Lecture 10
Mass transfer coupled with reaction

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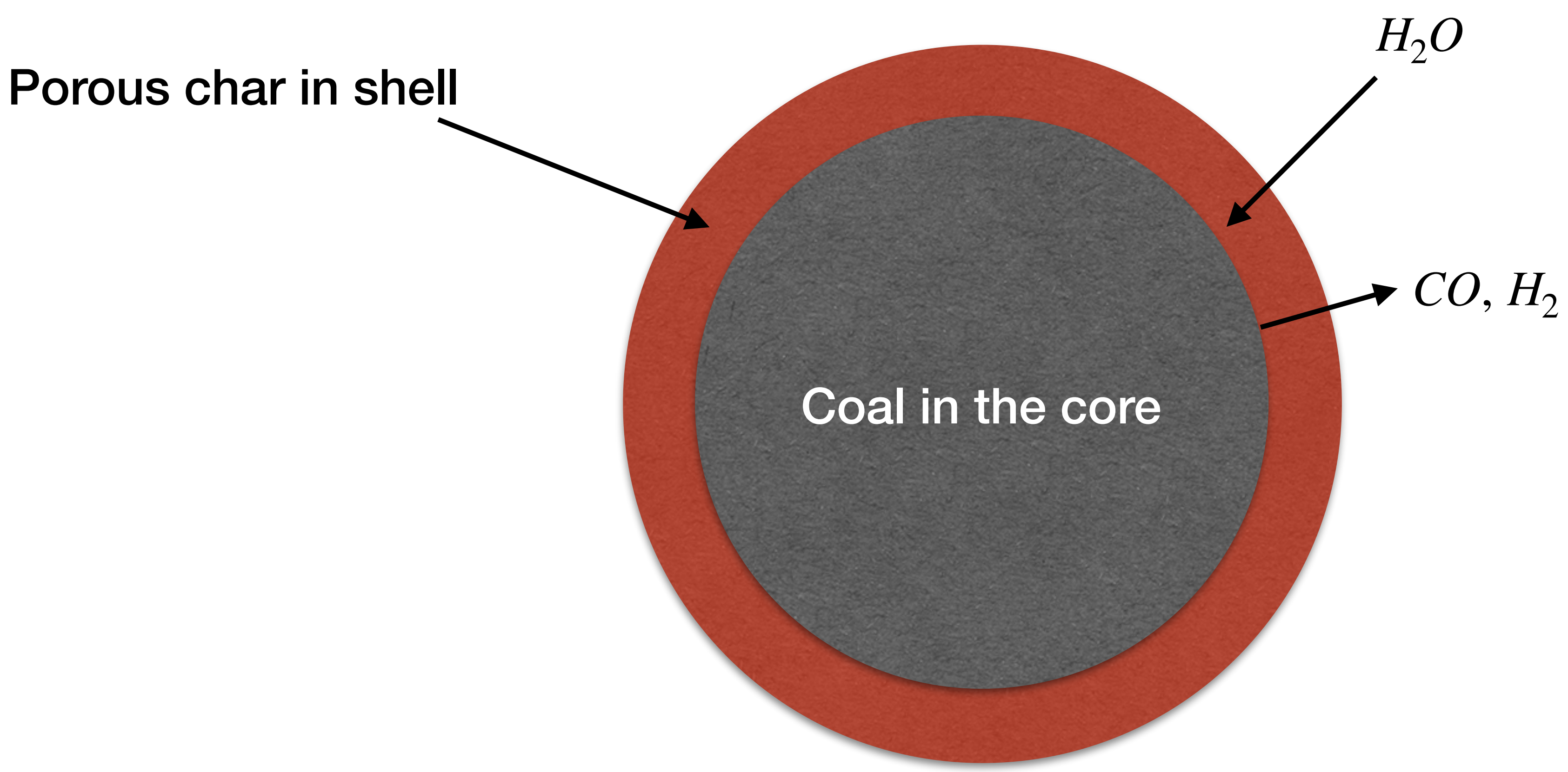
Intended Learning Outcomes

- 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

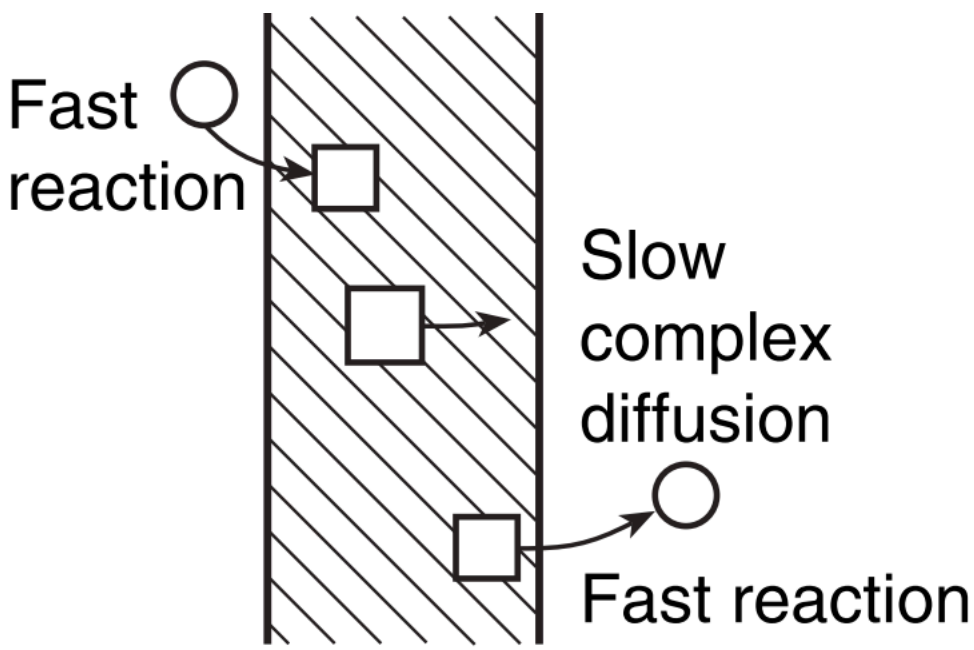
Reaction are diffusion-controlled when the diffusion time-scale is larger than that of reaction.

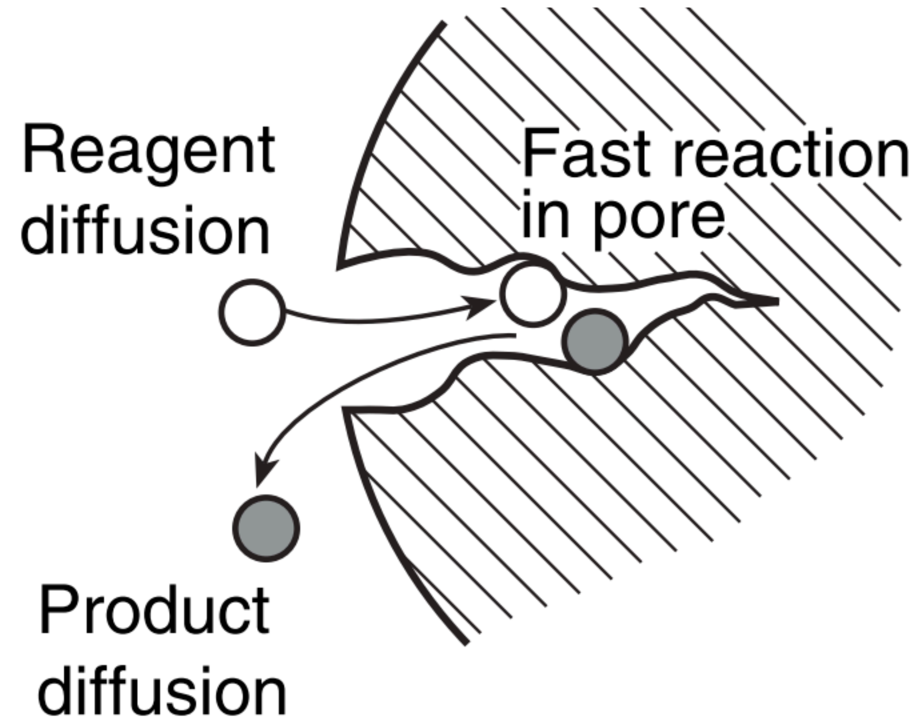
Gasification of coal to produce syngas



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

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

<u>While modeling reaction with diffusion, we need to understand a few things:</u>

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

<u>Homogeneous vs. Heterogeneous reactions</u>

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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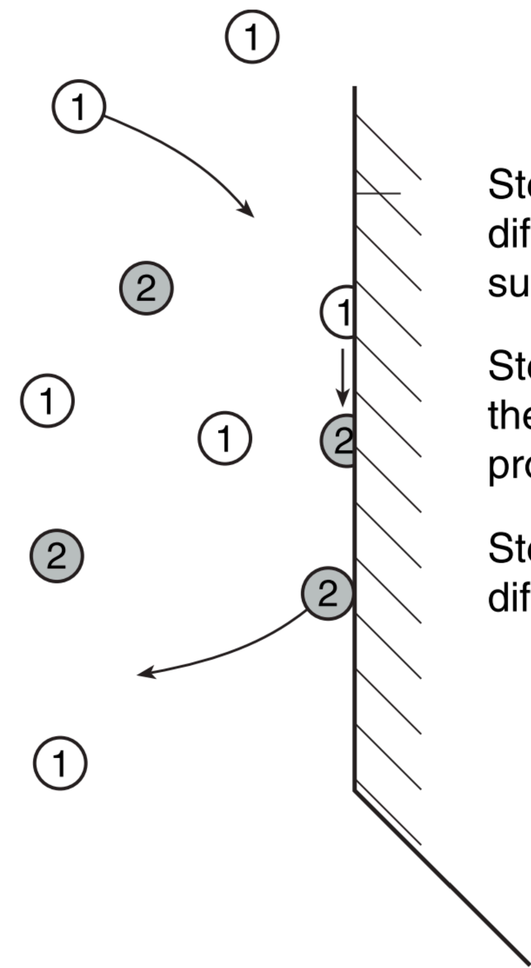
Diffusion and first-order heterogeneous reaction

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



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 $\mathrm{r}, \mathrm{c}_{1\mathrm{i}}, \mathrm{c}_{2\mathrm{i}}$

$$\mathrm{r} \ = \ \mathrm{k}_1(\mathrm{c}_1 - \mathrm{c}_{1\mathrm{i}}) \ = \ \kappa_2 \mathrm{c}_{1\mathrm{i}} - \kappa_{-2}\mathrm{c}_{2\mathrm{i}} \ = \mathrm{k}_3(\mathrm{c}_{2\mathrm{i}} - \mathrm{c}_2)$$

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

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

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

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

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

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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)

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

Comparison (resistances in series)

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

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

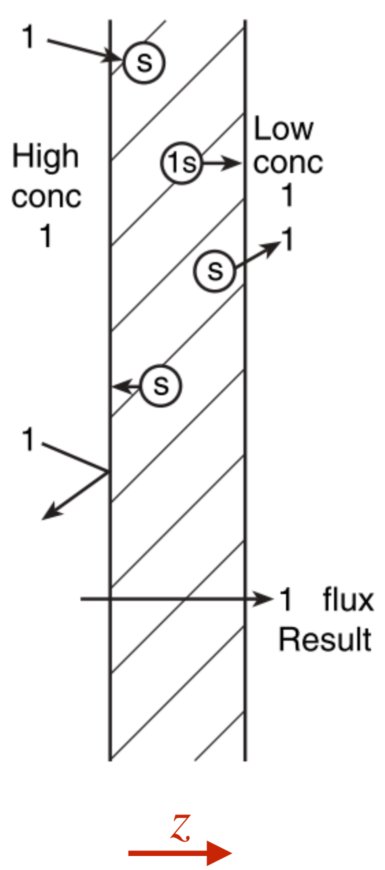
Overall mass transfer coefficient for conversion of a component
(reaction)

$$1 \rightarrow 2$$

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

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}

Accumulation = (flux in − flux out) + (mass gained by reaction)

Mathematical simplification : D is equal for all

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 does not leave membrane, or is not poisoned

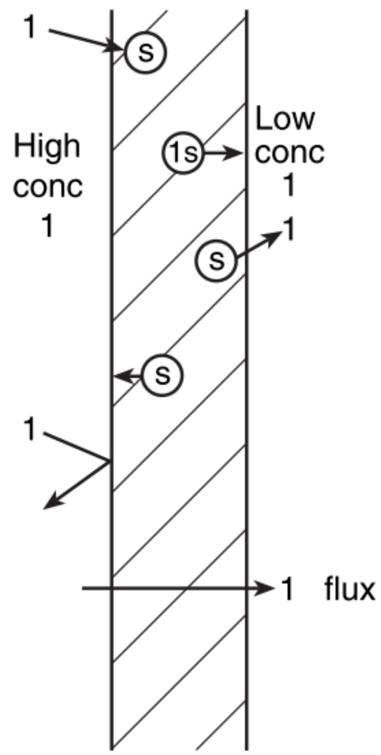
overall carrier concentration is conserved

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

$\bar{c}$ is known

c_s and c_{1s} are not known

$$c_{1s} = Kc_1 c_s$$



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

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

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

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

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

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

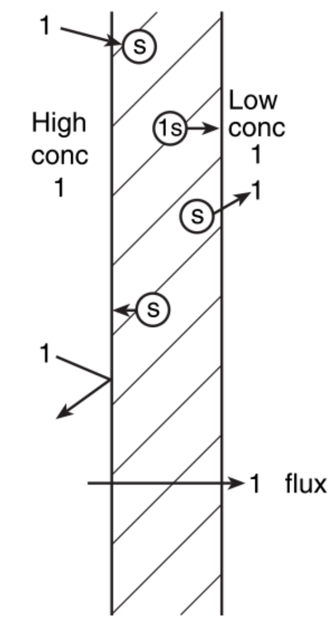
Overall flux of component 1

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

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

Facilitated transport membranes

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



More math with further simplifications

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

A few scenarios come out of this

when c_{10} is small

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

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

In-class exercise: 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 $\kappa_2 >> k_1, k_3$

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

(c) an irreversible reaction $K_2 = \frac{\kappa_2}{\kappa_{-2}} >> k_1, \kappa_2$

$$K = \frac{1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2}\right]} \qquad r = \frac{c_1}{\left[\frac{1}{k_1} + \frac{1}{\kappa_2}\right]}$$

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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.

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

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.

Solution to Exercise problem 1

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

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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

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

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.

Solution to exercise problem 2

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.

$$\boxed{\begin{aligned} \mathrm{r} &= \mathrm{K}\left(\mathrm{c}_1 - \frac{\mathrm{c}_2}{\mathrm{K}_2}\right) \\ \mathrm{K} &= \frac{1}{\left[\frac{1}{\mathrm{k}_1} + \frac{1}{\kappa_2} + \frac{1}{\mathrm{k}_3\mathrm{K}_2}\right]} \end{aligned}}$$

high temperature case: $\kappa_2 >> k_1, k_3$

$$\mathrm{K} = \frac{1}{\left[\frac{1}{\mathrm{k}_1} + \frac{1}{\mathrm{k}_3\mathrm{K}_2}\right]} \qquad \mathrm{r} = \frac{\left(\mathrm{c}_1 - \frac{\mathrm{c}_2}{\mathrm{K}_2}\right)}{\left[\frac{1}{\mathrm{k}_1} + \frac{1}{\mathrm{k}_3\mathrm{K}_2}\right]}$$

Answer: If you are already at high temperature, rate does not depend on κ_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 $4*10^{-6}$ cm^2/s

Mass transfer coefficient decreases over time in unsteady case

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

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

Solution to exercise problem 3

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$$\mathrm{K} = \frac{1}{\left[\frac{1}{\mathrm{k}_1} + \frac{1}{\kappa_2} + \frac{1}{\mathrm{k}_3\mathrm{K}_2}\right]}$$

For diffusion or mass transfer to be important:

$$k_1 \approx \kappa_2$$

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

Surface renewal theory:

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

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

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