# Lecture 9
# Mass transfer coupled with reaction

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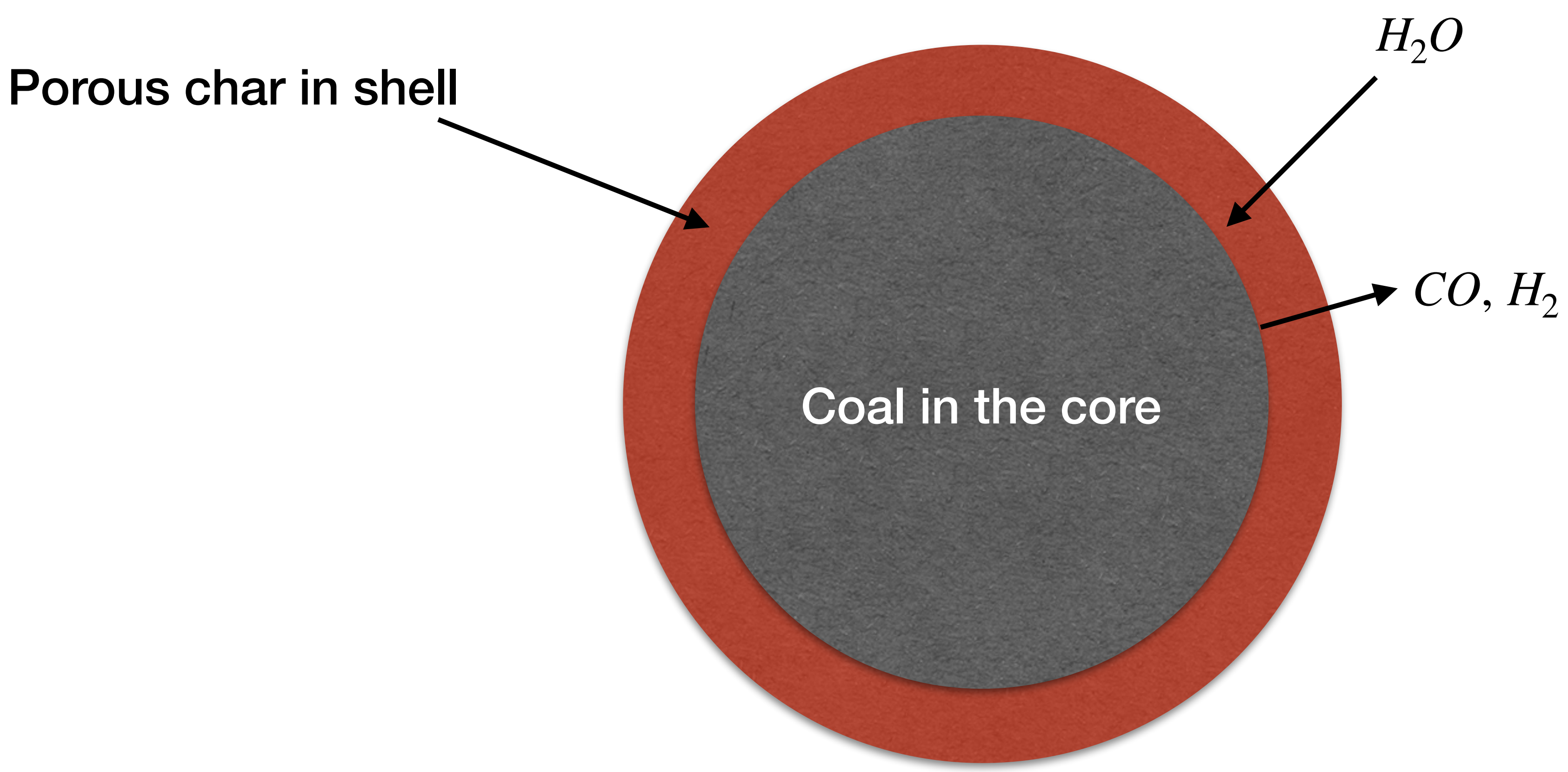
# Intended Learning Outcomes

- Analyze important difference between homogeneous and heterogeneous reaction.
- Derive expression for rate of heterogeneous reaction.
- Derive expression for overall mass transfer coefficient in the presence of heterogeneous reaction.
- Analyze facilitated transport in a membrane.

# Diffusion-controlled reaction

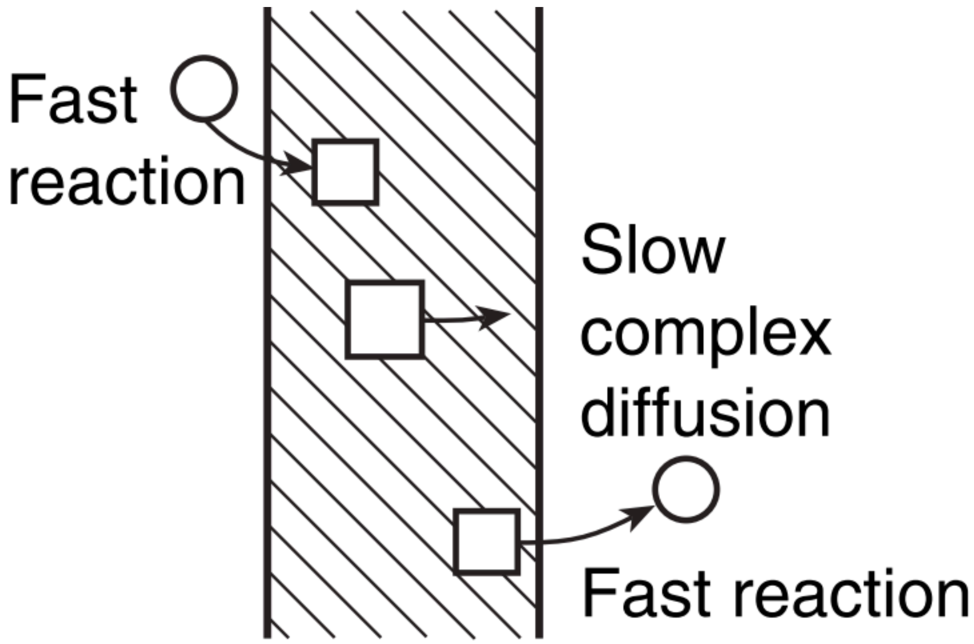
**Reaction are diffusion-controlled when the diffusion time-scale is larger than that of reaction.**

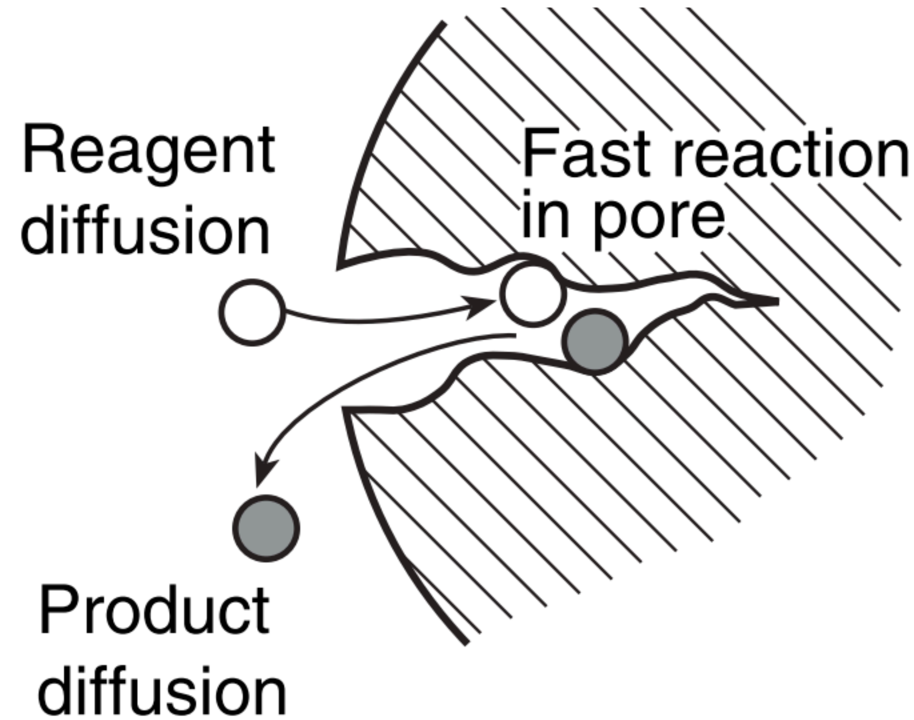
Gasification of coal to produce syngas




$$C + H_2O \rightarrow CO + H_2$$

# Diffusion-controlled reaction: other examples




**Facilitated transport**

$O_2$-hemoglobin complex

Facilitated transport membranes

**Reaction inside porous catalyst, materials**

zeolite for dehydrogenation of hydrocarbons

# Diffusion and reaction

While modeling reaction with diffusion, we need to understand a few things:

- Is the reaction heterogeneous or homogeneous?
- Is the reaction first-order, second-order, higher-order?

## Homogeneous vs. Heterogeneous reactions

**Heterogeneous reactions occur only on surface**

$$\text{rate per unit area} = \kappa_1(\text{concentration per unit area})$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

Reaction term appears in the boundary condition

**Homogeneous reactions occur throughout the volume**

$$\text{rate per unit volume} = \kappa_1(\text{concentration per unit volume})$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + r_1$$

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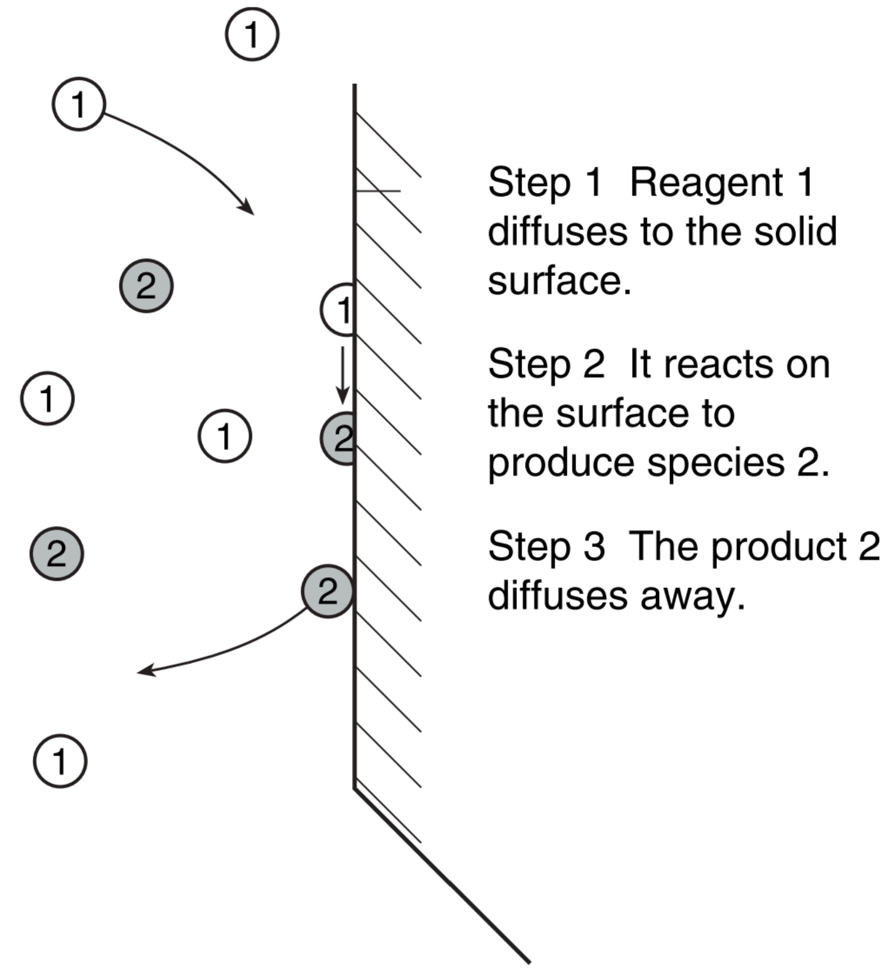
# Diffusion and first-order heterogeneous reaction

$$\text{species } 1 \underset{\kappa_{-2}}{\overset{\kappa_2}{\rightleftharpoons}} \text{species } 2 \qquad K_2 = \frac{\kappa_2}{\kappa_{-2}}$$




**At steady-state**

**Overall rate**

**= rate of diffusion to surface**

**= rate of reaction**

**= rate of diffusion away from surface**

$$r = k_1(c_1 - c_{1i}) = \kappa_2 c_{1i} - \kappa_{-2} c_{2i} = k_3(c_{2i} - c_2)$$

$c_{1i}$ and $c_{2i}$ are not known (easier to measure bulk concentrations)

**How will you calculate them?**

**3 equations, 3 unknowns** $r, c_{1i}, c_{2i}$

# Diffusion and first-order heterogeneous reaction

**3 equations, 3 unknowns** $\mathrm{r, c_{1i}, c_{2i}}$

$$\mathrm{r} = \mathrm{k_1(c_1 - c_{1i})} = \kappa_2 \mathrm{c_{1i}} - \kappa_{-2}\mathrm{c_{2i}} = \mathrm{k_3(c_{2i} - c_2)} \qquad K_2 = \frac{\kappa_2}{\kappa_{-2}}$$

**Go ahead and solve this to get rate in terms of known parameters** $(k_1, c_1, c_2, \kappa_2, \kappa_{-2})$

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# Diffusion and first-order heterogeneous reaction

**3 equations, 3 unknowns** $\mathrm{r, c_{1i}, c_{2i}}$

$$\mathrm{r} = \mathrm{k_1(c_1 - c_{1i})} = \kappa_2 \mathrm{c_{1i}} - \kappa_{-2}\mathrm{c_{2i}} = \mathrm{k_3(c_{2i} - c_2)}$$

$$K_2 = \frac{\kappa_2}{\kappa_{-2}}$$

$$-\mathrm{k_1} * \mathbf{c_{1i}} + 0 * \mathbf{c_{2i}} - \mathbf{r} = -\mathrm{k_1 c_1} \qquad \text{(Eq. 1)}$$

$$\mathrm{k_3} * \mathbf{c_{2i}} - \mathbf{r} = \mathrm{k_3 c_2} \qquad \text{(Eq. 2)}$$

$$\kappa_2 * \mathbf{c_{1i}} - \kappa_{-2} * \mathbf{c_{2i}} - \mathbf{r} = 0 \qquad \text{(Eq. 3)}$$

**Solving this, we get**

$$c_{1i} = \frac{k_1 k_3 c_1 + (k_1 c_1 + k_3 c_2)\kappa_{-2}}{(k_1 + \kappa_2)k_3 + k_1 \kappa_{-2}}$$

$$r = k_1(c_1 - c_{1i}) = \frac{\left(c_1 - \frac{c_2}{K_2}\right)}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}\right]}$$

# Diffusion and first-order heterogeneous reaction

$$r = k_1(c_1 - c_{1i}) = \frac{\left(c_1 - \frac{c_2}{K_2}\right)}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}\right]} = K\left(c_1 - \frac{c_2}{K_2}\right)$$

$$K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}\right]}$$

**Overall mass transfer coefficient**
**(with reaction)**

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}$$

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# Comparison (resistances in series)

**Overall mass transfer coefficient of a component in two phases (e.g. liquid/vapor)**
**(no reaction)**

$$\frac{1}{K_x} = \frac{1}{k_x} + \frac{1}{mk_y}$$

**Overall mass transfer coefficient for conversion of a component**
**(reaction)**

$$1 \rightarrow 2$$

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}$$

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# Diffusion and first-order heterogeneous reaction: 3 limits

$$r = K\left(c_1 - \frac{c_2}{K_2}\right)$$

$$K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}\right]}$$

Calculate the overall rate of reaction for

(a) fast stirring

(b) high temperature

(c) an irreversible reaction

(a) fast stirring $k_1, k_3 >> \kappa_2$ $K = \kappa_2$ $r = \kappa_2\left(c_1 - \frac{c_2}{K_2}\right) = \kappa_2 c_1 - \kappa_{-2} c_2$ $c_{1i} = c_1$, $c_{2i} = c_2$

(b) high temperature $\kappa_2 >> k_1, k_3$ $K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{k_3 K_2}\right]}$ $r = \frac{\left(c_1 - \frac{c_2}{K_2}\right)}{\left[\frac{1}{k_1} + \frac{1}{k_3 K_2}\right]}$

(c) an irreversible reaction $K_2 = \frac{\kappa_2}{\kappa_{-2}} >> k_1, \kappa_2$ $K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2}\right]}$ $r = \frac{c_1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2}\right]}$

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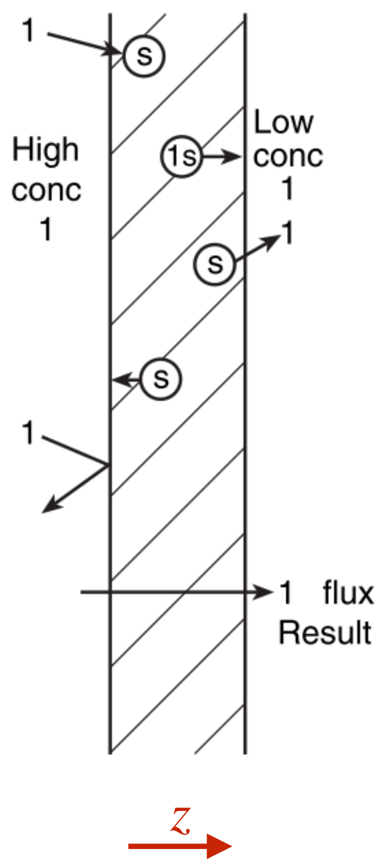
# Facilitated transport membranes

**Advantage: highly selective transport across membrane**




Step 1 Carrier s reacts with solute 1.

Step 2 The complexed carrier diffuses across the membrane.

Step 3 Because the adjacent solution is dilute, the solute–carrier reaction is reversed, releasing solute 1.

Step 4 The carrier returns across the membrane.

Step 5 Uncomplexed solute can not diffuse across the membrane because of low solubility.

The reaction with the mobile carrier enhances or "facilitates" the flux of solute.

$c_1, c_s$ **and** $c_{1s}$ **are function of z within the film**

**Steady-state mass balance for** $c_1, c_s, c_{1s}$

$$\text{Accumulation} = (\text{flux in} - \text{flux out}) \pm (\text{mass change by reaction})$$

**Mathematical simplification:** D is equal for all species

**Steady-state,** accumulation = 0

$$0 = D\frac{d^2c_1}{dz^2} - r_{1s}$$

$$0 = D\frac{d^2c_s}{dz^2} - r_{1s}$$

$$0 = D\frac{d^2c_{1s}}{dz^2} + r_{1s}$$

**Boundary conditions**

$$z = 0,\ c_1 = Hc_{10}$$

$$z = l,\ c_1 = 0$$

E. L. Cussler, Diffusion: Mass Transfer in Fluid Systems

# Facilitated transport membranes

Assuming the carrier neither leaves the membrane nor is poisoned

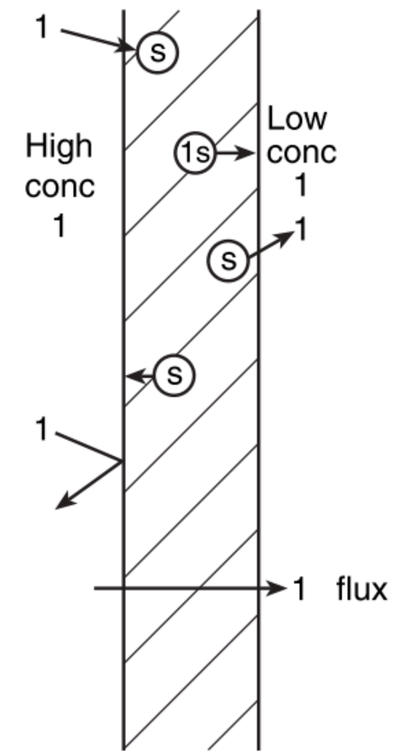
Overall carrier concentration is conserved

$$c_s + c_{1s} = \bar{c}$$

$\bar{c}$ is known; $c_s$ and $c_{1s}$ are not known

$$c_{1s} = K c_1 c_s$$

Equilibrium relationship




$$0 = D\frac{d^2 c_1}{dz^2} - r_{1s}$$

$$0 = D\frac{d^2 c_s}{dz^2} - r_{1s}$$

$$0 = D\frac{d^2 c_{1s}}{dz^2} + r_{1s}$$

Based on above 2 equation, we can estimate $c_{1s}$

$$\Rightarrow c_{1s} = Kc_1(\bar{c} - c_{1s}) \qquad \Rightarrow c_{1s} = \frac{Kc_1\bar{c}}{1 + Kc_1}$$

$$j_1 = -D\frac{dc_1}{dz} \qquad j_{1s} = -D\frac{dc_{1s}}{dz}$$

Overall flux of component 1

$$j_1 + j_{1s} = -D\left[\frac{dc_1}{dz} + \frac{dc_{1s}}{dz}\right] = \text{constant}$$

$$\Rightarrow j_1 + j_{1s} = -D\left[\frac{dc_1}{dz} + \frac{d}{dz}\left(\frac{Kc_1\bar{c}}{1 + Kc_1}\right)\right] = \text{constant}$$

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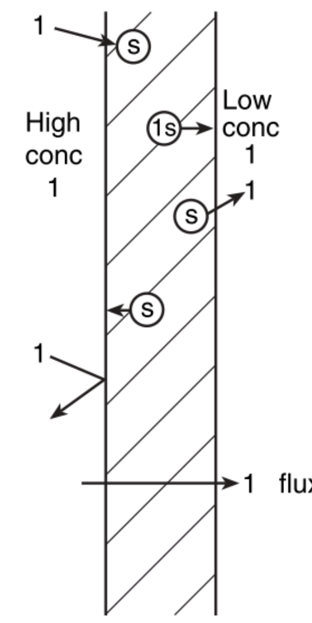
# Facilitated transport membranes

$$j_1 + j_{1s} = -D\left[\frac{dc_1}{dz} + \frac{d}{dz}\left(\frac{Kc_1\bar{c}}{1+Kc_1}\right)\right] = \text{constant} = \mathrm{A}_1$$




For integration, we can rearrange as follows

$$dc_1 + d\left(\frac{Kc_1\bar{c}}{1+Kc_1}\right) = -\frac{\mathrm{A}_1}{\mathrm{D}}\mathrm{dz}$$

Integration would give

$$c_1 + \left(\frac{Kc_1\bar{c}}{1+Kc_1}\right) = -\frac{\mathrm{A}_1}{\mathrm{D}}\mathrm{z} + \mathrm{A}_2$$

Boundary conditions

$$z = 0,\ c_1 = Hc_{10}$$

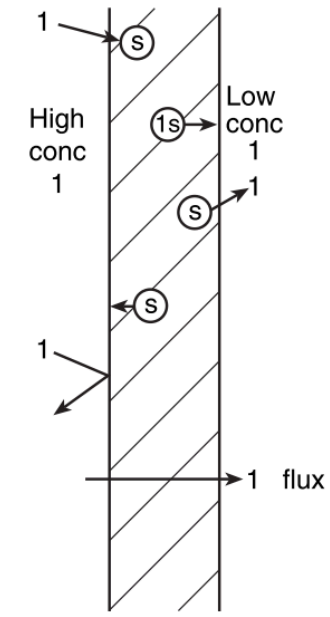
$$z = l,\ c_1 = 0$$

$$\Rightarrow A_2 = Hc_{10} + \frac{KHc_{10}\bar{c}}{1+KHc_{10}}$$

$$\Rightarrow A_1 = \frac{D}{l}A_2$$

$$\Rightarrow A_1 = j_1 + j_{1s} = \frac{DH}{l}c_{10} + \frac{DH}{l}\left[\frac{Kc_{10}\bar{c}}{(1+KHc_{10})}\right]$$

# Facilitated transport membranes




$$j_1 + j_{1s} = \frac{DH}{l}c_{10} + \frac{DH}{l}\left[\frac{Kc_{10}\,\bar{c}}{(1+KHc_{10})}\right]$$

**A few scenarios come out of this**

when $c_{10}$ is small

$$j_1 + j_{1s} = j_{1s} = \left(\frac{DHK\,\bar{c}}{l}\right)c_{10}$$

$j_1$ is neglected because $j_1 << j_{1s}$ especially for small $c_{10}$

when $c_{10}$ is large

$$j_1 + j_{1s} = \frac{DH}{l}c_{10} + \frac{D}{l}\bar{c}$$

Approaches constant value because $\bar{c} >> c_{10}$

when K is infinite

$$j_1 + j_{1s} = -D\left[\frac{dc_1}{dz} + \frac{d}{dz}\left(\frac{Kc_1\,\bar{c}}{1+Kc_1}\right)\right]$$

$$j_1 + j_{1s} = -D\left[\frac{dc_1}{dz} + 0\right]$$

$$j_1 + j_{1s} = \frac{DH}{l}c_{10}$$

No effect of facilitated transport
Poisoning of carrier

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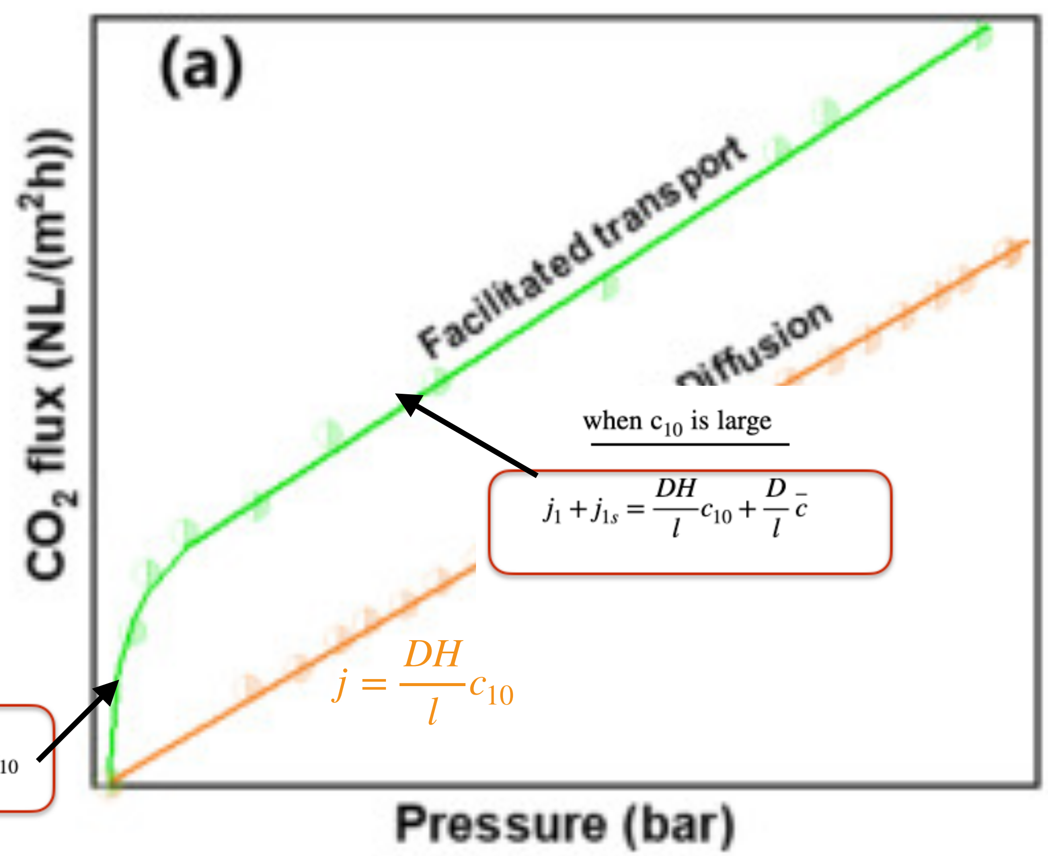
Can you explain the trend in $CO_2$ flux across a membrane as a function of its pressure. The orange line is thin film result without facilitation.

# Facilitated transport membranes for $CO_2/CH_4$ separation - State of the art

Hongfang Guo [a,b,c,d], Jing Wei [a,b,c,d], Yulei Ma [a,b,c,d], Jing Deng [e], Shouliang Yi [f,**], Bangda Wang [a,b,c,d], Liyuan Deng [g], Xia Jiang [a,b,c,d], Zhongde Dai [a,b,c,d,*]




when $c_{10}$ is large

$$j_1 + j_{1s} = \frac{DH}{l} c_{10} + \frac{D}{l} \bar{c}$$

$$j = \frac{DH}{l} c_{10}$$

when $c_{10}$ is small

$$j_1 + j_{1s} = j_{1s} = \left( \frac{DHK\bar{c}}{l} \right) c_{10}$$

$j_1$ is neglected because $j_1 << j_{1s}$ especially for small $c_{10}$

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# In-class exercise problem

You are trying to estimate the forward reaction rate constant $(\kappa_2)$ for the reduction of $CO_2$ at Pt surface at 500 ºC to form CO (total pressure = 1 bar). Pt is available as a spherical pellet.

The first experiment involved extremely rapid flow of $CO_2$ at 500 ºC where $c_1 = 0.9$ bar (tip: convert to mole/m$^3$ using ideal gas law) and rest being the product $c_2$. Let's say that the measured rate was $r$. The equilibrium constant, $K$, is 100.

The 2nd experiment involved exposing Pt to a steady flow of $CO_2$ but at 1000 ºC where the rate constant for the forward and backward reactions ($\kappa_2, \kappa_{-2}$) are both $10^5$ fold higher than those at 500 ºC. Here $c_1 = 0.6$ bar and rest was the product $c_2$. The mass transfer coefficients, $k_1, k_3$ were the same, estimated as 0.1 m/s. The measured overall rate was $10r$.

Based on the above information, calculate $\kappa_2$ at 500 ºC.

$$c = P/RT$$

At 500 ºC, fast mass transfer case

$$r = \kappa_2\left(c_1 - \frac{c_2}{K_2}\right) = \frac{\kappa_2(0.9 - 0.1/100) * 10^5}{8.31 * (273 + 500)}$$

At 1000 ºC (high reaction rate case)

$$10r = \frac{\left(c_1 - \frac{c_2}{K_2}\right)}{\left[\frac{1}{k_1} + \frac{1}{k_3 K_2}\right]} \Rightarrow 10r = \frac{\left(0.6 - \frac{0.4}{100}\right)}{\left[\frac{1}{0.1} + \frac{1}{0.1 * 100}\right]} \frac{10^5}{8.31 * (273 + 1000)}$$

$$\kappa_2 = 0.0045 \text{ m/s}$$

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# Exercise problem 1

## Estimate the reaction rate constant

You are studying a rapid electrochemical kinetics using a platinum electrode immersed in a flowing aqueous solution.

$$\mathrm{Fe(CN)_6^{4-}} \rightarrow \mathrm{Fe(CN)_6^{3-}} + \mathrm{e^-}$$

Estimate the rate constant of this reaction, when the overall rate constant was measured to be 0.009 cm/sec. The mass transfer coefficient for flow across electrode is calculated to be 0.01 cm/s.

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}$$

Rapid electrochemical reaction is irreversible

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{\kappa_2} \qquad \Rightarrow \frac{1}{0.009} = \frac{1}{0.01} + \frac{1}{\kappa_2} \qquad \Rightarrow \kappa_2 = 0.09 \text{ cm/s}$$

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# Exercise problem 2

## Explain the following:

Generally, increasing temperature increases the reaction rate for heterogeneous reaction in an exponential manner.

$$rate = \kappa c_1 \; = A \exp\left( -\frac{E}{RT} \right) c_1$$

However, in your reaction, increasing temperature leads to only a small increase in the reaction rate.

$$r = K\left( c_1 - \frac{c_2}{K_2} \right)$$

$$K = \frac{1}{\left[ \frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2} \right]}$$

(b) high temperature $\kappa_2 >> k_1, k_3$

$$K = \frac{1}{\left[ \frac{1}{k_1} + \frac{1}{k_3 K_2} \right]}$$

$$r = \frac{\left( c_1 - \frac{c_2}{K_2} \right)}{\left[ \frac{1}{k_1} + \frac{1}{k_3 K_2} \right]}$$

Answer: If you are already at high temperature, rate does not depend on $\kappa_2$

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# Exercise problem 3

The oxidation

$$Ce^{3+} \rightarrow Ce^{4+} + e^{-}$$

has a rate constant of 4*10^-4^ cm/s. You are carrying our this reaction by suddenly applying a potential across a stagnant volume of this solution. Estimate how long you can reliably measure the reaction kinetics before diffusion becomes important. Assume D as 4*10^-6^ cm²/s

Tip: Mass transfer coefficient decreases over time in transient case

$$r = K\left(c_1 - \frac{c_2}{K_2}\right)$$

$$K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}\right]}$$

For diffusion or mass transfer to be important:

$$k_1 \approx \kappa_2$$

$$k_1 = \kappa_2 = 4 * 10^{-4}\ \mathrm{cm/s}$$

Surface renewal theory:

$$k_1 = \sqrt{\frac{D_1}{\tau}}$$

$$\tau = \frac{D}{k_1^2} \approx 25\ \mathrm{s}$$