# Introduction to Chemical Reactors

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## 5. Design of Catalytic Reactors

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## Objectives

- Describe catalyst types and components, catalytic mechanisms, rate limiting steps and catalyst deactivation.
- List and describe the steps in a catalytic mechanism.
- Derive the reaction rate applicable when the limiting step is
  - external mass transfer,
  - pore diffusion, or
  - surface reaction.
- Use Langmuir-Hinshelwood kinetics to model a reaction rate.
- Apply isothermal reactor design heuristics for the different situations listed above.

## Sources for catalytic reactors

- Schmidt: Chapter 7
- (Fogler: Chapters 10, 11 and 12)

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## Motivation

Catalysts are substances that cause the reaction to *proceed faster* but that do not enter the reaction stoichiometry. Catalysts *cannot alter the equilibrium* (uniquely defined for a system), however, they can increase the rate of a desired reaction over other undesired reactions.

Most real reactors use catalyst to

- *operate at lower temperatures/pressures*

  (for a given conversion)

- *achieve a higher selectivity*

  (accelerating desired reactions/slowing down undesired reactions)

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## 5.1 Catalysts and their properties

## Catalysts

Catalysts can be
- homogeneous (same phase as reactants), or
- heterogeneous (in another phase, usually solid)

They can consist of:

1. **Active ingredients**
   - provide an alternate reaction path with a lower activation energy
2. **Promoters** (optional)
   - modify the behaviour of the active ingredients
3. **Support** (optional)
   - bind the active ingredients & promoters to keep them inside the reactor
   - facilitate mass transfer
   - increase surface area

## Catalyst deactivation

Catalysts can undergo changes in activity / selectivity due to:
- **Poisoning**
  - e.g. accumulation of Pb in automotive catalytic converter
  - e.g. S and Pb in petroleum feedstocks on petrochemical catalysts
- **Aging**
  - sintering of metal clusters (narrowing/closing of the pores),
  - dissolution in their support,
  - change in the surface crystal structure (crystal agglomeration)
  
  due to extreme operating conditions (high T and P).
- **Coking or fouling**
  
  e.g. formation of coke deposits on the catalyst surface (soot); the catalyst can be regenerated by burning off the coke.

## Catalytic reactors: packed bed reactor (PBR)

Most common industrial catalytic reactor.

*packed bed reactor*

Tank or pipe filled with catalysts pellets (catalyst is fixed in a bed) with fluid flowing in the void space and reacting in the pellets. Assume similar behaviour to PFR (i.e. no mixing)

$$u \frac{dC_j}{dz} = \nu_j r$$

But now the total reactor volume, $V_R$, is:

$$V_R = V_{fluid} + V_{catalyst}$$
$$V_{fluid} = \varepsilon V_R$$
$$V_{catalyst} = (1 - \varepsilon) V_R$$

(where $\varepsilon$ is the **void fraction** of the reactor occupied by the fluid).

## Other catalytic reactors: slurry and fluidised bed

In this case the fluid and the catalyst are stirred.

Assume similar behaviour to CSTR.

$$C_{A0} - C_A = \tau \, r \qquad\qquad \tau = \frac{V_{f\,luid}}{v} = \frac{\varepsilon V_R}{v}$$

- if fluid is a liquid and catalyst a solid – *slurry reactor*

- if fluid is a liquid and catalyst is a liquid – *emulsion reactor*

- if fluid is a gas and catalyst is a solid – *fluidised bed*

## Surface reaction rates

We will assume that all reactions occur on the surface of the catalyst with surface reaction rate r''

$$r = \left( \frac{area}{volume} \right) r''$$

r:  pseudohomogeneous rate [moles/(volume time)]

r'':  surface reaction rate, rate per catalyst area [moles/(area time)]

(area/volume):  surface area of catalyst per volume of reactor [length$^{-1}$]

$$\left( \frac{area}{volume} \right) = S_g \rho_c \frac{V_{catalyst}}{V_R} = S_g \rho_c (1 - \varepsilon)$$

$S_g$:  surface area per unit weight of catalyst [area/weight]

$\rho_c$:  density of catalyst [weight/volume]

$S_g \rho_c$: surface area of catalyst based on catalyst volume

## Rate per weight of catalyst

It is often easier to measure the area per unit weight of catalyst. Hence the rate per weight of catalyst, r', is also commonly used:

$$r = \left( \frac{weight}{volume} \right) r'$$

r:  pseudohomogeneous rate [moles/(volume time)]

r':  rate per weight of catalyst [moles/(weight time)]

(weight/volume):  weight of catalyst per reactor volume [weight/volume]

$$\left( \frac{weight}{volume} \right) = \rho_c \frac{V_{catalyst}}{V_R} = \rho_c (1 - \varepsilon)$$

$\rho_c$:  density of catalyst [weight/volume]

## Common catalyst materials

The ideal catalyst is one with the highest possible area (to minimise $V_R$), thus catalyst are formulated as a powder and pressed into pellets (spherical, cylindrical, …).

- Amorphous silica ($SiO_2$): very high surface area ($\approx 500$ m$^2$/g)

- High area alumina ($Al_2O_3$): surface area up to $\approx 200$ m$^2$/g

- Zeolites (aluminosilicates): have regular pore sizes, allowing to catalyse reactions with shape selectivity

- Carbon: from partially burned organic material, up to $\approx 500$ m$^2$/g

Supported noble metals (Pt, Pd, Ag, Rh, Ni, etc.): very expensive, thus deposited on high-area supports
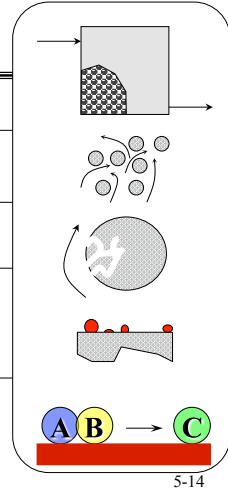
## 5.2 Heterogeneous catalytic reactions

There are several phenomena/mechanisms involved in catalytic reactors:

- – fluid flow (affecting **mass transfer**)

- – **diffusion** (through the pores of the catalyst)

- – **adsorption** (on the catalyst surface)

- – **surface reaction** (at the catalyst surface)

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## Length scales in a reactor

| | Order of magnitude | Variable of interest | Phenomena of interest |
|---|---|---|---|
| Reactor | 1 m | z or L in Reac. | position in reactor |
| Pellet | $10^{-2}$ m | x within pellet | flow around catalyst pellet |
| Pores | $10^{-4}$ m | $d_{pore}$ | diffusion within pores |
| Catalyst particles | $10^{-6}$ m | $d_{particle}$ | adsorption and reaction |
| Reaction molecules | $10^{-10}$ m | | atomic bonds and orbitals |

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Because of these varied phenomena, heterogeneous catalytic reactions can be better understood in terms of **several possible steps**.

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## Steps in heterogeneous catalytic reactions

1. Mass transfer of reactants from bulk fluid to the external surface of the pellet.
2. Diffusion of reactants into the pellet (through the pore).
3. Adsorption of reactants onto the catalyst surface.
4. Surface reaction of reactants to form products.
5. Desorption of products from the catalyst surface.
6. Diffusion of products from the pellet interior to the surface.
7. Mass transfer of products from pellet surface to the bulk fluid.
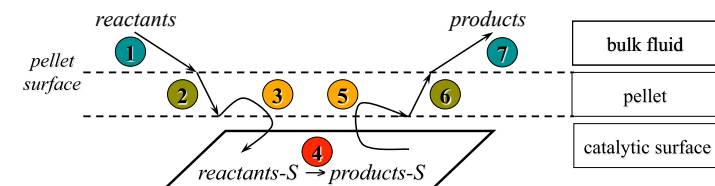
## Steady state

*At steady state the rates for all the steps must be exactly equal*

Since, in general, each of the steps has a different rate (different dynamics), this means that one of the steps is the *limiting step* in the reaction process.

The limiting step (the slowest link in the chain) determines in most cases the overall rate because the rest of the steps have a negligible rate with respect to it.

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Let's start the analysis of catalytic reactions with a simple case, one in which only

- mass transfer and
- surface reaction

are present because the catalysts (pellet) is nonporous, i.e. there is **no diffusion**.

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## I. Reaction in a nonporous pellet (1)

Consider a nonporous pellet, the reaction occurs on its surface:

$$\begin{bmatrix} \text{rate of mass transfer} \\ \text{from bulk fluid to surface} \end{bmatrix} = \begin{bmatrix} \text{rate of surface reaction} \end{bmatrix}$$

*solve*

$$\left(4\pi R^2\right) k_{mA}\left(C_{Ab} - C_{As}\right) = \left(4\pi R^2\right) r^{"} = \left(4\pi R^2\right) k^{"} C_{As} \quad \left[\tfrac{mole}{s}\right] \qquad C_{As} = \frac{1}{1 + \dfrac{k^{"}}{k_{mA}}} C_{Ab}$$

spherical pellet

mass transfer coefficient [m s$^{-1}$]

bulk gas concentration of A

surface concentration of A

assuming 1$^{st}$ order, irreversible reaction

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We have derived an expression to calculate the surface concentration $C_{As}$ as a function of the concentration in the bulk gas $C_{Ab}$, and the reaction rate and mass transfer coefficients ($k^{"}$ and $k_{mA}$).

Why is this useful?

Because $C_{As}$ is difficult, if not impossible, to measure.

Now we can express the reaction rate in terms of $C_{Ab}$, and an **"effective"** specific reaction rate $k_{eff}$ ...

## I. Reaction in a nonporous pellet (2)

Starting from
$$C_{As} = \dfrac{1}{1 + \dfrac{k^{"}}{k_{mA}}} C_{Ab}$$

substitute $C_{AS}$ into $r$":
$$r^{"} = k^{"} C_{As} = \dfrac{k^{"}}{1 + \dfrac{k^{"}}{k_{mA}}} C_{Ab} = k^{"}_{eff} C_{Ab}$$
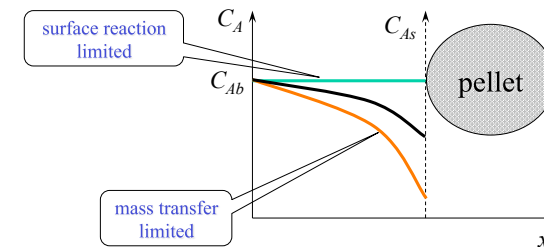
$$k^{"}_{eff} = \dfrac{k^{"}}{1 + \dfrac{k^{"}}{k_{mA}}} = \dfrac{k_{mA} k^{"}}{k_{mA} + k^{"}}$$

## I. Reaction in a nonporous pellet (3)

Now consider the two possible limiting cases:

• Reaction limited        $k^{"} \ll k_{mA}$        $r^{"} \cong k^{"} C_{Ab}$

• Mass transfer limited        $k_{mA} \ll k^{"}$        $r^{"} \cong k_{mA} C_{Ab}$

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How to interpret the plot in the last slide:
• when the process is **reaction limited**, i.e. the reaction rate is much slower than the mass transfer rate,
  – the overall rate depends on $k^{"}$ and
  – $C_{Ab} = C_{As}$

• when the process is **mass transfer limited**, i.e. the mass transfer rate is much slower than the reaction rate,
  – the overall rate depends on $k_{mA}$ and
  – $C_{Ab} \gg C_{As}$

There may be processes where neither mechanism dominates (middle line).

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## *(a very short review of mass transfer coefficients)*

The value of $k_{mA}$ can be calculated from: $Sh_d = \dfrac{k_{mA} d}{D_A}$

where $Sh_d$ is the Sherwood number [dimensionless], and
$D_A$ the diffusion coefficient of A in a fluid [m² s⁻¹].

$Sh_d$ depends on the reactor flow regime:

• laminar flow ($Re_d < 2100$)        $Sh_d = \dfrac{8}{3}$

• turbulent flow ($Re_d > 2100$)        $Sh_d = 0.023 \, Re_d^{0.8} \, Pr^{1/3}$

$$Re = \dfrac{\rho u d}{\mu}$$
$$Pr = \dfrac{\mu Cp}{k}$$

Let's continue the analysis by considering what happens in a porous pellet, i.e. there is **diffusion** through the pore.

As a first approximation we will consider first that all the **pores are equal in length and diameter** and that they are **straight and cylindrical**.

In order to model the variation of $C_A$ along the length of the pore, we set out a mass balance for A across a differential cross section of the pore (in terms of the flux of A and the reaction).

Note that one of the boundary conditions states that at the entrance of the pore $C_A = C_{As}$ and now we know how to estimate $C_{As}$ in terms of $C_{ab}$ .

## II. Reaction in a porous pellet

First consider a single pore of length $l$ and diameter $d_p$ with:

- uniformly reactive walls where $r'' = k''C_A(x)$
- assume the end of the pore to be unreactive, $\dfrac{dC_A}{dx} = 0$ @ $x = 0$

$$\big[\text{net flux IN @ x}\big] - \big[\text{net flux OUT @ x + dx}\big] = \big[\text{rxn on wall between x, x + dx}\big]$$

$$\frac{\pi d_p^2}{4} D_A \left(\frac{dC_A}{dx}\right)_x - \frac{\pi d_p^2}{4} D_A \left(\frac{dC_A}{dx}\right)_{x+dx} = -(\pi d_p)\, dx\, k'' C_A \qquad \left[\frac{\text{moles}}{\text{s}}\right]$$

diffusion coefficient [$m^2\,s^{-1}$]

$$\frac{d^2 C_A}{dx^2} = \frac{4k''}{D_A d_p} C_A = \lambda^2 C_A \qquad \lambda = \left(\frac{4k''}{D_A d_p}\right)^{1/2}$$

$$BCs: \quad \begin{vmatrix} C_A = C_{As} & @ & x = l \\ \dfrac{dC_A}{dx} = 0 & @ & x = 0 \end{vmatrix}$$

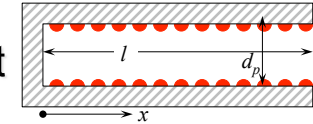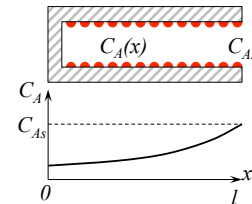The resulting 2nd order ODE is then solved obtaining an expression for $C_A$ in terms of the position along the pore.

Through the concept of **effectiveness factor η** (which in turn is a function of the Thiele modulus φ), we will be able to calculate the reaction rate in terms of $C_{As}$ ...

## II. Reaction in a porous pellet (2)

Solution: $C_A(x) = C_{As} \dfrac{e^{\lambda x} + e^{-\lambda x}}{e^{\lambda l} + e^{-\lambda l}} = C_{As} \dfrac{\cosh \lambda x}{\cosh \lambda l}$

since $C_A(x)$ is a function of position within the pore, a convenient way to relate it to the concentration at the pellet surface, $C_{As}$, is through the effectiveness factor $\eta$.

$$\eta = \frac{\text{actual rate}}{\text{ideal rate}} = \frac{r''}{r''_{ideal}} = \frac{\pi d_p \int_{x=0}^{x=l} k'' C_A(x)dx}{\pi d_p l\, k'' C_{As}} \qquad \boxed{\eta(\phi) = \frac{1}{\phi} \cdot \frac{e^\phi - e^{-\phi}}{e^\phi + e^{-\phi}} = \frac{\tanh \phi}{\phi}}$$

where $\phi$ is the (dimensionless) **Thiele modulus**: $\boxed{\phi = \lambda l = \left(\frac{4k''}{D_A d_p}\right)^{1/2} l}$
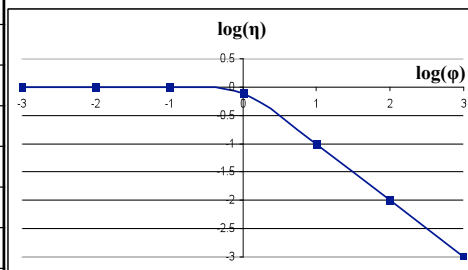
## Dependence of η (effectiveness factor) on φ (Thiele modulus)

| φ | η(φ) |
|---|---|
| 0.001 | 1.000 |
| 0.01 | 1.000 |
| 0.1 | 0.9967 |
| 1.0 | 0.7616 |
| 10 | 0.1000 |
| 100 | 0.0100 |
| 1000 | 0.0010 |

| log(φ) | log(η) |
|---|---|
| −3.0 | 0 |
| −2.0 | − 1.4E-5 |
| − 1.0 | −0.0014 |
| 0.0 | −0.1183 |
| 1.0 | −1.0 |
| 2.0 | −2.0 |
| 3.0 | −3.0 |

## Significance of the Thiele modulus

Solving for $r''$ we can calculate the reaction rate in terms of $C_{As}$
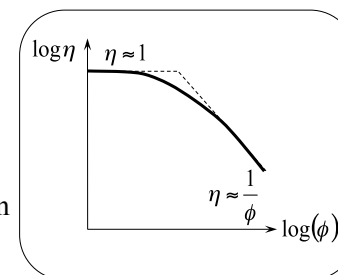
$$r'' = r''_{ideal}\,\eta(\phi) = k''C_{As}\,\eta$$

where we have a set of "interesting" values:

- not limited by pore diffusion

  $\phi \ll 1 \;\Rightarrow\; \eta = 1 \qquad (C_A(x) \cong C_{As})$

- some pore diffusion limitation

  $\phi = 1 \;\Rightarrow\; \eta = 0.762$

- strongly limited by pore diffusion

  $\phi \gg 1 \;\Rightarrow\; \eta = 1/\phi \qquad (C_A(x) \ll C_{As})$
  MT limits

## III. Irregular pores

The derivation we have made assumes that the catalyst has straight, cylindrical pores. However, pores are often irregular, for example when the pellets are made out of pressed spheres.

For straight, cylindrical pores

$$\phi = \left(\frac{4k''}{d_p D_A}\right)^{1/2} l \quad \Leftarrow \quad \left(\frac{area}{volume}\right) = \frac{\pi d_p l}{\pi \frac{1}{4}d_p^2 l} = \frac{4}{d_p}$$

For irregular pores (average diameter $d_p$)

$$\phi = \left(\frac{S_g \rho_c k''}{D_A}\right)^{1/2} l \quad \Leftarrow \quad \left(\frac{area}{volume}\right) = S_g \rho_c$$
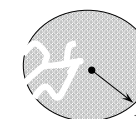
Catalyst surface area per unit volume of catalyst

## IV. $C_A$ in spherical pellets with irregular pores

The equations above for $C_A(x)$, $\eta$, and $\phi$ are valid for porous catalyst slabs of thickness $2l$.

For spherical pellets of radius $R_0$ (without derivation):

the $C_A(R)$ within the pellet is:

$$C_A(R) = C_{As}\,\frac{R_0}{R}\,\frac{\sinh \lambda R}{\sinh \lambda R_0}$$

with an effectiveness factor:

$$\eta = \frac{3}{\phi}\cdot\frac{\phi \coth \phi - 1}{\phi}$$

and a Thiele modulus:

$$\phi = \left(\frac{S_g \rho_c k''}{D_A}\right)^{1/2} R_0$$

## Summary: the three limiting cases (1)

We have identified three different rate expressions depending on which rate coefficients control/limit the overall process:

$$r''$$

- external mass transfer limited

$$r \cong \left(\frac{\text{area}}{\text{volume}}\right) k_{mA} C_{Ab}$$

- pore diffusion limited

$$r \cong \left(\frac{\text{area}}{\text{volume}}\right) k'' C_{Ab} \eta$$

- surface reaction limited

$$r \cong \left(\frac{\text{area}}{\text{volume}}\right) k'' C_{Ab}$$

## Summary: the three limiting cases (2)

- external MT limited

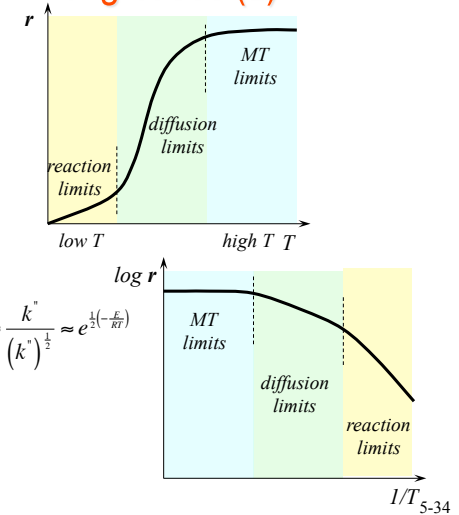$$r'' \cong k_{mA} C_{Ab} \cong fn\left(T^{1/2}\right)$$

($k_{mA}$ *weak function of T*)

- pore diffusion limited

$$r'' \cong k'' C_{Ab} \eta \cong fn\left(e^{-E/2RT}\right)$$

$$k'' \eta \approx \frac{k''}{\phi} \approx \frac{k''}{\left(k''\right)^{\frac{1}{2}}} \approx e^{\frac{1}{2}\left(-\frac{E}{RT}\right)}$$

- surface reaction limited

$$r'' \cong k'' C_{Ab} \cong fn\left(e^{-E/RT}\right)$$

## 5.3 Surface reactions
## (inclusion of adsorption/desorption)

## A more detailed view of surface reactions

So far we have assumed that surface reactions are first order in $C_{As}$, i.e. $r'' = k\, C_{As}$.

However, **surface reactions** are more complex, in principle they **are multistep processes** for which it is necessary to describe the concentrations of species adsorbed on the catalyst surface.

In order to proceed with the analysis we need to define:

$\Theta_j$ : coverage of adsorbed molecules

$$\Theta_j \equiv \frac{n_j}{n_{j0}}$$

*"sort of" concentration*

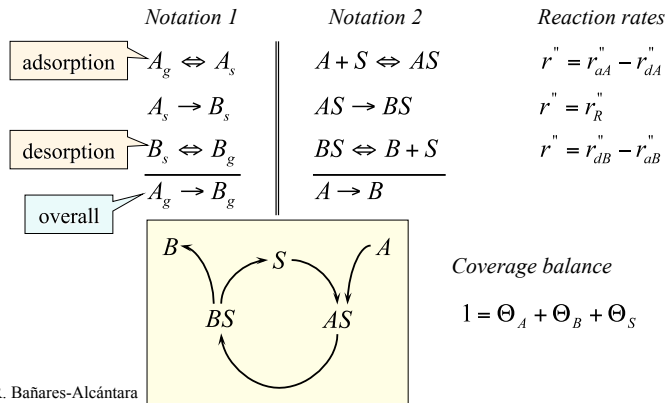$n_j$ : density of adsorbed molecules of species $j$ on the catalyst surface [moles cm$^{-2}$]

$n_{j0}$ : maximum n$_j$ packed in a 2-D layer, i.e. a monolayer

## Unimolecular surface reactions

Consider the following *unimolecular, catalysed, irreversible surface reaction* where $A_g$ and $B_g$ are the species in the gas phase:
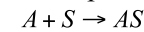
| | Notation 1 | Notation 2 | Reaction rates |
|---|---|---|---|
| adsorption | $A_g \Leftrightarrow A_s$ | $A + S \Leftrightarrow AS$ | $r'' = r''_{aA} - r''_{dA}$ |
| | $A_s \rightarrow B_s$ | $AS \rightarrow BS$ | $r'' = r''_R$ |
| desorption | $B_s \Leftrightarrow B_g$ | $BS \Leftrightarrow B + S$ | $r'' = r''_{dB} - r''_{aB}$ |
| overall | $A_g \rightarrow B_g$ | $A \rightarrow B$ | |



Coverage balance

$$1 = \Theta_A + \Theta_B + \Theta_S$$

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## Unimolecular surface reactions: mass balances

- Adsorption

  second order in "$C_A$" and "$C_S$"
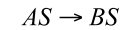
  $A + S \rightarrow AS$ $\qquad r''_{aA} = k_{aA} p_A \Theta_S = k_{aA} p_A \left(1 - \Theta_A - \Theta_B\right)$

- Desorption
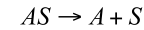
  $AS \rightarrow A + S$ $\qquad r''_{dA} = k_{dA} \Theta_A$

- Surface reaction

  $AS \rightarrow BS$ $\qquad r''_R = k_R \Theta_A$

Mass balances on adsorbed A and B:

$$\frac{d\Theta_A}{dt} = r''_{aA} - r''_{dA} - r''_R = k_{aA} p_A \left(1 - \Theta_A - \Theta_B\right) - k_{dA}\Theta_A - k_R\Theta_A$$

$$\frac{d\Theta_B}{dt} = r''_{aB} - r''_{dB} + r''_R = k_{aB} p_B \left(1 - \Theta_A - \Theta_B\right) - k_{dB}\Theta_B + k_R\Theta_A$$

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## Unimolecular surface reactions: steady state

At steady state $\quad \dfrac{d\Theta_A}{dt} = \dfrac{d\Theta_B}{dt} = 0$

and we have 2 algebraic equations in $p_A$, $p_B$, $\Theta_A$ and $\Theta_B$.

Solve one of them for $\Theta_B$ and substitute $\Theta_B$ into the other to get $\Theta_A$. Then, recalling that for $r''_R = k_R \Theta A$:

$$r''_R = k_R \Theta_A = \frac{k_R K'_A p_A}{1 + K'_A p_A + K'_B p_B}$$

where

$$K'_A = \frac{k_{aA}}{\left(k_{dA} + k_R\right)} \qquad\qquad K'_B = \frac{k_{aB}}{\left(k_{dB} + k_R\right)}$$

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The equation obtained for the rate of a unimolecular, irreversible, surface reaction A → B

$$r''_R = \frac{k_R K'_A p_A}{1 + K'_A p_A + K'_B p_B}$$

is in terms of the concentrations of A and B in the gas (partial pressures; easy to measure) and a combination of specific rate constants

- for adsorption/desorption: $k_{aA}$, $k_{dA}$, $k_{aB}$, $k_{dB}$,
- for surface reaction $k_R$.

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# 5.4 Langmuir-Hinshelwood isotherms and kinetics (modelling of surface reactions)

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## Sir Cyril Norman Hinshelwood (1897 –1967)

Professor of Chemistry at the University of Oxford, he studied at Balliol College and was a tutor at Trinity College.

Hinshelwood was jointly awarded the **Nobel Prize in Chemistry** in 1956 for his researches into the mechanism of chemical reactions.

He never married. He was fluent in 7 classical and modern languages and his main hobbies were painting, collecting Chinese pottery, and foreign literature.

[from Wikipedia]

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As usual, we will start with the simplest case:

the adsorption, without reaction, of a single component A on a surface.

The resulting expression is known as the **Langmuir-Hinshelwood adsorption isotherm** and it models the coverage of adsorbed A in terms of the partial pressure of A.

As expected, coverage is proportional to the partial pressure of A …

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## Langmuir-Hinshelwood isotherms

The expression for the coverage of _pure species A_ on the surface, $\Theta_A$, can be derived from the adsorption/desorption rates:

$$A + S \Leftrightarrow AS \qquad r^{"} = r^{"}_{aA} - r^{"}_{dA} = k_{aA} p_A \Theta_S - k_{dA} \Theta_A$$
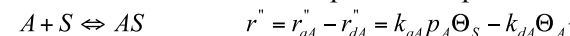
coverage balance: $\qquad 1 = \Theta_A + \Theta_S \quad \Rightarrow \quad \Theta_A = 1 - \Theta_S$

at equilibrium: $\qquad r^{"}_{aA} = r^{"}_{dA}$

$$k_{aA} p_A \left(1 - \Theta_A\right) = k_{dA} \Theta_A$$

$$K_A = \frac{k_{aA}}{k_{dA}} \qquad K_A p_A \left(1 - \Theta_A\right) = \Theta_A$$

**Langmuir-Hinshelwood adsorption isotherm**

$$\Theta_A = \frac{K_A p_A}{1 + K_A p_A}$$
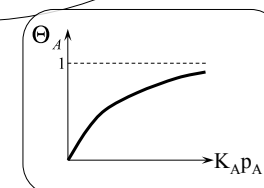
Let us include surface reaction; furthermore, let us assume it is the limiting step.

Now we have two chemical species, *A and B*.

They not only participate in the surface reaction, but *also compete for surface sites*.

## Langmuir-Hinshelwood kinetics (1)

A similar result to the one for *unimolecular surface reactions with two adsorbed species* can be derived using L-H isotherms (assume the surface reaction step is limiting,

i.e. $k_R \ll k_{aA}, k_{dA}, k_{aB}, k_{dB}$).

Again, assume that the adsorption and desorption steps of A and B reach thermodynamic equilibrium, i.e.

$$0 = r''_{aA} - r''_{dA} = r''_{dB} - r''_{aB}$$

$$= k_{aA} p_A (1 - \Theta_A - \Theta_B) - k_{dA}\Theta_A = k_{dB}\Theta_B - k_{aB} p_B (1 - \Theta_A - \Theta_B)$$

Solving for $\Theta_A$ we obtain the *Langmuir-Hinshelwood adsorption isotherm* for species A:

$$\Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}$$

where

$$K_A = \frac{k_{aA}}{k_{dA}}$$

$$K_B = \frac{k_{aB}}{k_{dB}}$$

## Langmuir-Hinshelwood kinetics (2)

Recalling that $r'' = k_R\Theta_A$ we can also obtain the *Langmuir-Hinshelwood rate expression* for the unimolecular reaction A→B

$$r''_R = k_R\Theta_A = \frac{k_R K_A p_A}{1 + K_A p_A + K_B p_B}$$

It relies on the following <u>assumptions</u>:

1. Adsorbed species compete for surface sites but do not interact otherwise.
2. There is only one type of adsorption site for all species.
3. Maximum coverage is of one monolayer.

The expression obtained for unimolecular surface reaction is a function of the partial pressures of A and B (the reactant and product of the reaction).

Now let's add a third component C and assume that it is an *inert* in the reaction *but competes with A and B for surface sites*.

This is an important case in real-world applications.
Can you think why?

## An explanation for catalyst poisoning

It can be shown that when an inert component $C$ adsorbs on the same sites as A and B the coverage of A is:

$$\Theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B + K_C p_C}$$

If $(K_C p_C) >> 1$, $(K_A p_A)$ and $(K_B p_B)$

$$r_R^{"} = \frac{k_R K_A}{K_C}\frac{p_A}{p_C} = k_{eff}^{"} p_A p_C^{-1}$$

The reaction rate is inversely proportional to $p_C$.
In effect, a strong adsorption of the inert species $C$ in the catalyst surface ($K_C$ high) and the presence of such an inert, strongly inhibits the reaction rate, i.e. it becomes a catalyst **poison**.

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The following table analyses different possible outcomes from the expression for a unimolecular reaction in the presence of an inert species.

The observed (or apparent) rate of reaction, i.e.
- its effective rate, and
- the order of the reaction

depends on which of the terms dominates in the expression.

Notice that this model *explains* the existence of *zero- and negative order* with respect to some of the species.

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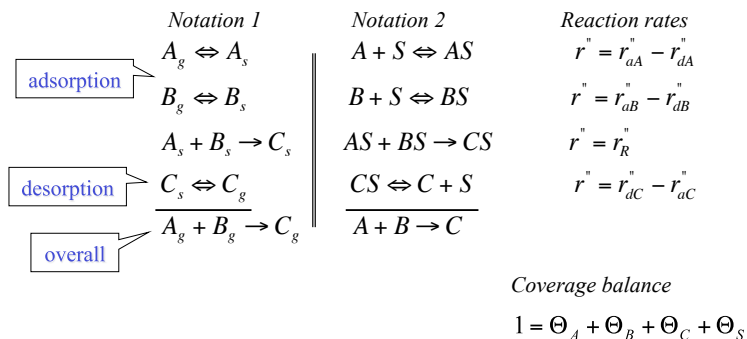## Effective reaction rates for unimolecular rxns

$$\boxed{A \rightarrow B} \qquad r^{"} = k_R \Theta_A = k_R \frac{K_A p_A}{1 + K_A p_A + K_B p_B + K_C p_C}$$

| Approximation | $k^{"}_{eff}$ | Pressure dependence | Coverages |
|---|---|---|---|
| $1 >> K_A p_A, K_B p_B$ | $k_R K_A$ | $(p_A)^{+1}$ | $\Theta_A, \Theta_B << 1$ |
| $K_A p_A >> 1, K_B p_B$ | $k_R$ | $(p_A)^0$ | $\Theta_A = 1$ |
| $K_B p_B >> 1, K_A p_A$ | $k_R K_A / K_B$ | $(p_A)^{+1} (p_B)^{-1}$ | $\Theta_B = 1$ |
| $K_C p_C$  large | $k_R K_A / K_C$ | $(p_A)^{+1} (p_C)^{-1}$ | $\Theta_C = 1$ |

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Lastly, these modelling technique can be extended to more complicated stoichiometries, for example a bimolecular surface reaction

$$A + B \rightarrow C$$

## Bimolecular surface reactions (1)

Consider the following bimolecular catalysed, irreversible, surface reaction where $A_g$ and $B_g$ are species in the gas phase:

*Notation 1*

adsorption

$A_g \Leftrightarrow A_s$

$B_g \Leftrightarrow B_s$

$A_s + B_s \to C_s$

desorption

$C_s \Leftrightarrow C_g$

overall

$A_g + B_g \to C_g$

*Notation 2*

$A + S \Leftrightarrow AS$

$B + S \Leftrightarrow BS$

$AS + BS \to CS$

$CS \Leftrightarrow C + S$

$A + B \to C$

*Reaction rates*

$r'' = r''_{aA} - r''_{dA}$

$r'' = r''_{aB} - r''_{dB}$

$r'' = r''_R$

$r'' = r''_{dC} - r''_{aC}$

*Coverage balance*

$$1 = \Theta_A + \Theta_B + \Theta_C + \Theta_S$$
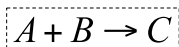
## Bimolecular surface reactions (2)

If we assume adsorption-desorption equilibrium, i.e. if the surface reaction is limiting ($r_a = r_d \gg r_R$) the resulting *Langmuir isotherm* for species J is:

$$\Theta_j = \frac{K_j p_j}{1 + K_A p_A + K_B p_B + K_C p_C}$$

And the reaction rate is:

$$r''_R = k_R \Theta_A \Theta_B = \frac{k_R K_A K_B p_A p_B}{\left(1 + K_A p_A + K_B p_B + K_C p_C\right)^2}$$

## Effective reaction rates for bimolecular reactions

$$A + B \to C \qquad r''_R = k_R \Theta_A \Theta_B = k_R \frac{K_A K_B p_A p_B}{\left(1 + K_A p_A + K_B p_B + K_C p_C\right)^2}$$

| Approximation | $k''_{eff}$ | Pressure dependence | Coverages |
|---|---|---|---|
| $1 \gg K_A p_A, K_B p_B$ | $k_R K_A K_B$ | $(p_A)^{+1}(p_B)^{+1}$ | $\Theta_A, \Theta_B \ll 1$ |
| $K_A p_A \gg 1, K_B p_B$ | $k_R K_A^{-1} K_B$ | $(p_A)^{-1}(p_B)^{+1}$ | $\Theta_A = 1$ |
| $K_B p_B \gg 1, K_A p_A$ | $k_R K_A K_B^{-1}$ | $(p_A)^{+1}(p_B)^{-1}$ | $\Theta_B = 1$ |
| $K_C p_C$ large | $k_R K_A K_B K_C^{-2}$ | $(p_A)^{+1}(p_B)^{+1}(p_C)^{-2}$ | $\Theta_C = 1$ |

## 5.5 Design of catalytic reactors

## SUMMARY
## general expression for the design of catalytic reactors

$$r = \left(\frac{area}{volume}\right)r'' = \left(\frac{area}{volume}\right)\frac{k''}{1 + k''/k_m}C_{Ab}\eta(\phi)$$

$k''$: reaction rate

$$k'' = k_0'' \exp\left(-E/RT\right)$$

$k_m$: external diffusion

$$k_m = \frac{Sh_d D_A}{d}$$

$\eta(\phi)$: pore diffusion

$$\eta = \frac{3}{\phi} \cdot \frac{\phi \coth\phi - 1}{\phi}$$

$\phi$: Thiele modulus

$$\phi = \left(\frac{S_g \rho_c k''}{D_A}\right)^{1/2} R_0$$

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## Design heuristics for catalytic reactors (1)

Optimum performance = maximum reaction rate

- $k''$ increases as we increase temperature, but mass transfer and/or pore diffusion can limit the rate

- best operation point usually
  - when reactor begins to be mass transfer limited, i.e. $k_m \sim k''$ or
  - when pore diffusion just begins to affect the rate, i.e. $\phi \sim 1$

- catalyst load should be as small as possible (save money)

- pellet size should be as large as possible (minimise P drop)

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## Design heuristics for catalytic reactors (2)

- Increase flow velocity ($u$) to increase external mass transfer rate
- Porous catalyst are often chosen / designed to have different distributions of pore diameters
  - macropores to promote diffusion
  - micropores to provide a high surface area, also size selectivity