B.C.: $\begin{cases} z = 0, & y_1 = y_{10} \\ z = l, & y_1 = y_{1l} \end{cases}$

Total flux: $\boxed{n_1 = \frac{Dc}{l}\ln\left(\frac{1-y_{1l}}{1-y_{10}}\right)}\left[\frac{mol}{sm^2}\right]$

Convective flux: $c_1 v^* = n_1 - j_1$
Diffusive flux: $j_1 = \frac{Dc}{l}\ln\left(\frac{1-y_{1l}}{1-y_{10}}\right)(1 - y_1)$ with $\frac{1-y_1}{1-y_{10}} = \left(\frac{1-y_{1l}}{1-y_{10}}\right)^{z/l}$

Catalytic cracking of molecules (s. 3.30):

Methane gas is cracked at the surface of a solid catalyst forming hydrogen and a solid carbon deposit (for example). The reaction is: $CH_{4(g)} \to C_{(s)} + 2H_{2(g)}$

From MB: $n_1 = -Dc\frac{\partial y_1}{\partial z} + c_1\left(-k\frac{n_1}{c}\right)$

With B.C.: $\begin{cases} z = 0, & y_1 = y_{10} \\ z = l, & y_1 = y_{1l} \end{cases}$

Total flux:

$$\boxed{n_1 = -\frac{Dc}{k \cdot l}\ln\left(\frac{1 + k \cdot y_{1l}}{1 + k \cdot y_{10}}\right)}$$

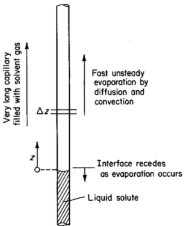Where k is the difference between the number of products formed and the reagents (for $CH_4 \to k = 2 - 1 = 1$).
Note: $n_1 \cdot \frac{MM_1}{\rho_1} \cdot$ time = thickness For a reaction:

- $A \to B + C: n_p = -2n_e \to k = 2 - 1 = 1$
- $AB_4 \to A + 4B: n_p = -4n_e \to k = 4 - 1 = 3$
- $A \to 2B: n_p = -2n_e \to k = 2 - 1 = 1$

Nickel film cracking (s. 3.42-46):

Fast Diffusion into Semi-Infinite Slab (s. 3.34):

A volatile liquid solute evaporates into a long capillary

From MB: $\frac{\partial c_1}{\partial t} = -\frac{\partial n_1}{\partial z}$ and $\frac{\partial c_2}{\partial t} = -\frac{\partial n_2}{\partial z}$

With B.C.: $\begin{cases} t = 0, & \forall z, c_1 = 0 \\ t > 0, & z = 0 : c_1 = c_{1,sat} \\ & z = \infty : c_1 = 0 \end{cases}$

We define so:

$$\Phi = -\frac{1}{2}\left(\frac{\bar{V}_1(\frac{\partial c_1}{\partial \zeta})}{1 - c_1 \bar{V}_1}\right)_{\zeta=0} \quad \text{and} \quad \zeta = \frac{z}{\sqrt{4Dt}}$$

Integrating we obtain: $\frac{c_1}{c_{1,sat}} = \frac{1 - erf(\zeta - \Phi)}{1 + erf(\Phi)}$

Equation for Φ: $\bar{V}_1 c_{1,sat} = \left(1 + \frac{1}{\sqrt{\pi}(1 + erf(\Phi))\Phi \exp(\Phi^2)}\right)^{-1}$

Interfacial flux:

$$N_1 = n_{1|z=0} = -D\left(\frac{\partial c_1}{\partial z}{1 - c_1 \bar{V}_1}\right) = \sqrt{\frac{D}{\pi t}} c_{1,sat} \frac{1}{1 - \bar{V}_1 c_{1,sat}} \frac{\exp(-\Phi^2)}{1 + erf(\Phi)}$$

Note: Φ is a dimensionless velocity characterizing the convection by diffusion and the movement of the interface. If $\Phi = 0$, the problem reduces to that of diffusion in dilute concentrations!

General Mass Balance

$$(\text{accumulation}) = (\text{flow in}) - (\text{flow out}) + (\text{mass produced})$$

$$\frac{\partial}{\partial t}(A\Delta z c_1) = (An_{1|z}) - (An_{1|z+\Delta z}) + r_1$$

Mass balance equation (for species 1)

Cartesian: $\frac{\partial c_1}{\partial t} = -\frac{\partial n_{1x}}{\partial x} - \frac{\partial n_{1y}}{\partial y} - \frac{\partial n_{1z}}{\partial z} + r_1$

Cylindrical: $\frac{\partial c_1}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(rn_{1r}) - \frac{1}{r}\frac{\partial n_{1\theta}}{\partial \theta} - \frac{\partial n_{1z}}{\partial z} + r_1$

Spherical: $\frac{\partial c_1}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 n_{1r}) - \frac{1}{r \sin(\theta)}\frac{\partial}{\partial \theta}(n_{1\theta}\sin(\theta)) - \frac{1}{r\sin(\theta)}\frac{\partial n_{1\phi}}{\partial \phi} + r_1$

Continuity equation (for all species)

Cartesian: $\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}(\rho v_x) - \frac{\partial}{\partial y}(\rho v_y) - \frac{\partial}{\partial z}(\rho v_z)$

Cylindrical: $\frac{\partial \rho}{\partial t} = -\frac{1}{r}\frac{\partial}{\partial r}(\rho r v_r) - \frac{1}{r}\frac{\partial}{\partial \theta}(\rho v_\theta) - \frac{\partial}{\partial z}(\rho v_z)$

Spherical: $\frac{\partial \rho}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}(\rho r^2 v_r) - \frac{1}{r\sin(\theta)}\frac{\partial}{\partial \theta}(\rho v_\theta \sin(\theta)) - \frac{1}{r\sin(\theta)}\frac{\partial}{\partial \phi}(\rho v_\phi)$

Mass balance equation for constant density systems (dilute $\to v_i^0 = 0$)

Cartesian: $\frac{\partial c_1}{\partial t} + v_x^0\frac{\partial c_1}{\partial x} + v_y^0\frac{\partial c_1}{\partial y} + v_z^0\frac{\partial c_1}{\partial z} = D[\frac{\partial^2 c_1}{\partial x^2} + \frac{\partial^2 c_1}{\partial y^2} + \frac{\partial^2 c_1}{\partial z^2}] + r_1$

Cylindrical: $\frac{\partial c_1}{\partial t} + v_r^0\frac{\partial c_1}{\partial r} + \frac{v_\theta^0}{r}\frac{\partial c_1}{\partial \theta} + v_z^0\frac{\partial c_1}{\partial z} = D[\frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial c_1}{\partial r}) + \frac{1}{r^2}\frac{\partial^2 c_1}{\partial \theta^2} + \frac{\partial^2 c_1}{\partial z^2}] + r_1$

Spherical: $\frac{\partial c_1}{\partial t} + v_r^0\frac{\partial c_1}{\partial r} + \frac{v_\theta^0}{r}\frac{\partial c_1}{\partial \theta} + \frac{v_\phi^0}{r\sin(\theta)}\frac{\partial c_1}{\partial \phi} =$
$= D[\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial c_1}{\partial r}) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial \theta}(\sin(\theta)\frac{\partial c_1}{\partial \theta}) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2 c_1}{\partial \phi^2}] + r_1$

Flux near a spinning disk (s. 5.17-20):

Dissolving pill (s. 5.22-24):

Estimation of diffusitives

Diffusion coefficient of gases (s. 6.9-18 & TAB sk. 118/121/123):

Average molecular velocity: $\overline{v} = \sqrt{\frac{8k_B T}{\pi m}}$

Mean free path: $\lambda = \frac{\overline{v}}{z} = \frac{k_B T}{\sqrt{2}\pi\sigma^2 p} = \frac{1}{\sqrt{2}\pi\sigma^2 c}$, z: Collision freq. $z = c\pi\sigma^2 \underbrace{\sqrt{2}\overline{v}}_{\overline{v}_{rel}}$

σ = Collision diameter, c = conc. $[\frac{\#molec.}{V}]$, $k_B = 1.38 \cdot 10^{-16}[\frac{gcm^2}{s^2 K}]$

Self-diffusivity: $D_{AA} = \frac{2}{3}\sqrt{\frac{k_B^3 N_A}{\pi^3}} \cdot \frac{\sqrt{T^3/M_A}}{p\sigma_A^2}$

Chapman Enskog: $D_{AB} = 1.858 \cdot 10^{-3}\frac{\sqrt{T^3(\frac{1}{M_A} + \frac{1}{M_B})}}{p\sigma_{AB}^2\Omega_{AB}}$ (non-polar molec.)

with $D[\frac{cm^2}{s}]$, $T[K]$, $p[atm]$, $M[\frac{g}{mol}]$, $\sigma_{AB}[\text{Å}]$, $1\text{Å} = 2 \cdot 10^{-8}$ cm

Collision diameter: $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)$

Energy of interaction: $\frac{\epsilon_{AB}}{k_B} = \sqrt{\frac{\epsilon_A}{k_B}\frac{\epsilon_B}{k_B}}$

Fuller, Schettler & Giddings: $D_{AB} = 10^{-3}\frac{T^{1.75}(1/MM_1 + 1/MM_2)^{1/2}}{p[(\sum_i V_{i1})^{1/3} + (\sum_i V_{i2})^{1/3}]^2}$

Note: $D(T_1) = D(T_2) \cdot \left(\frac{T_1}{T_2}\right)^{\frac{3}{2}}\frac{p_2}{p_1}$

Diffusivity in liquids (s. 31-38 & TAB sk. 127):

Stokes-Einstein: $D = \frac{\overline{x^2}}{2t} = \frac{\overline{u^2}t}{\beta t} = \frac{\overline{u^2}m}{f} = \frac{k_B T}{f}$ with:

- $f = 6\pi\mu_{liquid}R_0$ in continuum regime $(d_p \gg \lambda), [\mu_l] = \frac{g}{cm \cdot s}$
- $f = \frac{8}{3}R_0^2\rho\sqrt{\frac{2\pi k_B T}{m}}[1 + \frac{\pi a}{8}]$ in free molec. regime with $a = 0.9$

Note: $R_0 = \frac{\sigma}{2}$ or $R_0 = \sqrt[3]{\frac{3\sum_i V_i}{4\pi}}$

MTC (sk. 250 for dimeslos numbers)

$N_1 = k_1(c_{1i} - c_1)$ Often used: $N_1 At = c_1 V$ or: $N_1 A = V\frac{\partial c_1}{\partial t}$ or $N = \frac{\rho L}{MM \cdot \Delta t}$

N_1 : flux at the interface (Diffusion + Convection)
c_{1i}: concentration at the interface c_1: concentration in the bulk. If stirred $k = 0$

Humidification (s. 7.6 & sk. 238):

Normal Tube:

Length L, inner diameter $d = 2R$, thick δ, fluid velocity v^0 along z, steady.
Note: $1[\frac{L}{min}] = \frac{50}{3}[\frac{cm^3}{s}]$
Using MB: $0 = \pi R^2 \cdot v^0 \cdot (c_{1|z} - c_{1|z+\Delta z}) + k \cdot 2\pi \cdot R \cdot \Delta z \cdot (c_{bath} - c_1)$

- k from MTC (TAB sk. 252/254). **Attention** when k also depend on z (s. 8.27 & sk. 253 wetted column)
- $c_1(z) = c_{bath} + (c_{10} - c_{bath}) \cdot e^{-\frac{4k}{v^0 d}z}$

Using Fick's Law and MB: $\Delta J_1 = -2\pi r \cdot \Delta z \cdot D\frac{dc_1}{dr} \to \frac{\Delta J_1}{\Delta z} = \frac{2\pi D}{\ln\frac{R+\delta}{R}} \cdot c_1$

Inserting in MB: $v^0 \cdot \pi \cdot R^2 \cdot (c_{1|z} - c_{1|z+\Delta z}) - \Delta J_1 = 0$, dividing for Δz:

- D from Table/Calculate as in chapter 5
- Assuming $c_{bath} = 0$, $c_1(z) = c_{10} \cdot \exp\{-\frac{2D}{v^0 R^2 \ln\frac{R+\delta}{R}}z\}$

Packet Bed (s. 7.12-18):

Length L, inner diameter $d = 2R$, thick δ, fluid velocity v^0 along z, steady,
ϵ = bed porosity, $\phi = 1 - \epsilon$ = deg. filling bed, $a = \frac{\text{surface area}}{\text{bed volume}}[\frac{cm^2}{cm^3}]$

Note: $1[\frac{L}{min}] = \frac{50}{3}[\frac{cm^3}{s}]$

Average MTC: using MB: $N_1 \cdot a \cdot (1 - \epsilon) \cdot L \cdot A \cdot t = A \cdot v^0 \cdot c_1 \cdot t$
At entrance of bed: $N_1 = k(c_{bath} - 0) \to k = \frac{v^0 c_1}{a(1-\epsilon)Lc_{bath}}$

Local MTC: using MB:
$0 = \pi R^2 \cdot v^0 \cdot (c_{1|z} - c_{1|z+\Delta z}) + k \cdot \pi \cdot R^2 \cdot \Delta z \cdot a \cdot \rho_{part} \cdot (1 - \epsilon) \cdot (c_{bath} - c_1)$:

- $k \propto (v^0)^{0.58} \propto (L)^{0.58}$ (using k from MTC TAB sk. 252/254)
- $c_1(z) = c_{bath} + (c_{10} - c_{bath}) \cdot e^{-\frac{k \cdot a \cdot (1-\epsilon)\rho_{particle}}{v^0}z}$
- Pressure Drop: $\Delta P = \alpha L$
- If particles have k_{part}, partition $H \to k_{tot} = \frac{1}{\frac{1}{k} + \frac{H}{k_{part}}}$

Bubbles in tank (s. 7.19 & sk. 246):

Oxigen bubble with diameter d arising from sparger with velocity v^0, tank with height H, using MB:

$$(\text{mass flux of } O_2 \text{ transferred from bb}) = k \cdot (c_{bath} - c_{bb}) \cdot A_{inter}$$

- Residence time: $\tau = \frac{H}{v^0}$
- $\dot{V}_{air} = \frac{N_{bb} \cdot V_{bb}}{\tau}$
- $N_1 \cdot A_{inter} = N_1 \cdot N_{bb} \cdot \pi d^2 = (\text{mass } O_2 \text{ consumed per time}) = \dot{m}_{O_2}$

For varing concentrations in the bubbles with partition H:

- First in bubbles and $c_{bath} = const \to$, MB: $V_{bb}\frac{dc_{bb}}{dt} = kA_{bb}(c_{bath} - \frac{c_{bb}}{H})$
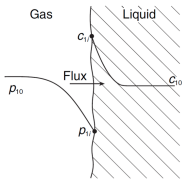- For the bath, MB: $V_{bath}\frac{dc_{bath}}{dt} = \dot{V}_{air} \cdot (c_{bath} - c_{bb}(t = \tau))$

Different units of MTC:

Liquids: $N_1 = \underbrace{k}_{[\frac{cm}{s}]}(c_{1i} - c_1) \overset{k_x = k \cdot c_{tot}}{\longrightarrow} N_1 = \underbrace{k_x}_{[\frac{mol}{cm^2 s}]}(x_{1i} - x_1)$

Gases: $N_1 = \underbrace{k_p}_{[\frac{mol}{cm^2 s Pa}]}(p_{1i} - p_1) \overset{k_y = k_p \cdot p_{tot}}{\longrightarrow} N_1 = \underbrace{k_y}_{[\frac{mol}{cm^2 s}]}(y_{1i} - y_1)$

Note: $k_p = \frac{k}{RT}$

The overall MTC (s. 8.8-10):

Flux in gas: $N_1 = k_p(p_{10} - p_{1i})$
Flux in liquid: $N_1 = k_L(c_{1i} - c_{10})$
Inserting $p_{1i} = Hc_{1i}$ yields: $c_{1i} = \frac{k_p p_{10} + k_L c_{10}}{k_p H + k_L}$
$\to N_1 = \frac{1}{\frac{1}{k_p} + \frac{H}{k_L}}(p_{10} - Hc_{10})$
$\to K_p = \frac{1}{\frac{1}{k_p} + \frac{H}{k_L}}$ = overall gas-side MTC

Two possibilities to write flux:
(1) $N_1 = K_p(p_{10} - p_1^*)$ $p_1^* = Hc_{10}$ $K_p = \frac{1}{\frac{1}{k_p} + \frac{H}{k_L}}$
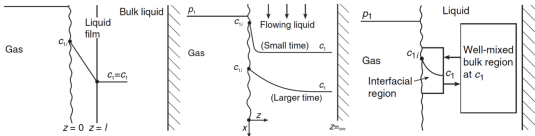
(2) $N_1 = K_L(c_1^* - c_{10})$ $c_1^* = \frac{p_{10}}{H}$ $K_L = \frac{1}{\frac{1}{k_L} + \frac{1}{k_p H}}$

Note:

- $V_m = \frac{\overline{R}T}{p}$ at standard cond.: $V_m = 22.4 \frac{L}{mol}$
- $p_1 = Hx_1$, $y_1 = mx_1$, $c_{1,gas} = H'c_{1,liquid}$ with H, m, H': partition coefficients, x_1: mole frac. in liquid, y_1: mole frac. in gas. Henry's law: $p_1 = Hc_1$

Boundary layers (sk. 299 for correlation of k)

The film theory (s. 9.8-10):

Steady state flux across film:

$N_1 = \frac{D}{l}(c_{1i} - c_1)$ with $k = \frac{D}{l}$, $Sh := \frac{kl}{D} = 1$

Resistances in series:
$R = \frac{1}{K} = \underbrace{\frac{1}{k_p}}_{R_G} + \underbrace{\frac{H}{k_L}}_{R_L}$, $k_p = \frac{D_p}{l_p \overline{R} T}$, $k_L = \frac{D_L}{l_L}$

Advantages: Simple, good base for extension
Disadvantages: Film thickness l is unknown

The penetration theory (s. 9.11-13):

Steady state flux at specific x: $N_1 = \sqrt{\frac{Dv_{max}}{\pi x}}(c_{1i} - c_1)$

Average flux: $N_1 = 2\sqrt{\frac{Dv_{max}}{\pi L}}(c_{1i} - c_1)$ $\rightarrow$ $k = 2\sqrt{\frac{Dv_{max}}{\pi L}}$

Contact time: $t_{contact} = \frac{L}{v_{max}} = \frac{4D}{\pi k^2}$

Advantages: Simplest including flow
Disadvantages: Contact time usually unknown

Surface renewal theory (s. 9.14-18):

Flux: $N_1 = \sqrt{\frac{D}{\pi t}}(c_{1i} - c_1)$ $\rightarrow$ $k = \sqrt{\frac{D}{\tau}} = \sqrt{\frac{D}{\pi t}}$

Advantages: Similar math to penetration theory, but better physical picture
Disadvantages: Surface-renewal rate (τ) unknown

Theories for concentraded solutions (s. 9.31-33):

MTC for concentraded sol.: $k = \frac{v^0}{\exp(v^0 \cdot \frac{L}{D}) - 1}$ vs dilute sol.: $k^0 = \frac{D}{L}$

Ratio: $\frac{k}{k^0} \approx \frac{1}{1 + \frac{1}{2}v^0/k/0}$
Note:

- If a large convective flux (blows/sucks) (from/into) the interface into the bulk liquid (positive/negative z), then v^0 is (positive/negative) and k is (less/greater) than k^0.
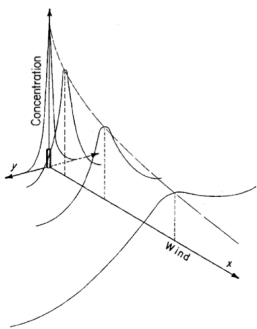- In general, k can be either increased or decreased in concentrated solution.

Mass transfer in Boundary Layers (s. 10. 20):

1. Calculate the velocity profile in the B.L.
2. Calculate the concentration profile in the B.L.
3. Calculate the flux at the interface $j = -D\frac{\partial c}{\partial y}|_{y=0}$ and set it equal to $k\Delta c$ to obtain k

Dispersion (TAB s. 13.16)

Dispersion in one or more dimensions (s. 11.15-17):

The source of the plume is at (0,0) and wind is blowing at speed v^0 in the x-direction. Average pollutant concentration at (x, y):

$$c_1 = \underbrace{\frac{M/A}{\sqrt{4\pi \cdot E_y \cdot t}}}_{=c_{max}} \cdot \exp\{-\frac{y^2}{4E_y t}\}$$

Note:

- $t = x/v^0$
- $\frac{c_{max}(y_2)}{c_{max}(y_1)} = \exp\{-\frac{(y_2 - y_1)^2}{4Et}\}$
- Since $c_{max} \sim \frac{1}{\sqrt{t}}$: $\frac{c_1(\max \text{ at } t_2)}{c_1(\max \text{ at } t_1)} = \sqrt{\frac{t_1}{t_2}} \rightarrow \frac{c_1(\max \text{ at } x_2)}{c_1(\max \text{ at } x_1)} = \sqrt{\frac{x_1}{x_2}}$

Chemical Reactions

Reactions and Mass transfer (s. 12.10-15):

Given a reaction: $\sum \nu_j' X_j \leftrightarrow \sum \nu_j'' X_j$ we have:

Reaction rate: $r = k_f \prod_i c_{X_i}^{\nu_i'} - k_r \prod_i c_{X_i}^{\nu_i''}$

If wer have equilibrium $r = 0$. solve for $K = \frac{k_f}{k_r}$

Concentration ODE: $\frac{dc_{X_i}}{dt} = (\nu_i'' - \nu_i') \cdot r$
Comparing the speed of mass transfer with that of reaction allows to determine the rate-limiting step and if rxn have to be accounted for:

1. if $r \gg$ mass transfer rate $\Rightarrow$ neglect reactions
2. if $r \ll$ mass transfer rate $\Rightarrow$ neglect mass transfer
3. if $r \approx$ mass transfer rate $\Rightarrow$ include both

Activation energy:

Activation energy is required for the reaction to start and to carry on (supplied by heat or sometimes UV light).
A catalyst lowers the activation energy and increases the speed of the reaction at a certain temperature. The catalyst (typically a solid, but could also be a liquid) is not consumed after the reaction.

Heterogeneous & homogeneous reactions (s.12.12-15):

Heterogeneous reactions take place at an interface (e.g. solid catalyst surface, coal combustion) and diffusion and reaction occur by steps **in series**:
$r = [\frac{mol}{m^2 s}]$. Heterogeneous rct. & transport: $\frac{\partial c_1}{\partial t} = D\nabla^2 c_1 - \nabla c_1 v^0$
The reaction is introduced at the boundary conditions, treated together with the MTCs!
For 1st order reaction: $\kappa = [m/s]$ (as MTC)
Homogeneous reactions take place throughout the volume in the same phase (fuel combustion in engine). Diffusion and reaction occur by steps partially in **parallel**: $r = [\frac{mol}{m^3 s}]$.

Homogeneous rct. & transport: $\frac{\partial c_1}{\partial t} = D\nabla^2 c_1 - \nabla c_1 v^0 + r_1$
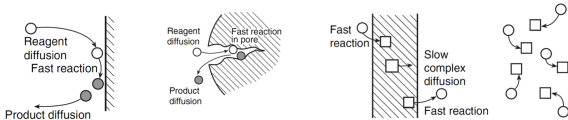For 1st order reaction: $\kappa = [1/s]$
Note: If reaction limited $\rightarrow \nabla^2 c_1 = 0$.

Diffusion-controlled reaction (s. 12.16-19):

Every diffusion-controlled process involves multiple steps. E.g. in dehydrogenation of C2H6 on Pt crystals:
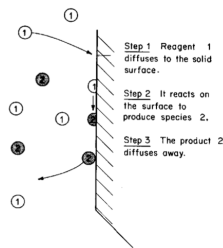
- C_2H_6 diffuses to Pt surface
- C_2H_6 reacts on the surface
- Product diffuses away from the surface

If $t_{step,1} \gg t_{step,2} \rightarrow$ diffusion-controlled reaction.

1. Diffused-controlled heterogeneous reaction where the reactant diffuses to a (e.g. hot or catalytic) surface, reacts and the product diffuses away.
2. Porous particle and the reactant diffuses to catalytically active sites where it reacts and the product diffuses away while reaction continues (important in catalysis scrubbing and extraction).
3. Low-moving molecules react with more mobile ones facilitating the transport of the former across a membrane (example: oxygen uptake by hemoglobin in the lungs).
4. Molecules are well mixed and react upon contact. The reaction rate depends on the Brownian motion of the molecules (acid/base reactions, CH_4 combustion etc.)

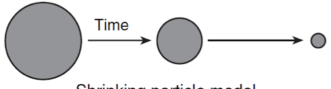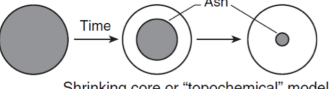### Diffusion and 1st order heterogeneous rcts. (dilute solutions, s. 12.20):

Surface reaction: Species $1 \leftrightarrow$ Species 2
Reaction constant κ_2 and κ_{-2}.
Reaction rate: $r_2 = \kappa_2 c_{1i} - \kappa_{-2} c_{2i}$ and from MTC
$r_2 = n_1 = K(c_1 - \frac{c_2}{K_2})$. Combining this two and using $K_2 = K_e q = \frac{k_f}{k_r} = \frac{\kappa_2}{\kappa_{-2}}$ we get:

$$K = \frac{1}{\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}} \quad \text{with } \kappa_2 [\frac{cm}{s}]$$

(1) Fast stirring (k_1, k_3 large, $K_2 \rightarrow \kappa_2$): $r_2 = \kappa_2(c_1 - \frac{c_2}{K_2})$

(2) High temperature ($1/\kappa_2 \rightarrow 0$): $r_2 = \frac{1}{\frac{1}{k_1} + \frac{1}{k_3 K_2}}(c_1 - \frac{c_2}{K_2})$

(3) Irreversible reactions ($\kappa_{-2} = 0, K_2 \rightarrow \infty$): $r_2 = \frac{1}{\frac{1}{k_1} + \frac{1}{\kappa_2}}c_1$

Rate of ferrocyanide oxidation (s. 12.26):

Cholesterol solubilization in bile (s. 12.28-32):

Mechanism of irreversible heterogeneous reactions (TAB sk. 466):

Physical situation	Rate-controlling step	Size $R = f$(time, reagent)	Size = f(temperature)	Size = f(flow)	Remarks
A Shrinking particle	Reaction	$R \propto c_1 t$	strong temperature variation	Independant of flow	Other reaction stoichiometries can be found easily
B Shrinking particle	External diffusion	$R^2 \propto (c_1 t)$ small particles $R^{3/2} \propto (c_1 t)$ larger particles	Weak temperature variation	Independent for small particles only	The exact variation with flow depends on the mass transfer coefficient
C Shrinking core[a]	Reaction	$R \propto c_1 t$	strong temperature	Independent of flow	This is the same as case A, except for ash formation
D Shrinking core[a]	External diffusion	$R \propto c_1 t$	Weak	Usually about square root of flow	This case is uncommon
E Shrinking core[a]	Ash diffusion	$R \propto (c_1 t)^{1/2}$	Weak	Independant of flow	This case is common, an interesting contrast with the previous one

Surface reaction controls (Cases A & C, s. 12.35):

$$(\text{gas species 1}) + (\text{solid species 2}) \rightarrow (\text{products})$$

As the solid concentration c_2 is constant, the reaction is 1st order w.r.t c_1.
MB: $\frac{d}{dt}\left(\frac{4}{3}\pi r^3 c_2\right) = r^* 4\pi \cdot r^2$ with $c_2 = \frac{\rho}{MM}$

- For a more general reaction attention when r^* depends on r!
- With $r^* = -\kappa_2 c_1 c_2 \Rightarrow$ $\boxed{r = R_0 - \kappa_2 c_1 t}$ $\Rightarrow \frac{d(r)}{dt} = const$
- We can use this reaction also with a slow reaction with ash.

Diffusion outside of a shrinking particle controls (Case B, s. 12.36):

Use MTC correlation for (i.e.) forced convection around solid sphere:

$$\frac{kd}{D} = 2 + 0.6\left(\frac{dv^0}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3} = 2 + 0.6(Re)^{1/2}(Sc)^{1/3}$$

- **Small particles:** $Re \rightarrow 0$, so: $\frac{kd}{D} = 2 \rightarrow k = \frac{D}{r}$
  MB: $\frac{d}{dt}\left(\frac{4}{3}\pi r^3 c_2\right) = -4\pi \cdot r^2(c_1 - \cancel{c_i}) \Rightarrow$ $\boxed{r^2 = R_0^2 - \left(\frac{2Dc_1}{c_2}\right)t}$ $\Rightarrow \frac{d(r^2)}{dt} = const$
- **Large particles:** $\frac{kd}{D} \approx 0.6\left(\frac{dv^0}{\nu}\right)^{1/2} \cdot \left(\frac{\nu}{D}\right)^{1/3}$ and so:
  $k \approx 0.42\left(\frac{(v^0)^{1/2}D^{2/3}}{\nu^{1/6}}\right) \cdot r^{-1/2} \Rightarrow$ $\boxed{r^{\frac{3}{2}} = R_0^{\frac{3}{2}} - \left(\frac{0.64 v^{\frac{1}{2}}D^{\frac{2}{3}}}{\nu^{\frac{1}{6}}}\right)\left(\frac{c_1}{c_2}\right)t}$ $\Rightarrow \frac{d(r^{3/2})}{dt} = const$

Note: We can always write $c_i = \rho_i/MM_i$

Diffusion in the surrounding bulk fluid controls (Case D, s. 12.39):

Use MTC correlation for (i.e.) forced convection around solid sphere:

$$\frac{kd}{D} = 2 + 0.6\left(\frac{dv^0}{\nu}\right)^{1/2}\left(\frac{\nu}{D}\right)^{1/3} = 2 + 0.6(Re)^{1/2}(Sc)^{1/3}$$

MB: $\frac{d}{dt}\left(\frac{4}{3}\pi r^3 c_2\right) = -4\pi r^2 k(c_1 - \cancel{c_i}) \Rightarrow$ $\boxed{r = R_0 - (k\frac{c_1}{c_2})t}$ $\Rightarrow \frac{d(r)}{dt} = const$

- Now, particle overall radius (core c_1 + shell c_2) relevant for mass transfer is constant, thus k constant.
- We can always write $c_i = \rho_i/MM_i$

Diffusion in the ash (or shell) controls (Case E, s. 12.40):

Use film model to describe MTC: $k = \frac{D}{R_0 - r}$, where D is the effective diffusivity through the shell.
MB: $\frac{d}{dt}\left(\frac{4}{3}\pi r^3 c_2\right) = -4\pi r^2 \frac{D}{R_0-r}(c_1 - \cancel{c_i}) \Rightarrow$ $\boxed{r = R_0 - \left(\frac{2Dc_1}{c_2}t\right)^{\frac{1}{2}}}$ $\Rightarrow \frac{d(r^2)}{dt} = const$
Note: c_1 core (bulk), c_2 shell, $c_i = \rho_i/MM_i$

Dissolution of particle for fast reactions (s. 4.8):

Since we have fast reaction $r = 0$:
Shrinking particle: Fick's 2nd law $\rightarrow 0 = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right)$ with

B.C.: $\begin{cases} r = R_0, & c_1 = c_{1,sat} \\ r = \infty, & c_1 = c_{bath} \end{cases}$

$$c_1(r) = (c_{1,sat} - c_{bath})\frac{R_0}{r} + c_{bath} \quad \text{and} \quad j_1(r) = \frac{D(c_{1,sat} - c_{bath})R_0}{r^2}$$

MB with Fick's Law: $\frac{1}{MM}\frac{\rho \cdot d(\frac{4\pi R_0^3}{3})}{dt} = -4\pi R_0^2 \cdot j_1|_{r=R_0}$

MB with MTC: $\frac{1}{MM}\frac{\rho \cdot d(\frac{4\pi R_0^3}{3})}{dt} = -4\pi R_0^2 k(c_i - c_{bath})$

- Using Fick's Law: $\frac{R_0^2}{2} - \frac{R_{0,0}^2}{2} = \frac{MM \cdot D(c_{bath} - c_{1,sat})}{\rho}t$
- Using MTC: $R_0 = R_{0,0} - \frac{k\Delta c \cdot MM}{\rho}t$

Shrinking core: Particle with total radius r_{out} and core radius $r_{out} - d_{shell} = r_{in}$, shell with permeability $H = \phi$. Fick's 2nd law as before but with:

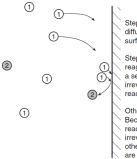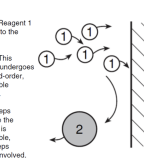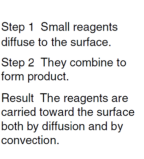B.C.: $\begin{cases} r = r_{in}, & c_1 = 0 \\ r = r_{out}, & c_1 = c_0 \end{cases}$

$$c_1(r) = \frac{c_0 r_{in} r_{out}}{r_{in} - r_{out}}\left(\frac{1}{r} - \frac{1}{r_{in}}\right) \text{ and } j_1(r) = -D\frac{c_0 r_{in} r_{out}}{r_{out} - r_{in}}\frac{1}{r^2}$$

MB with Fick's: $\frac{d}{dt}\left(\frac{\rho}{MM}\cdot\frac{4}{3}\pi r_{in}^3 \cdot \phi\right) = 4\pi r_{in}^2 \cdot j_1|_{r=r_{in}}$

We get so: $\left(\frac{r_{in}^3}{3} - \frac{r_{out}r_{in}^2}{2}\right) - \left(\frac{r_{in,0}^3}{3} - \frac{r_{out}r_{in,0}^2}{2}\right) = \frac{MM \cdot D \cdot r_{out} \cdot c_0 \cdot t}{\phi\rho}$

Barium Tank (s. 4.6):

Heterogeneous reactions of unusual stoichiometries

Irreversible second-order heterogeneous reaction (s. 12-42):

Overall reaction rate (no more resistance series adding):

$r_1 = k_1 c_1\left[\frac{k_1}{2c_1\kappa_2}\left(\sqrt{1 + \frac{4\kappa_2 c_1}{k_1}} - 1\right)\right]$ (First image)
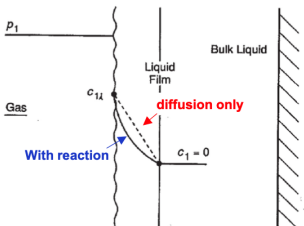
Heterogeneous Reactions in Concentrated Solutions (s. 12.44):

For concentrated solutions we cannot assume anymore that $k \neq f(r_2)$. In the figure are 2 examples of that: Cracking of hydrocarbons and Reforming.

- In cracking, convection is **away** from the surface: The reacting species must diffuse **against** the current of product species ($\nu > 1$).
- In reforming, convection is **towards** the surface as reaction "pulls" reactants. The product must diffuse away ($\nu < 1$).
- $\nu = 1$ treat as before

We get so: $r_1 = n_1 = -\frac{k_1 c}{\nu - 1}\ln\left(\frac{1 + \frac{(\nu-1)n_1}{\kappa_2 c}}{1 + \frac{(\nu-1)c_1}{c}}\right)$ with $k_1 = \frac{D}{l}$

Note: $1 mol\ e^- = 96500C = 96500As \rightarrow j_1\left[\frac{mol}{cm^2 s}\right] = \frac{i\left[\frac{A}{cm^2}\right]}{96500\left[\frac{As}{mol}\right]}$

Homogeneous Chemical Reactions

Mass Transfer with 1st order chemical reactions (s. 13.4):

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \rightarrow r = [k_1 c_{O_2}^2]c_{CH_4}$ where $[kc_{O_2}^2] = $ pseudo 1st order rate constant.

Irreversible reactions (s. 13.5 without rcts, s. 13.13.6 with rcts.):

With chemical reaction:
- $\frac{c_1}{c_{1i}} = \frac{\sinh[\sqrt{\frac{\kappa_1}{D}}\cdot(l-z)]}{\sinh[\sqrt{\frac{\kappa_1}{D}}\cdot l]}$
- $j_1 = -D\frac{\partial c_1}{\partial z} = \sqrt{Dk_1}\cdot c_{1i}\cdot\frac{\cosh[\sqrt{\frac{\kappa_1}{D}}\cdot(l-z)]}{\sinh[\sqrt{\frac{\kappa_1}{D}}\cdot l]}$
- $\frac{k}{k^0} = 1 + \frac{D_2 c_{2l}}{v D_1 c_{1i}}$

Without chemical reaction: $c_1 = c_{1i}(1 - \frac{z}{l}) \Rightarrow j_1 = \frac{D}{l}(c_{1i} - 0) \Rightarrow$ $\boxed{k^0 = \frac{D}{l}}$

For slow reactions: $\kappa_1 \rightarrow 0 \quad \Rightarrow \frac{k}{k^0} = 1 + \frac{D\kappa_1}{3(k^0)^2} + \cdots$
For fast reactions: $\kappa_1 \rightarrow \infty \quad \Rightarrow k = \sqrt{D\kappa_1}$

Note: $erf(\infty) = 1$, for $k \rightarrow 0 \Rightarrow erf(x) \approx \left(\frac{2x}{\sqrt{\pi}}\right)^{1/2}$

Coupling between mass transfer and reaction greatly affects the temperature-dependence of k: If κ_1 doubles every $10°$, then k doubles every $20°$. In the absence of reaction k doubles every $50°$! (see s.13.9)

Variation of mass transfer with fluid flow (s. 13.10-15):

Mass Transfer with $2nd$ order homogeneus reaction (s. 13.16-18):

Species 1 MB: $0 = D_1\frac{d^2 c_1}{d_z^2} - \kappa_1 c_1 c_2$

Species 2 MB: $0 = D_2\frac{d^2 c_2}{d_z^2} - \kappa_1 c_1 c_2$

with BC: $z = 0 : c_1 = c_{1i}, \frac{dc_2}{dz} = 0, z = l : c_1 = 0, c_2 = c_{2i}$
If fast and irreversible: $\nu n_1 + n_2 = 0 \Rightarrow n_1 = \frac{D_1}{l}(1 + \frac{D_2 c_{2l}}{\nu D_1 c_{1i}})c_{1i}$ with

$k^0 = \frac{D_1}{l}$ and $\boxed{\frac{k}{k^0} = 1 + \frac{D_2 c_{2l}}{\nu D_1 c_{1i}}}$

SO_2 absorption in a packed tower (s. 13-19-24):

Diffusion Controlled Reactions (s. 13.25-29):

Acid-Base reactions and combustion reactions are so fast that they are always diffusion controlled. Reaction rate: $r = -\kappa_1 c_1 c_2$ with:
$\boxed{\kappa_1 = 4\pi(D_1 + D_2)\sigma_{12}N_{AV}}$, $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$

Note: $pH = -\log_{10}(c_H \cdot \frac{l}{mol})$