Chemical Reactions & Mass Transfer

- Definitions: Reaction rate, order reaction & equilibrium constant
- Heterogeneous & Homogeneous reactions

- Diffusion-Controlled Reaction
- Diffusion and 1st Order Heterogeneous Reactions
- Mechanism of Irreversible Heterogeneous Reactions
- Heterogeneous Reactions of Unusual Stoichiometries

A chemical reaction is a conversion of one set of chemical substances into another: \[ AB + CD \rightarrow AD + BC \]
The reaction rate is the decrease in reactant concentration or the increase in product concentration with time:

$$ r_\rightarrow = - \frac{dc_{AB}}{dt} = - \frac{dc_{CD}}{dt} = \frac{dc_{AD}}{dt} = \frac{dc_{BC}}{dt} \quad (1) $$

The reaction rate is proportional to the concentration of reactants:

$$ r_\rightarrow \sim c_{AB} \cdot c_{CD} \quad \text{or} \quad r_\rightarrow = \kappa_\rightarrow \cdot c_{AB} \cdot c_{CD} \quad (2) $$

With $\kappa$ being the rate constant.

Many chemical reactions are reversible. Forward and reverse reactions finally lead to an equilibrium:

$$ AB + CD \rightleftharpoons AD + BC $$

We can define (1) and (2) also for the reverse reaction:
Now, the rate of the total reaction is the difference in the rates of the forward and reverse reactions:

\[ r = r_\rightarrow - r_\leftarrow \]

If \( r_\rightarrow = r_\leftarrow \) and \( r = 0 \)

the reaction has reached chemical equilibrium and the ratio of rate constants is the equilibrium constant of the chemical reaction:

\[ K_1 = \frac{K_\rightarrow}{K_\leftarrow} = \frac{c_{AD} \cdot c_{BC}}{c_{AB} \cdot c_{CD}} \]
Reaction order

Apart from temperature and pressure, the reaction rate can depend on the concentration of the reactants.

A reaction rate depending on the concentration of one reactant is a *first order reaction*, e.g.:

\[ r_\rightarrow = \kappa_\rightarrow \cdot c_{AB} \]

one depending on two concentrations is of second order:

\[ r_\rightarrow = \kappa_\rightarrow \cdot c_{AB} \cdot c_{CD} \]

For an irreversible second order reaction

\[ r_\leftarrow \to 0: r = r_\rightarrow, \quad \kappa_\leftarrow \to 0 \text{ and } \kappa = \kappa_\rightarrow: r = \kappa \cdot c_{AB} \cdot c_{CD} \]
The forward reaction

\[ \text{H}_2 + 2 \text{Cl} \rightarrow 2 \text{HCl} \]

is third order, since:

\[ \kappa \rightarrow \cdot c_{\text{H}_2} \cdot c_{\text{Cl}} \cdot c_{\text{Cl}} = \kappa \rightarrow \cdot c_{\text{H}_2} \cdot c_{\text{Cl}}^2 \]

*Note: Reactions typically occur in a series of multiple reactions. One step is the rate determining one. Therefore, the overall reaction would be of second or first order. (depending also on concentration)*

A reaction rate not depending on any concentration is called a zero order reaction.
Reactions and mass transfer

Chemical reactions are always coupled with mass transfer since the reactants have to travel to the location where the conversion takes place ("sink" for the reactants) while the products have to travel away ("source" for the products).

Comparing the speed of mass transfer with that of reaction allows to determine the rate-limiting step and if rxns have to be accounted for:

- reaction rate \( \gg \) mass transfer \( \rightarrow \) neglect reactions
- mass transfer \( \gg \) reaction rate \( \rightarrow \) include reactions

When reaction rate and mass transfer are comparable then we need to incorporate reaction into the models.

\[
\frac{\partial c_i}{\partial t} = D \nabla^2 c_i - \nabla \cdot c_i v^0 + r_i
\]  
(see: Generalized Mass Balances)
Activation energy

Activation energy is required for the reaction to start and to carry on. The activation energy is typically supplied as heat (higher temperature) but sometimes it can be other electromagnetic radiation, such as 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.

Examples of chemical reactions

• Combustion (gaseous, liquid or solid fuels)
• Production of chemicals (catalysts)
• Fuel cells, batteries (catalysts)
• Gas cleaning (e.g. removal of $SO_2$ by $CaO$)
• (Nano-) particle synthesis
• …
Heterogeneous & Homogeneous reactions

*Heterogeneous reactions* take place AT an interface (e.g. solid catalyst surface, coal combustion) and diffusion and reaction occur by steps IN SERIES.

*Homogeneous reactions* take place THROUGHOUT the volume in the same phase (fuel combustion in engine). Diffusion and reaction occur by steps partially in PARALLEL.

*For simplification* of mass transfer problems some heterogeneous reactions can be treated as homogeneous ones, depending on the definition of the observation space.
For example, in combustion of coal particles in fluidized beds initially reaction takes place AT the coal surface – so heterogeneous reaction.

Later on, however, a highly porous inorganic structure (e.g. fly ash) develops and combustion takes place THROUGHOUT the particle.
Even though microscopically the reaction still is a surface reaction, macroscopic observation of the entire particle gives the picture of reactions occurring homogeneously throughout the particle.

Thus, this case can be described as a homogeneous reaction and the “homogeneous reaction model” can be applied:

\[
\frac{\text{Combustion rate}}{\text{particle volume}} = \kappa \rightarrow \left( \frac{\text{Oxygen concentration per unit volume}}{\text{of pore or particle}} \right)
\]

So the assignment of the reaction type can be subjective!

Combustion is an irreversible reaction, so \( \kappa = K^- \).
In summary, coal particle combustion can be described as:

a) **Heterogeneous** reaction and transport:

\[
\frac{\partial c_1}{\partial t} = D \nabla^2 c_1 - \nabla \cdot c_1 \nu^0
\]

The reaction is introduced at the boundary conditions!

b) **Homogeneous** (homogeneous-like) reaction model and transport:

\[
\frac{\partial c_1}{\partial t} = D \nabla^2 c_1 - \nabla \cdot c_1 \nu^0 + r_1
\]
Examples of reaction assignment

Oxidation of lead sulfide (semiconductor) particles:  **Heterogeneous**

\[ \text{PbS particles} \xrightarrow{\text{heat}} \text{porous PbO} \]

Removal of ammonia from off-gas:  **Homogeneous**

\[ \text{NH}_3 / \text{air} + \text{H}_2\text{O} \xrightarrow{\text{scrubbing}} \text{NH}_4\text{OH} \]

Adsorption of sulfur dioxide (from combustion off-gas):  **Not sure**

\[ \text{SO}_2 + \text{Ca(OH)}_2/\text{H}_2\text{O} \xrightarrow{\text{scrubbing using Ca(OH)}_2\text{ slurry}} \text{CaSO}_4 \]
10.1 Diffusion-Controlled Reaction

Every diffusion-controlled process involves multiple steps. E.g. in dehydrogenation of C₂H₆ on Pt crystals

1. C₂H₆ diffuses to Pt surface
2. C₂H₆ reacts on the surface
3. Product diffuses away from the surface

When step 1 takes much longer than step 2 then we have a diffusion-controlled reaction.
In a) we have a diffusion-controlled heterogeneous reaction where the reactant diffuses to a (e.g. hot or catalytic) surface, reacts and the product diffuses away.

In b) we have a porous particle and the reactant diffuses to catalytically active sites where it reacts and the product diffuses away while reaction continues. Very important in catalysis, scrubbing and extraction (homogeneous reaction model).
In c) a slow-moving molecules react with more mobile ones facilitating the transport of the former across a membrane (example: oxygen uptake by hemoglobin in the lungs).

In case d), 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.)
Goal: To find the overall rate of the process
A first-order reaction with respect to a reactant is one where the reaction rate is proportional to the reactant concentration:

\[ r_i = \kappa \cdot c_i \]

At the steady state the overall reaction rate/area equals the diffusion fluxes

\[ n_1 = k_1(c_1 - c_{1i}) \]
\[ = -n_2 = k_3(c_{2i} - c_2) \]
\[ = r_2 \]
The surface reaction is

\[
\text{Species 1} \quad \overset{\kappa_2}{\leftrightarrow} \quad \text{Species 2} \quad \overset{\kappa_{-2}}{\leftrightarrow}
\]

And the reaction rate is given by

\[
r_2 = \kappa_2 c_{1i} - \kappa_{-2} c_{2i}
\]

Note that the equilibrium constant is

\[
K_2 = \frac{\kappa_2}{\kappa_{-2}}
\]

To find the overall reaction we must eliminate the surface (or interfacial) concentrations that are hard to measure.
Following the analysis of the mass transfer across interfaces ("overall MTC") we obtain:

\[ r_2 = n_1 = K\left( c_1 - \frac{c_2}{K_2} \right) \]

Where the overall MTC or "resistance" is:

\[ K = \frac{1}{\frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{(k_3K_2)}} \]
Similarities/differences with interfacial mass transfer:

1. The resistances $1 / k_1$, $1 / k_2$ and $1 / (k_3 K_2)$ add to the total resistance $1/K$

\[
c_2 / K_2 \Leftrightarrow \begin{cases} 
\text{concentration of species 1} \\
\text{in equilibrium with the existing} \\
\text{bulk concentration of species 2}
\end{cases}
\]

2. Henry’s law constant (partition coefficient) characterizes distribution between phases: $K_2 \leftrightarrow H$

$K_2$ and $H$ vary over a wide range. Here, similarly to $H$, the $K_2$ determines the relative impact of $k_1$ and $k_3$. 
Example 10.2.1: Limiting cases of 1st order reactions

Determine overall rate of the process when:

(a) Fast stirring

$k_1$ and $k_3$ are large, so $K \rightarrow \kappa_2$. Then,

$$r_2 = \kappa_2 \left( c_1 - \frac{c_2}{K_2} \right)$$

(b) High temperature

Usually at high $T$ the reactions are fast so $1/\kappa_2$ is very small and can be neglected

$$r_2 = \frac{1}{1/k_1 + 1/(k_3K_2)} \left( c_1 - \frac{c_2}{K_2} \right)$$

(c) Irreversible reaction $\kappa_2 = 0$ so $K_2 \rightarrow \infty$

$$r_2 = \frac{1}{1/k_1 + 1/\kappa_2} c_1$$

Note that ONLY in this case the resistances are simply additive.
Example 10.2.2: Cholesterol solubilization in bile

Bile* is the body’s "detergent" for fat digestion through cholesterol excretion. Failure of bile leads to cholesterol gallstones. Typically, gallstones are removed by surgery. However, lab data show that gallstones can be dissolved by administering certain components of the bile.

Goal: Find dissolution ("reaction") rate of gallstone
As a cholesterol gallstone is a solid, mass transfer/chemical reaction at a solid/fluid interface needs to be understood: rotating (spinning) disk apparatus for cholesterol dissolution rates.

*Bile = Galle (in German)
cholesterol dissolution rate = \(5.39 \times 10^{-9}\) g/(cm\(^2\) s) = \(r_2\)

solubility = \(1.48 \times 10^{-3}\) g/cm\(^3\) = \(c_1\)

\(D\) = \(2 \times 10^{-6}\) cm\(^2\)/s

disk diameter, \(d\) = 1.59 cm

\(Re\) = 11200

bile kinematic viscosity, \(\nu\) = 0.036 cm\(^2\)/s

cholesterol solution, \(\Delta\rho\) density over the bile = \(1 \times 10^{-5}\) g/cm\(^3\)

If the reaction is irreversible find:

a) surface reaction rate constant
b) dissolution rate of a 1 cm radius cholesterol gallstone
(a) For this case

\[ K = \frac{1}{1/k_1 + 1/\kappa_2} \]

\[ r_2 = K \cdot c_1 \rightarrow K = \frac{r_2}{c_1} = \frac{5.39 \times 10^{-9} \text{ g/(cm}^2\text{s})}{1.48 \times 10^{-3} \text{ g/cm}^3} \]

Find \( k_1 \) from the appropriate mass transfer coefficient using the correlation for the spinning disk:

\[ k_1 = 0.62 \frac{D}{d} \left( \frac{d^2 \omega}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3} = 2.16 \times 10^{-3} \text{ cm/s} \]

So \( \kappa_2 \) can be obtained from \( k_1 \) and \( K \) as \( \kappa_2 = 3.6 \times 10^{-6} \text{ cm/s} \).
(b) dissolution rate of a 1 cm radius cholesterol gallstone

The 1 cm cholesterol gallstone is assumed to stand still, but the density gradient between cholesterol and bile results in flow by free convection so the mass transfer coefficient is:

\[
\frac{k_1 d}{D} = 2 + 0.6 \left( \frac{d^3 \Delta \rho \ g}{\rho \ \nu^2} \right)^{1/4} \left( \frac{\nu}{D} \right)^{1/3}
\]

\[
\frac{k_1 \cdot 1 \text{cm}}{2 \cdot 10^{-6} \text{ cm}^2 / \text{s}} = 2 + 0.6 \left( \frac{(1 \text{cm})^3 \ 1 \cdot 10^{-5} \text{ g/cm}^3 \cdot 980 \text{ cm/s}^2}{1 \text{ g/cm}^3 (0.036 \text{ cm}^2 / \text{s})^2} \right) \cdot (18000)^{1/3}
\]

\[
k_1 = 5.6 \cdot 10^{-5} \text{ cm/s}
\]
As we are still dealing with irreversible reactions:

\[
K = \frac{1}{1/k_1 + 1/k_2}
\]

\[
= \frac{1}{1/5.6 \cdot 10^{-5} \text{ cm/s} + 1/3.6 \cdot 10^{-6} \text{ cm/s}}
\]

\[
= 3.4 \cdot 10^{-6} \text{ cm/s}
\]

In an unstirred bile, the rate is also controlled by the reaction.
10.3 Finding the Mechanism of Irreversible Heterogeneous Reactions

Typically, the reaction mechanism is not known so it has to be inferred.

\[
\text{gaseous species 1} + \text{solid species 2} \rightarrow \text{products}
\]

The surface reaction takes place as

- **Shrinking particle model**
- **Shrinking core or “topochemical” model**
<table>
<thead>
<tr>
<th>Physical situation</th>
<th>Rate-controlling step</th>
<th>Size ( R = f(\text{time, reagent}) )</th>
<th>Size = ( f(\text{temperature}) )</th>
<th>Size = ( f(\text{flow}) )</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Shrink particle</td>
<td>Reaction</td>
<td>( R \propto c_1 t )</td>
<td>strong temperature variation</td>
<td>Independant of flow</td>
<td>Other reaction stoichomerties can be found easily</td>
</tr>
<tr>
<td>B Shrink particle</td>
<td>External diffusion</td>
<td>( R^2 \propto (c_1 t) ) small particles</td>
<td>Weak temperature variation</td>
<td>Independent for small particles only</td>
<td>The exact variation with flow depends on the mass transfer coefficient</td>
</tr>
<tr>
<td>C Shrink core(^a)</td>
<td>Reaction</td>
<td>( R \propto c_1 t )</td>
<td>strong temperature</td>
<td>Independant of flow</td>
<td>This is the same as case A, except for ash formation</td>
</tr>
<tr>
<td>D Shrink core(^a)</td>
<td>External diffusion</td>
<td>( R \propto c_1 t )</td>
<td>Weak</td>
<td>Usually about square root of flow</td>
<td>This case is uncommon</td>
</tr>
<tr>
<td>E Shrink core(^a)</td>
<td>Ash diffusion</td>
<td>( R \propto (c_1 t)^{1/2} )</td>
<td>Weak</td>
<td>Independant of flow</td>
<td>This case is common, an interesting contrast with the previous one</td>
</tr>
</tbody>
</table>

Notes: \(^a\)This is often called the topochemical model. The size \( R \) refers to the cone
Cases A and C: surface reaction controls

\[ r_2 = -\kappa_2 c_1 c_2 \]

As the solid concentration \((c_2)\) is constant the reaction is 1\(^{\text{st}}\) order with respect to \(c_1\).

Mass balance per particle:

\[
\frac{d}{dt} \left( \frac{4}{3} \pi r^3 c_2 \right) = r_2 \cdot 4\pi r^2
\]

\[
4\pi r^2 c_2 \frac{dr}{dt} = -\kappa_2 c_1 c_2 4\pi r^2
\]

\[
\frac{dr}{dt} = -\kappa_2 c_1
\]

Be careful, distinguish between radius \(r\) and reaction rate \(r_2\)!

If the gas phase concentration \(c_1\) is constant and the particle has an initial radius \(R_0\)

\[
r = R_0 - \kappa_2 c_1 \cdot t
\]
Case B: Diffusion outside of a shrinking particle controls

Identify correlation (forced convection around solid sphere)

\[
\frac{k_d}{D} = 2 + 0.6 \left( \frac{dv}{\nu} \right)^{1/2} \left( \frac{\nu}{D} \right)^{1/3}
\]

B.1) For very small particles \( Re \to 0 \), so

\[
\frac{k_d}{D} = 2 \rightarrow k = \frac{D}{r}
\]

Mass balance:

\[
\frac{d}{dt} \left( \frac{4}{3} \pi r^3 c_2 \right) = -k \cdot 4\pi r^2 (c_1 - c_{1i})
\]

\[
4\pi r^2 c_2 \frac{dr}{dt} = -4\pi r^2 \frac{D}{r} c_1
\]

\[
r \frac{dr}{dt} = -\frac{D}{c_2} c_1
\]

\[
r^2 = R_0^2 - \left( \frac{2Dc_1}{c_2} \right) \cdot t
\]
B.2) For large particles

\[
\frac{k_1 d}{D} \approx 0.6 \left( \frac{d v}{v} \right)^{1/2} \left( \frac{v}{D} \right)^{1/3}
\]

\[
k_1 \approx 0.42 \left( \frac{v^{1/2} D^{2/3}}{v^{1/6}} \right) \cdot r^{-1/2}
\]

Similarly,

\[
c_2 \cdot r^{1/2} \frac{dr}{dt} = -0.42 \left( \frac{v^{1/2} D^{2/3}}{v^{1/6}} \right) \cdot c_1
\]

\[
r^{3/2} = R_{0}^{3/2} - \left( \frac{0.64 \times v^{1/2} D^{2/3}}{v^{1/6}} \right) \left( \frac{c_1}{c_2} \right) \times t
\]
Cases C, D, and E: shrinking core model:
Two diffusional resistances in series

Physical situation | Rate-controlling step
--- | ---
A | Reaction
Shrinking particle
B | External diffusion
Shrinking particle
C | Reaction
Shrinking core<sup>a</sup>
D | External diffusion
Shrinking core<sup>a</sup>
E | Ash diffusion
Shrinking core<sup>a</sup>
Case D: Diffusion in the surrounding bulk fluid controls

Mass balance: \[
\frac{d}{dt} \left( \frac{4}{3} \pi r^3 c_2 \right) = -4\pi r^2 \cdot kc_1
\]

\[
4\pi r^2 c_2 \frac{dr}{dt} = -4\pi r^2 kc_1
\]

\[
r = R_0 - \left( k \frac{c_1}{c_2} \right) \cdot t
\]

Similar dependence of \( r \) with \( t \) as with cases A and C. Dependence on flow (through \( k \)) but weak dependence on temperature.
Case E: Diffusion in the ash (or shell) controls

Here the thickness of the shell is important. Film model:

\[ k = \frac{D}{R_0 - r} \]

where \( D \) is the effective diffusivity through the shell.

Mass balance:

\[ \frac{d}{dt} \left( \frac{4}{3} \pi r^3 c_2 \right) = -4\pi r^2 \cdot \frac{D \cdot c_1}{R_0 - r} \]

\[ r = R_0 - \left( \frac{2D \cdot c_1}{c_2} \cdot t \right)^{1/2} \]
10.4 Heterogeneous Reactions of Unusual Stoichiometries

10.4.1 Irreversible second-order heterogeneous reaction (additivity of resistances)

Step 1 Reagent 1 diffuses to the surface.

Step 2 This reagent undergoes a second-order, irreversible reaction.

Other steps Because the reaction is irreversible, other steps are not involved.
Steady-state mass transfer to the surface:

\[ r_1 = n_1 = k_1(c_1 - c_{1i}) \]

Surface reaction:

\[ r_1 = \kappa_2 \cdot c_{1i}^2 \]

Find the \( c_{1i} \) by equating the above

\[ \kappa_2 \cdot c_{1i}^2 + k_1 \cdot c_{1i} - k_1 \cdot c_1 = 0 \]

\[ c_{1i} = \frac{k_1}{2\kappa_2} \left( \sqrt{1 + \frac{4\kappa_2 c_1}{k_1}} - 1 \right) \]

So the overall reaction rate is:

\[ r_1 = k_1 c_1 \left[ 1 - \frac{k_1}{2c_1\kappa_2} \left( \sqrt{1 + \frac{4\kappa_2 c_1}{k_1}} - 1 \right) \right] \]
Compare this with the corresponding first order reaction:

\[
r_1 = k_1 c_1 \left[ 1 - \frac{k_1}{2c_1\kappa_2} \left( \sqrt{1 + \frac{4\kappa_2 c_1}{k_1}} - 1 \right) \right]
\]

second order reaction

\[
r_1 = \frac{1}{1/k_1 + 1/\kappa_2} \cdot c_1
\]

first order reaction
10.4.2 Heterogeneous Reactions in Concentrated Solutions

Until now we assumed that $k_1 \neq f(r_2)$. This is good for dilute solutions.

Example:

**Cracking of hydrocarbons:**

1 mol of species $1 \xrightarrow{\kappa_2} n$ moles of species $2$, $n > 1$

- Step 1: A large reagent diffuses to the surface.
- Step 2: It reacts to produce many smaller products.
- Result: The reagent must swim upstream against the flux of product.

**Reforming**

1 mol of species $1 \xrightarrow{\kappa_2} n$ moles of species $2$, $n < 1$

- Step 1: Small reagents diffuse to the surface.
- Step 2: They combine to form product.
- Result: The reagents are carried toward the surface both by diffusion and by convection.

In both cases we must account for CONVECTION in the calculation of mass transfer.
In cracking, convection is AWAY from the surface: The reacting species must diffuse AGAINST the current of product species. In reforming, convection is TOWARDS the surface as reaction "pulls" reactants. The product must diffuse away.

\[
\nu > 1 \text{ cracking} \\
\nu < 1 \text{ reforming} \\
\nu = 1 \text{ treat as before}
\]

**Goal:** To calculate the overall rate!
Overall rate of reaction across this film is:

\[ r_1 = n_1 = -\frac{n_2}{v} = \kappa_2 \cdot c_{1i} \]

We must calculate the flux \( n_1 \) for concentrated solutions:

\[ n_1 = -D \frac{dc_1}{dz} + c_1 v^0 \]

Now the flux from convection is

\[ c v^0 = n_1 + n_2 = (1 - v)n_1 \]

So the equation for flux \( n_1 \) can be written as:

\[ \frac{dc_1}{dz} + \frac{v - 1}{Dc} n_1 c_1 + \frac{n_1}{D} = 0 \]
B.C.’s: \( z = 0: \quad c_1 = c_{10} \)
\( z = l: \quad c_1 = c_{1i} \)

Solving for \( n_1 \) gives:

\[
1 + (v - 1)n_1/(\kappa_2 \cdot c) = \ln \left( \frac{1 + (v - 1)c_{10}/c}{1 + (v - 1)c_{10}/c} \right)
\]

where \( k_1 = \frac{D}{l} \)

For diffusion control \((\kappa_2 \cdot c_{10}/n_1 \text{ is large})\) the following diagram shows the rate relative to that of dilute solutions:
Consider studying cracking of oil by flowing it over a hot plate. If the molecular weight of the product is only 25% of that of the oil, by how much the convection introduced mass transfer changes the cracking reaction rate?

1 molecule oil = ν x 0.25 molecules of the product. So ν ≈ 4

As only oil is flowing (c_{10}/c) = 1. So 1 + (ν - 1) c_{10}/c ≈ 4 From the above figure:

\[
\frac{\text{actual rate}}{1:1 \text{ reaction rate}} = 40\% 
\]

The convection REDUCES the reaction rate when the effect of reaction on the mass transfer coefficient is neglected.