Heterogeneous catalysis (C9981)

1. Kinetics
2. Mechanisms of catalytic reactions
3. Diffusional limitations on heterogeneous catalysts
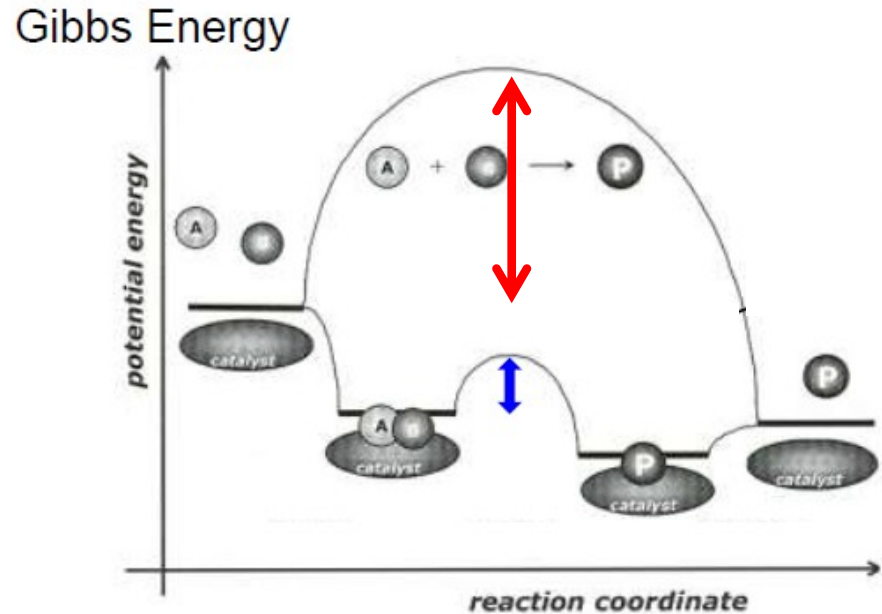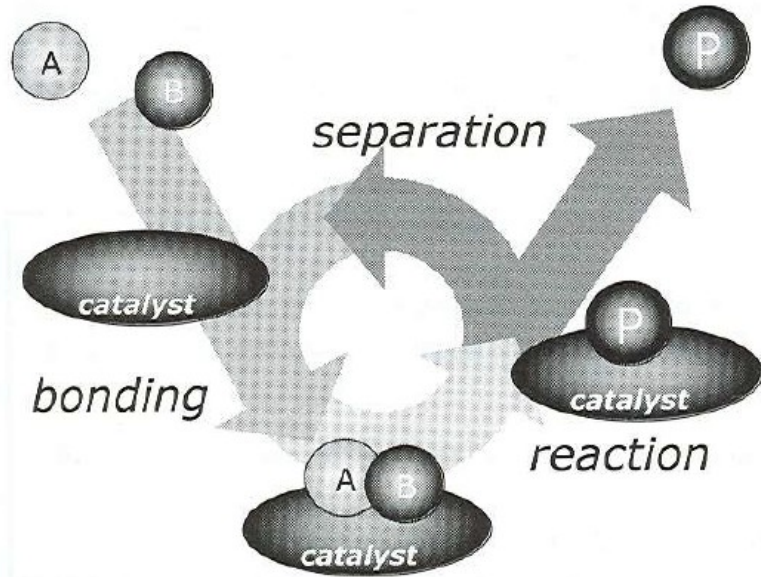
Definition

- Catalyst is…
  - A substance that speeds up a chemical reaction
  - Without being consumed or changed

- We get our products
  - In shorter time; at lower rxn temperature; at lower pressure
  - **cheaper; economical; ecological**
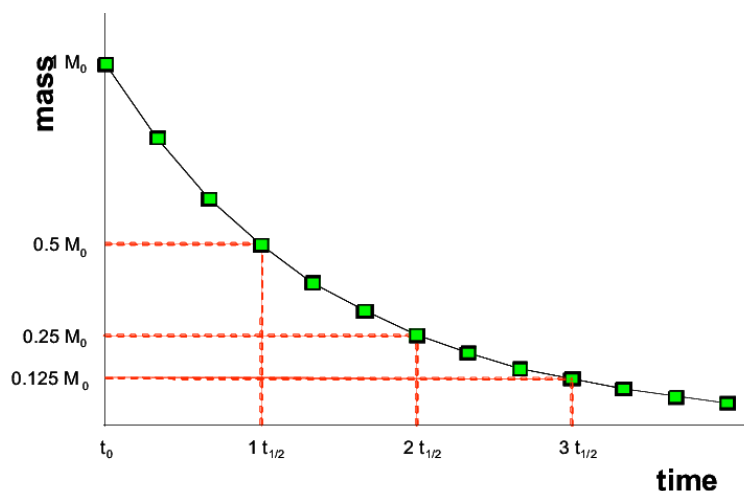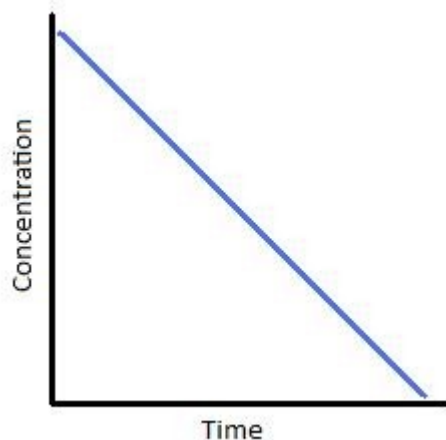
Catalytic cycle

A + B → P

$E_a \gg E_a(cata);\ k = A \cdot e^{-Ea/RT}$

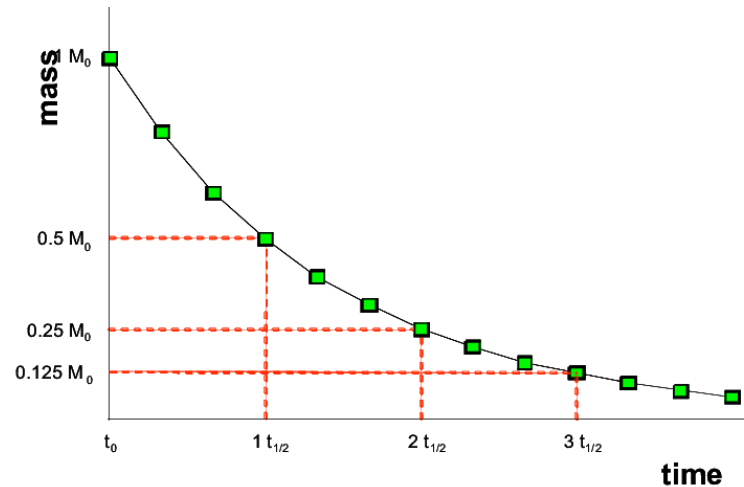$\Delta G = \Delta G(cata);\ \Delta G = -RT \cdot \ln K$

Kinetics

- We know kinetics☺ (#ChemKin)
- Rxns of zero order, first order, and second order

- But in catalysis also 0.39 order... (many steps, all contribute!)
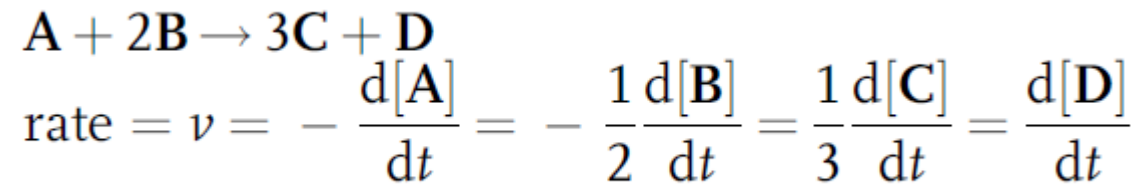
Kinetics

- An important consideration: type of the reactor
  - **Batch**
  - **Continuous** (plug flow (fixed bed) reactor (PFR) or continuous stirred tank reactor (CSTR))
    - Steady-state approximation (complicated math behind!)
    - It is not possible to follow changes of concentrations in time

Kinetics

- Important terms
  - Rate

$$\mathbf{A} + 2\mathbf{B} \rightarrow 3\mathbf{C} + \mathbf{D}$$
$$\text{rate} = v = -\frac{d[\mathbf{A}]}{dt} = -\frac{1}{2}\frac{d[\mathbf{B}]}{dt} = \frac{1}{3}\frac{d[\mathbf{C}]}{dt} = \frac{d[\mathbf{D}]}{dt}$$
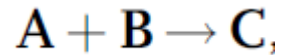
  - Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

Kinetics

- Important terms
  - Reaction order

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C},$$

$$- r_A = k[\mathbf{A}]^\alpha [\mathbf{B}]^\beta$$

overall reaction order is $n = \alpha + \beta$.

  - For elementary reactions α, β = whole numbers (integers)
  - For non-elementary reactions (i.e. catalytic reactions) α, β = non-integers
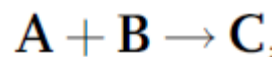
Kinetics

- Important terms
  - Reaction order
    - Can be negative!

If a compound slows the reaction or enhances the reverse reaction, partial reaction orders can even be negative. For example, in the water-gas shift reaction, the CO_2 product competes with the reactants for the same active site, and so the reaction shows a negative order in CO_2 [8]. Note that reaction orders of nonelementary reactions must be determined by experiment. You cannot deduce the order of a nonelementary reaction from the stoichiometric equation.

Kinetics

- ## Important terms
  - ### Reaction order
    - #### Example: Determination of reaction order

$$A + B \rightarrow C$$

$$\text{rate} = k[A]^{\alpha}[B]^{\beta}$$

Table 2.1 Measured concentrations of alkene **A** over time.

Run	$[A]_0/M$	$[B]_0/M$	$v_0/M \text{ min}^{-1}$
1	1.00	1.00	0.0162
2	1.00	2.00	0.0324
3	2.00	2.00	0.0324

$$\text{rate} = k[A]^0[B]^1 = \boxed{k[B]}$$

Kinetics

- Back to Arrhenius equation
- k – is the reaction rate constant
- k – is not a constant in fact
  - It depends on temperature and pressure
  - Its units differ according to the reaction order

$$k = A\mathrm{e}^{-\frac{E_a}{RT}}$$

Kinetics

- ## Important terms
  - – Reaction pseudo-order
    - Application of one (or more) of the reactants in a big excess so that its concentration in time t virtually equals concentration in time 0
    - Simplification of reaction rate equation

Kinetics

- **CAUTION!** Comparing k values between different types of reactions is an all-too-common mistake. Although we use the same letter k for both first-order and second-order rate constants, their units differ! A first-order rate constant has units of $[\text{time}]^{-1}$, while a second-order one has units of $[\text{time}]^{-1}$ $[\text{concentration}]^{-1}$. Comparing these two numbers is like comparing apples and tomatoes – it is nonsense. This is also the reason why comparing the rate constants of a reaction with and without a catalyst is meaningless: Consider, for example, the noncatalytic reaction $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$ that obeys the second-order rate law shown in Eq. (2.21).

$$\left.\begin{array}{l} \mathbf{A} + \mathbf{B} \rightarrow \mathbf{C} \\ \text{rate} = k[\mathbf{A}][\mathbf{B}] \end{array}\right\} \tag{2.21}$$

- If we add a catalyst, the reaction rate will change, but so will the rate law! Most likely, the new rate equation will depend on the catalyst's concentration, Eq. (2.22).

$$\left.\begin{array}{l} \mathbf{A} + \mathbf{B} \xrightarrow{\text{catalyst}} \mathbf{C} \\ \text{rate} = k[\text{catalyst}]^{\alpha}[\mathbf{A}]^{\beta}[\mathbf{B}]^{\gamma} \end{array}\right\} \tag{2.22}$$

Kinetics

- Depending on the type of catalyst and the new steps involved, the new overall reaction order may be $n = 2$, $n = 3$, or even $n = 2.5$. The units of the two rate constants k are different, so comparing their magnitudes makes no sense (and likewise for A values). There are other measures for comparing reaction rates: for example, the reaction half-life time, $\tau_{1/2}$, or the degree of conversion at a given time t. Differences in $\tau_{1/2}$ with and without a catalyst can be considerable. For example, the noncatalytic decarboxylation of orotic acid at $25\,°C$ has a half-life time of 78 million years. Adding the enzyme orotidine $5'$-phosphate decarboxylase enhances the reaction rate by a factor of 10^{17}, reducing $\tau_{1/2}$ to 0.02 seconds [13,14]!

Kinetics

$$k = Ae^{-\frac{E_a}{RT}}$$

- E_a (apparent) and A can be estimated by plotting ln k vs. 1/T = Arrhenius plot
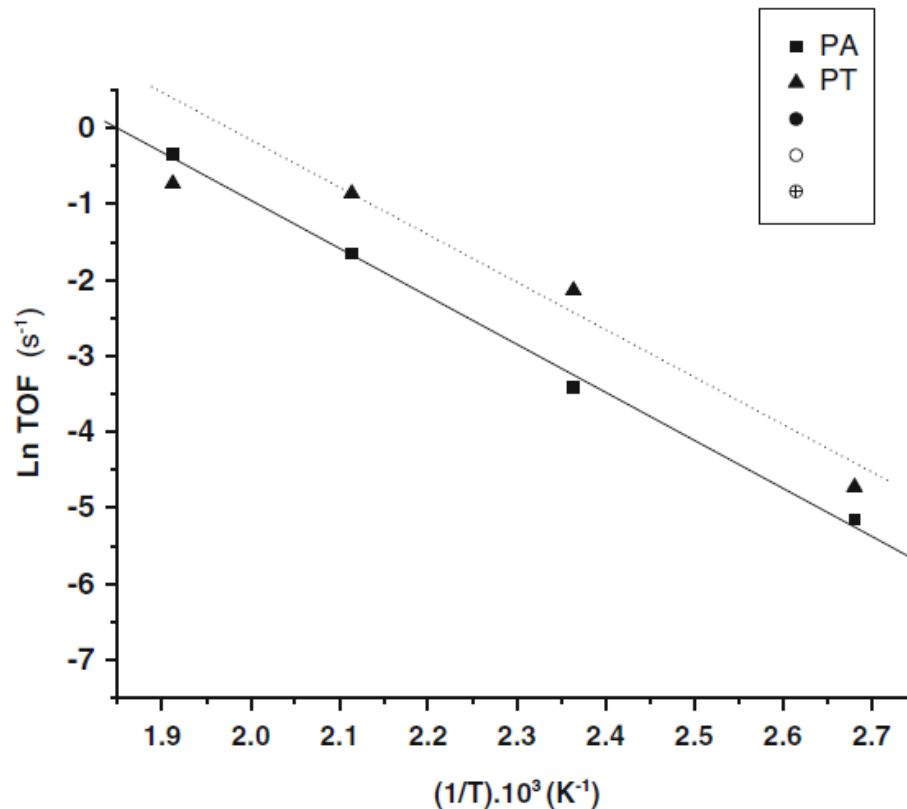
Kinetics

- Summary

If we look at the entire reaction system as a "black box," it seems that the catalyst simply "lowers the activation energy." We now know that this is true in only a few cases. In most cases, the catalyst actually opens an alternative reaction pathway. This pathway is often more complicated, and includes several catalytic intermediates. However, the highest activation barrier in the catalytic pathway is still lower than that of the noncatalytic one.

Homework 1

3. The synthesis of lineatin, a pheromone of the insect *Trypodendron lineatum*, involves the enantioselective addition of methane to the double bond of alkene **A** in the presence of a chiral rhenium catalyst on silica (Re*/silica; see Figure 2.19). Michael performed eight separate experiments for this reaction in a 500 mL high-pressure stirred autoclave reactor using liquid methane as a solvent and 0.05 mmol catalyst. The results are shown in Table 2.2.

In a second study, Abdelhafid performed five experiments in a 500 mL stirred tank reactor at 20 °C, using an inert organic solvent, 0.05 mmol catalyst, 1.000 mM alkene **A** and 1 atm of methane. In all these five experiments it was found that the reaction fitted a second-order rate law.

(a) Write out the rate equation that fits Michael's results.
(b) Calculate the value of the rate constant that Michael found.
(c) Write out the rate equation fits Abdelhafid's results.
(d) What is the reason for the different results observed by Michael and Abdelhafid?
(e) Both students repeated their first experiment again without changing conditions but using CD_4 instead of methane. What did they observe? Will the kinetics change?

alkene **A** + CH_4 →(Re*/silica, liquid methane)→ lineatin
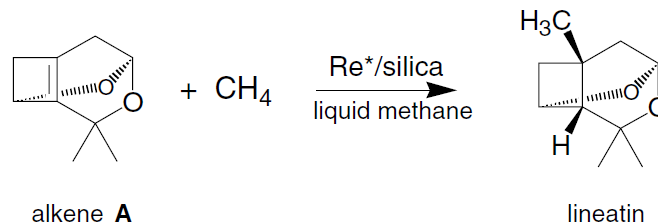
Homework 1

Table 2.2 Measured concentrations of alkene **A** over time.

Experiment	Time/min	[A]/mM	Time/min	[A]/mM
1	0.0	0.500	120.0	0.248
2	0.0	1.000	120.0	0.503
3	0.0	1.200	120.0	0.611
4	0.0	1.600	120.0	0.788
5	0.0	2.000	120.0	0.986
6	0.0	3.200	120.0	1.603
7	0.0	4.400	120.0	1.566
8	0.0	6.000	120.0	2.989

Mechanisms of catalytic reactions

- Langmuir (monomolecular)
  - A(adsorbed) → P(adsorbed)
- Langmuir-Hinshelwood (bimolecular)
  - A(adsorbed) + B(adsorbed) → P(adsorbed)
- Eley-Rideal (bimolecular)
  - A(adsorbed) + B(gas phase) → P(adsorbed)
- Mars-van Krevelen (special case)

Mechanisms of catalytic reactions

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Langmuir

- Hypotheses identical as for Langmuir adsorption isotherm
  - Monolayer
  - One molecule per active site
  - The enthalpy of adsorption independent on surface coverage Θ
    - All sites identical
    - No interactions between molecules of adsorbate
  - Adsorption and desorption in equilibrium

Langmuir

rate

Reaction Controls
(large P_A or θ_A)

Reaction Controls (Small P_A or θ_A)
or Adsorption A Controls

P_A
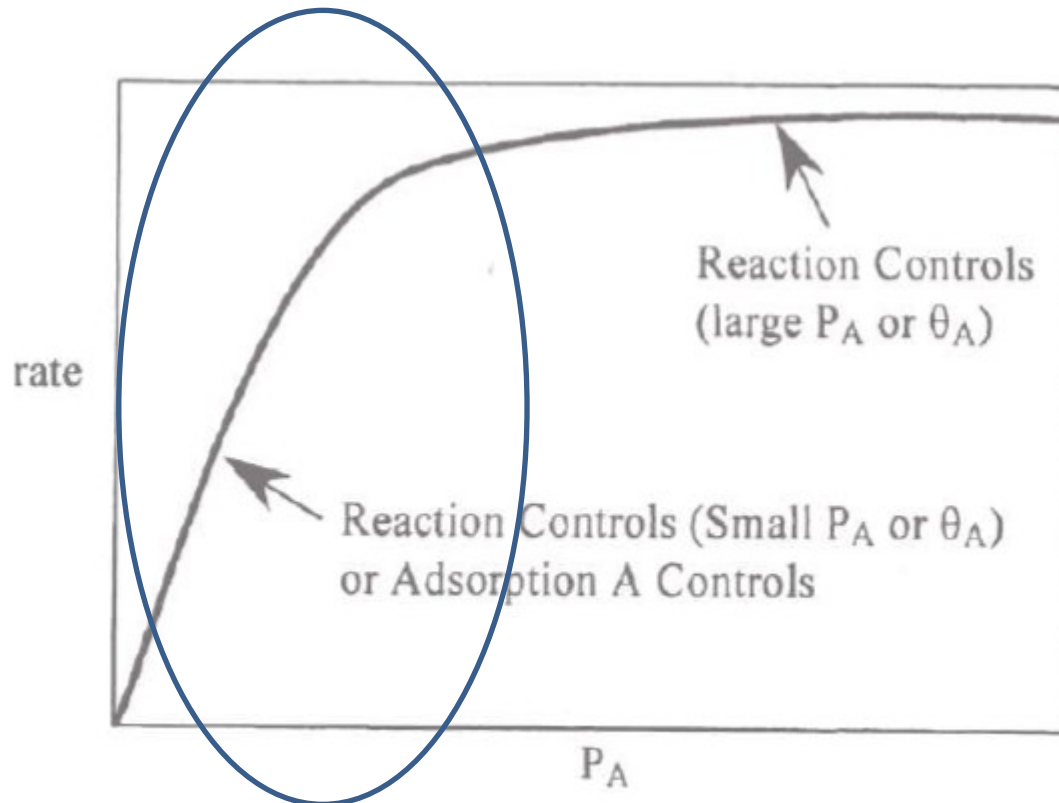
Reaction rate ≈ k·[A]

First order reaction

Note:

k can be $k_{A \to P}$

Or

$k_{A\text{-adsorption}}$

Langmuir

Surface is fully covered with A

No change with increasing [A]

Reaction rate ≈ k

Zero order reaction

rate

Reaction Controls
(large P_A or θ_A)

Reaction Controls (Small P_A or θ_A)
or Adsorption A Controls
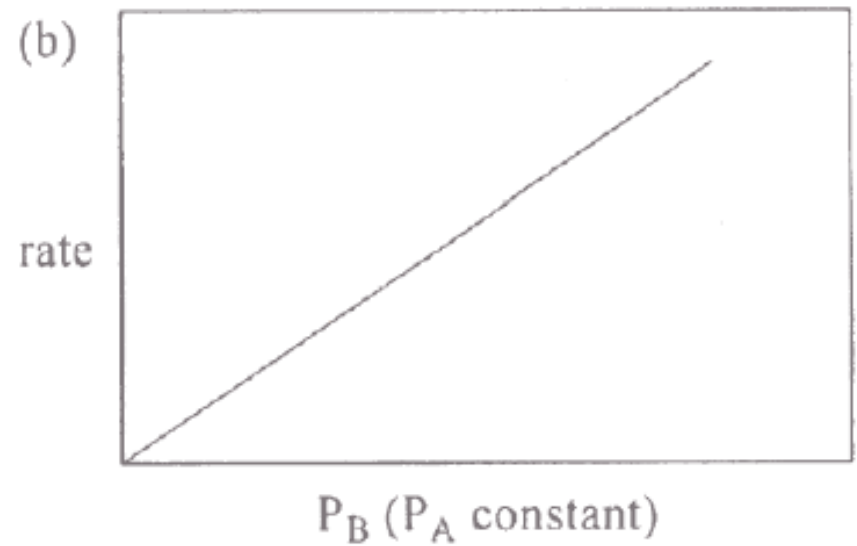
P_A
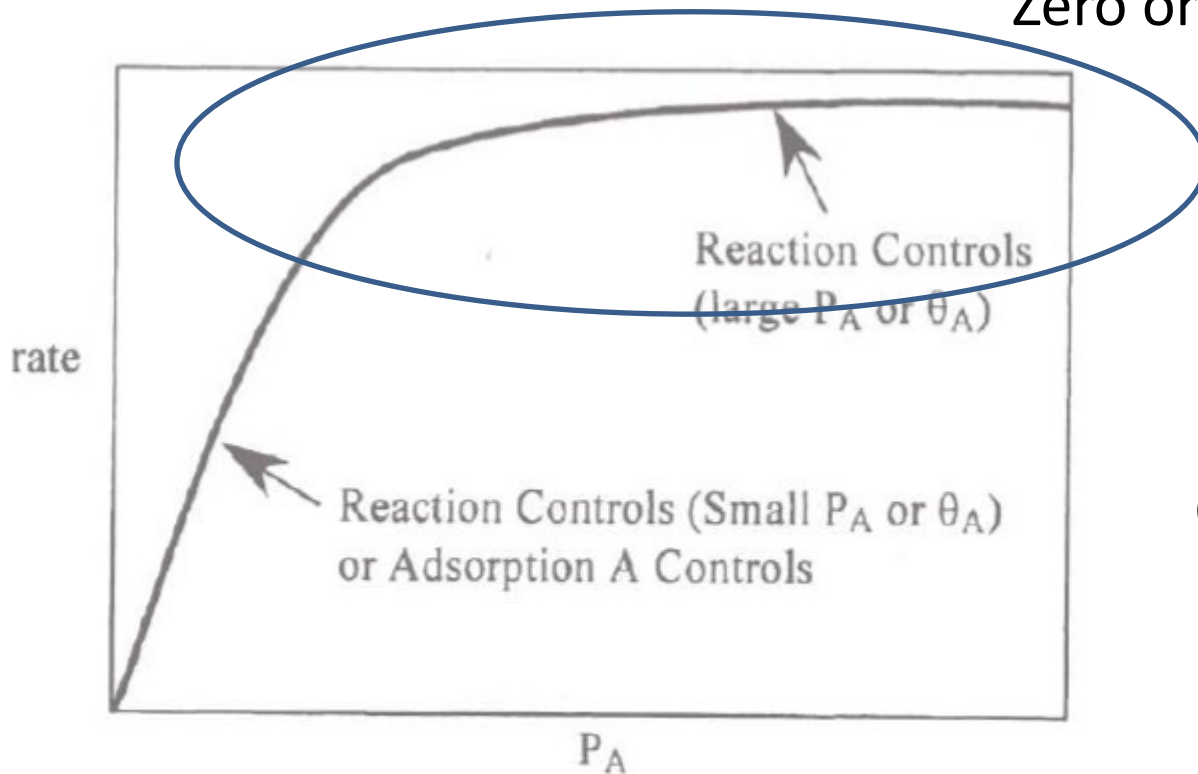
Note:

k can be $k_{A \rightarrow P}$

Or

$k_{P\text{-desorption}}$

Mechanisms of catalytic reactions

- Langmuir (monomolecular)
  - A(adsorbed) → P(adsorbed)
- **Langmuir-Hinshelwood (bimolecular)**
  - **A(adsorbed) + B(adsorbed) → P(adsorbed)**
- Eley-Rideal (bimolecular)
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- Mars-van Krevelen (special case)

Langmuir-Hinshelwood

- Competition between A and B adsorbates for adsorption sites
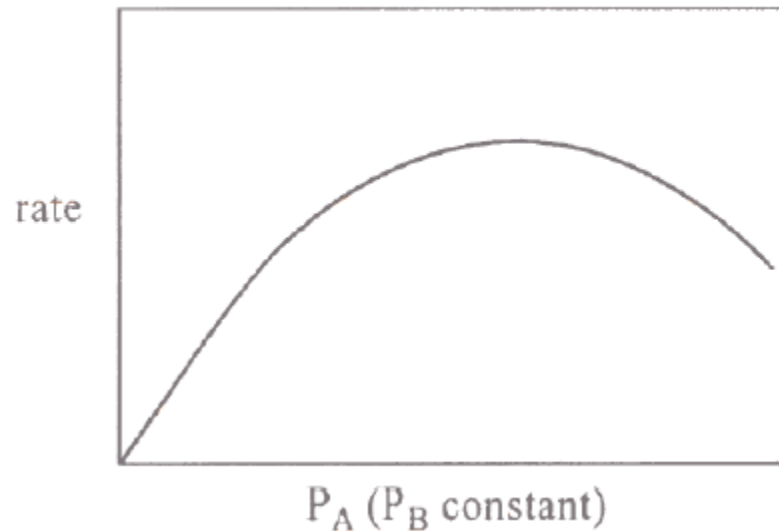
rate

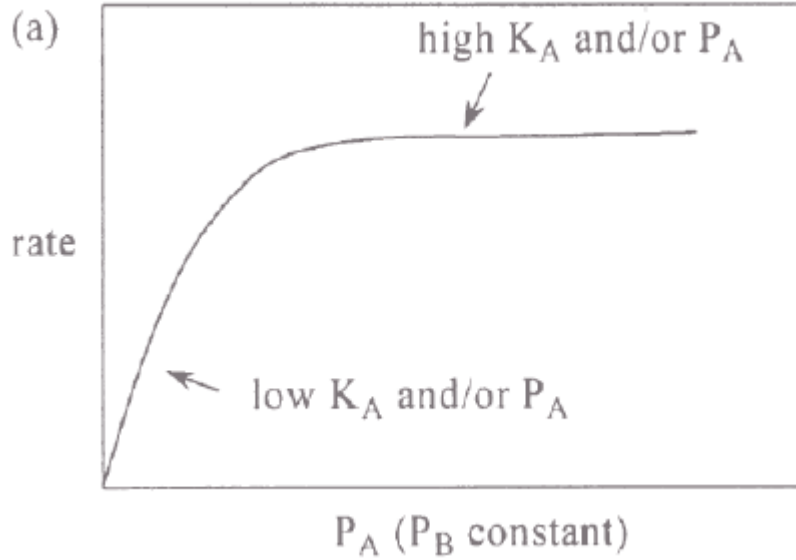P_A (P_B constant)

Mechanisms of catalytic reactions

- Langmuir (monomolecular)
  - A(adsorbed) → P(adsorbed)
- Langmuir-Hinshelwood (bimolecular)
  - A(adsorbed) + B(adsorbed) → P(adsorbed)
- **Eley-Rideal (bimolecular)**
  - **A(adsorbed) + B(gas phase) → P(adsorbed)**
- Mars-van Krevelen (special case)

Eley-Rideal

(a) high K_A and/or P_A

rate

low K_A and/or P_A

P_A (P_B constant)

(b)

rate

P_B (P_A constant)

Mechanisms of catalytic reactions

- Langmuir (monomolecular)
  - A(adsorbed) → P(adsorbed)
- Langmuir-Hinshelwood (bimolecular)
  - A(adsorbed) + B(adsorbed) → P(adsorbed)
- Eley-Rideal (bimolecular)
  - A(adsorbed) + B(gas phase) → P(adsorbed)
- **Mars-van Krevelen (special case)**

Mars-van Krevelen

- Example: oxidation of toluene over V_2O_5
  - Oxygen comes from crystal lattice (confirmed by isotope studies)
    - Creation of oxygen vacancies
    - Regeneration of catalyst with O_2 in the feed

V_2O_{5-x}

O_2

V_2O_5

$+ H_2O$
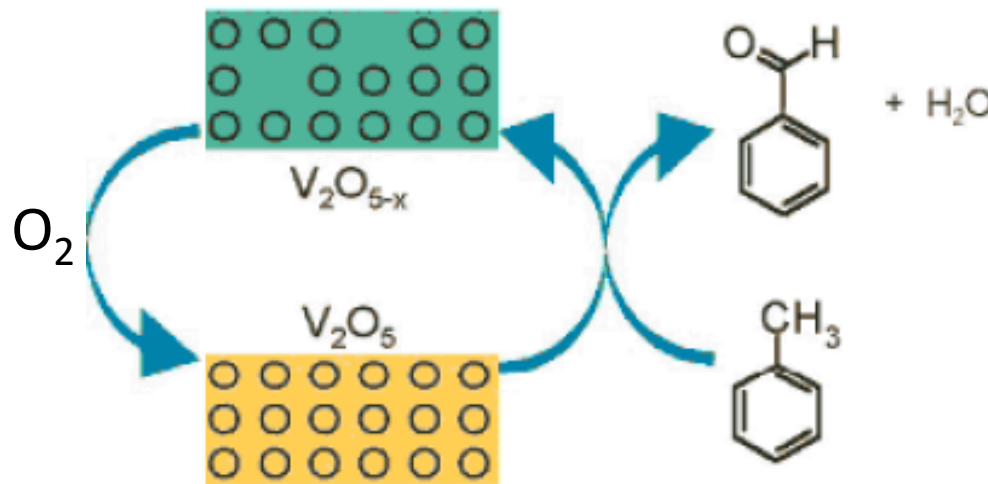
Note:

1. Catalyst should not change during catalysis!
2. Compare with Langmuir-Hinshelwood and Eley-Rideal

Mars-van Krevelen

- Possible only with metal oxides, sulphides, etc., where metal can achieve variable oxidation states and coordinations

- Catalyst works as a „bank"
  - It can borrow you oxygen if needed
  - It can save oxygen for worse times…

- Selectivity might be very high
  - Specific oxidation species within the crystal lattice

- Diffusion in solids needs to be considered
  - Vacancies play an important role

Mars-van Krevelen

- Possible only with metal oxides, sulphides, etc., where metal can achieve variable oxidation states and coordinations:

  – Oxidation of propylene to acrolein over MoO_{3-x}

  – Reduction of benzoic acid to benzaldehyde over MoO_{3-x}

  – Hydrodesulfurization of DBT do DB over $NiMoS_{2-x}$

  – Oxidation and reduction of gases in car exhausts over CeO_2-Ce_2O_3
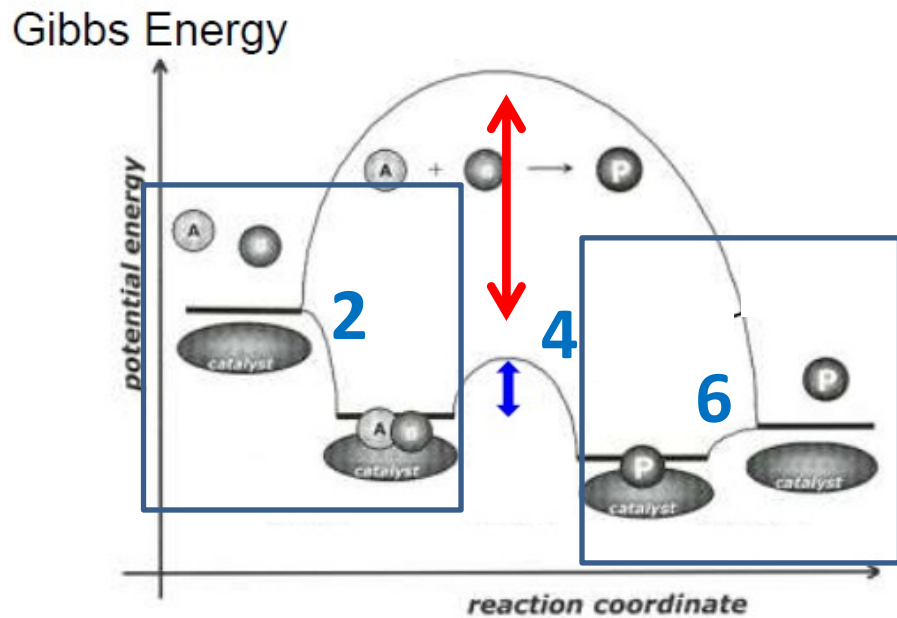
Thermodynamics + steps of cat reaction

A + B → P
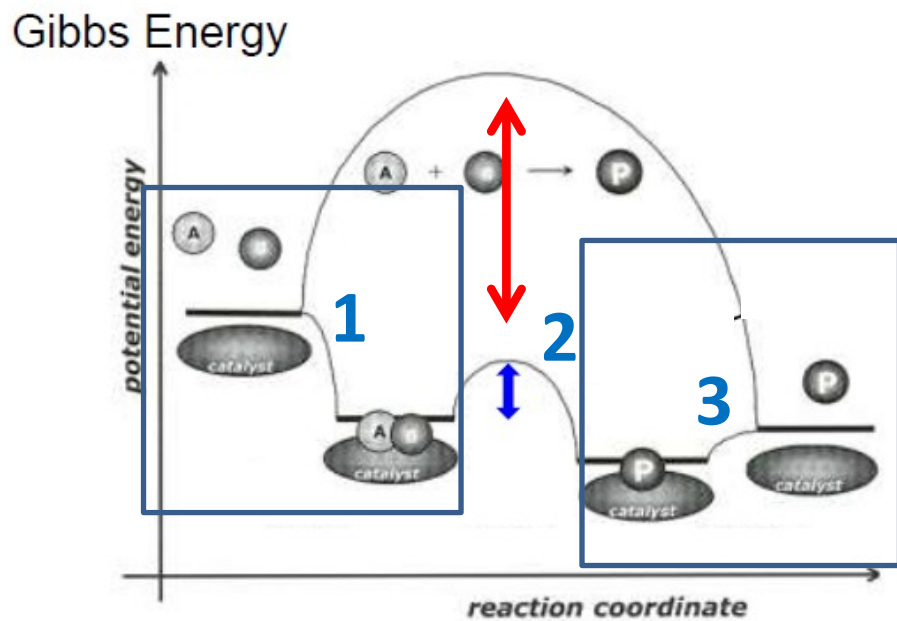
1: Adsorption of reactants on catalyst surface
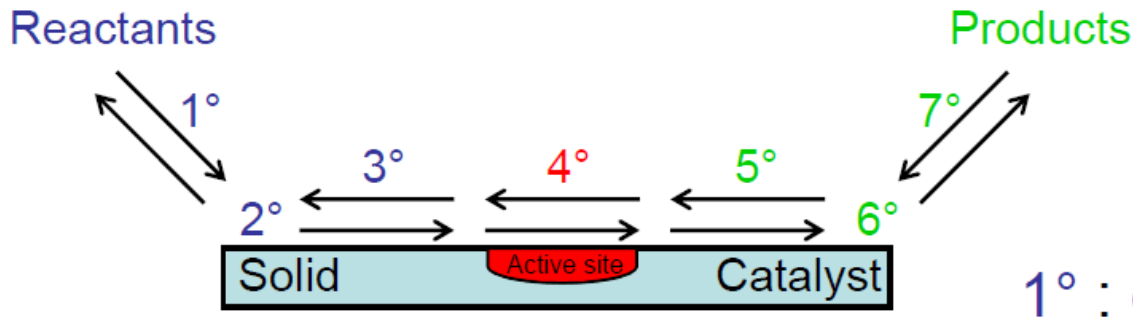
2: Reaction on active site

3: Desorption of products from catalyst surface

Steps of catalytic rxns

A + B → P

1: Diffusion medium→catalyst

2: Adsorption of reactants

(**3:** Diffusion on cat. surface)

4: Reaction on active site

(**5:** Diffusion on cat. surface)

6: Desorption of products

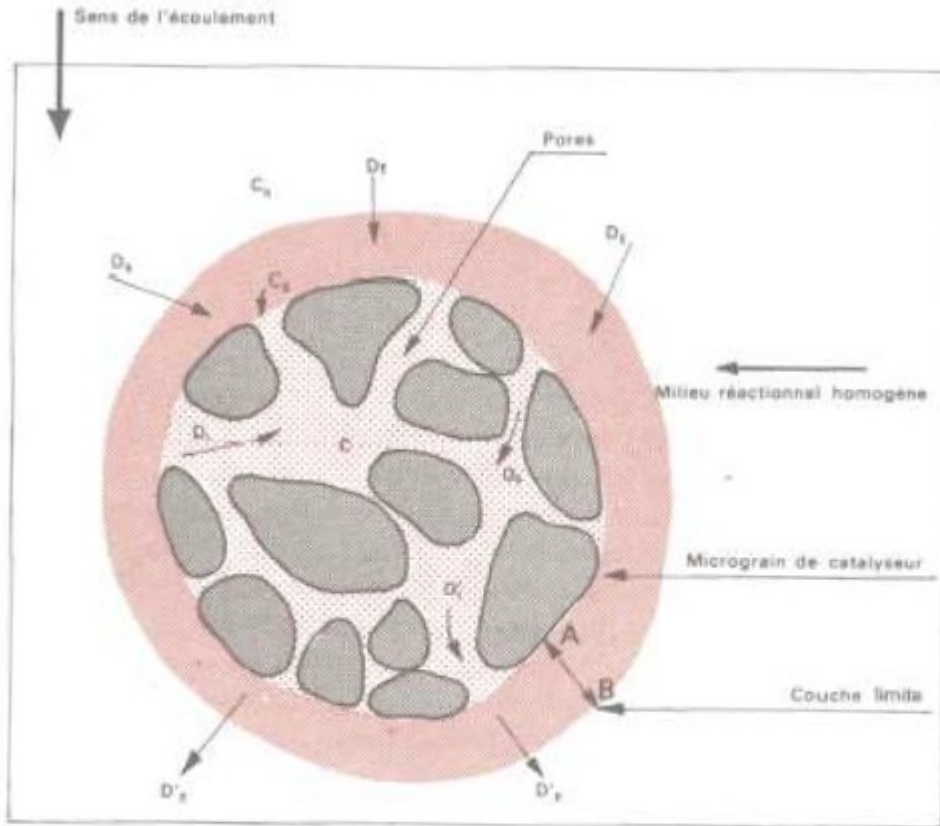**7:** Diffusion catalyst→medium

Steps of catalytic rxns

FIG. I.1 Processus de diffusion en catalyse hétérogène.

D_r : diffusion intragranulaire des réactifs — D_j : diffusion intragranulaire des produits — D_E : diffusion extragranulaire des réactifs — D_x : diffusion extragranulaire des produits — C_k : concentration d'un réactif en phase homogène — C_x : concentration de ce réactif au niveau de la surface extérieure — C : concentration à l'intérieur des pores.

En pointillé, couche laminaire immobile dont l'épaisseur (AB) varie selon le régime d'écoulement ou l'agitation du milieu réactionnel $(AB$ compris entre 10^{-1} at 10^{-2} mm).

1a: Diffusion of the reactant in the fluid film surrounding the catalysts grain (**External diffusion**; macroporosity)

1b: Diffusion of the reactant in porous network until reaching surface (**Internal diffusion**; micro- and mesopores)

2: Adsorption of reactants

(**3:** Diffusion on cat. surface)

4: Reaction on active site

(**5:** Diffusion on cat. surface)

6: Desorption of products

7a: Diffusion of the product in the porous network until reaching the aperture of the pore (**Internal diffusion**)

7a: Diffusion of the product in the fluid film (**External diffusion**)

Rate determining step

- Total: Up to 9 steps; 6 of them diffusion!
- All of them more or less contribute to the final reaction rate ($k_{apparent}$ and $E_{apparent}$)
- Slowest step???

Rate determining step

- 6 steps based on diffusion
  - Fick laws
  - **Low** dependance on temperature
  - E_a = 4–8 kJ mol^{-1}

- 3 steps based on chemistry
  - **High** dependance on temperature $\mathbf{k = A \cdot e^{-Ea/RT}}$
  - E_a = 20–200 kJ mol^{-1}

Slowest step of the catalytic reaction???

Depends on the temperature!!!

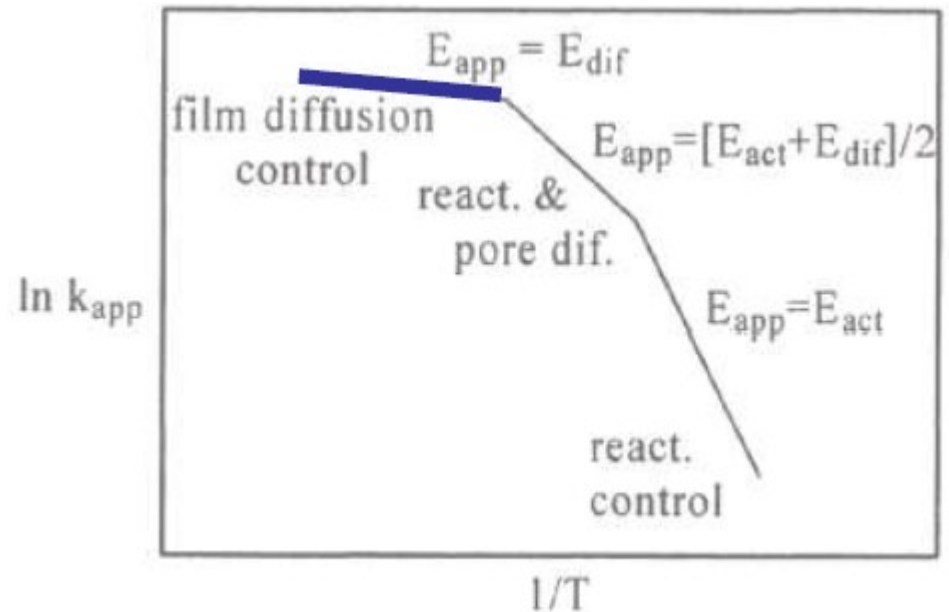# Rate determining step

- ## Low temperature
  - Chemical steps are limiting
 - $E_{app} = E_a$ of the reaction step
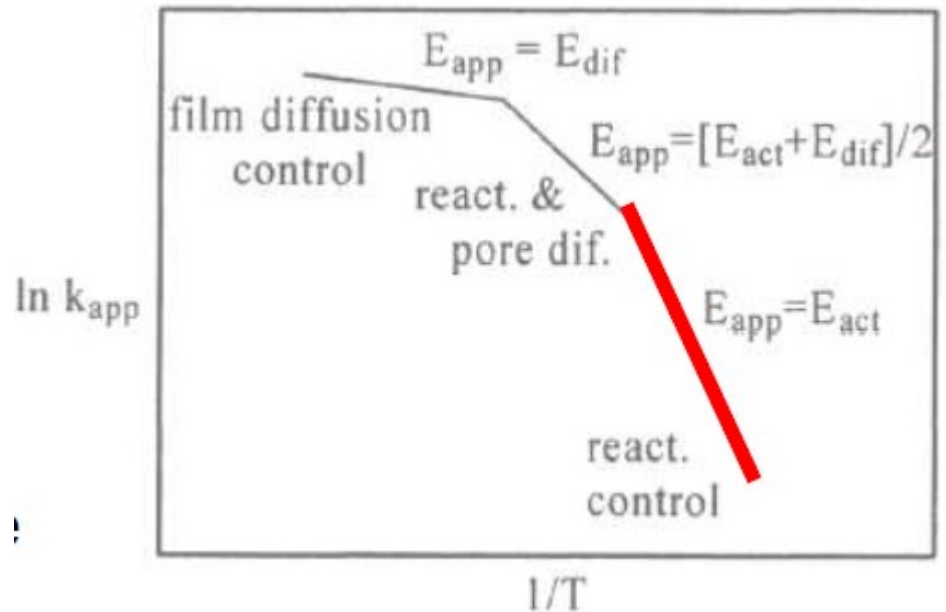
Rate determining step

- ## High temperature
  - The chemical reaction is fast
  - There is no time for **internal diffusion** to take place, only external surface employed in catalysis
  - Diffusional steps are limiting
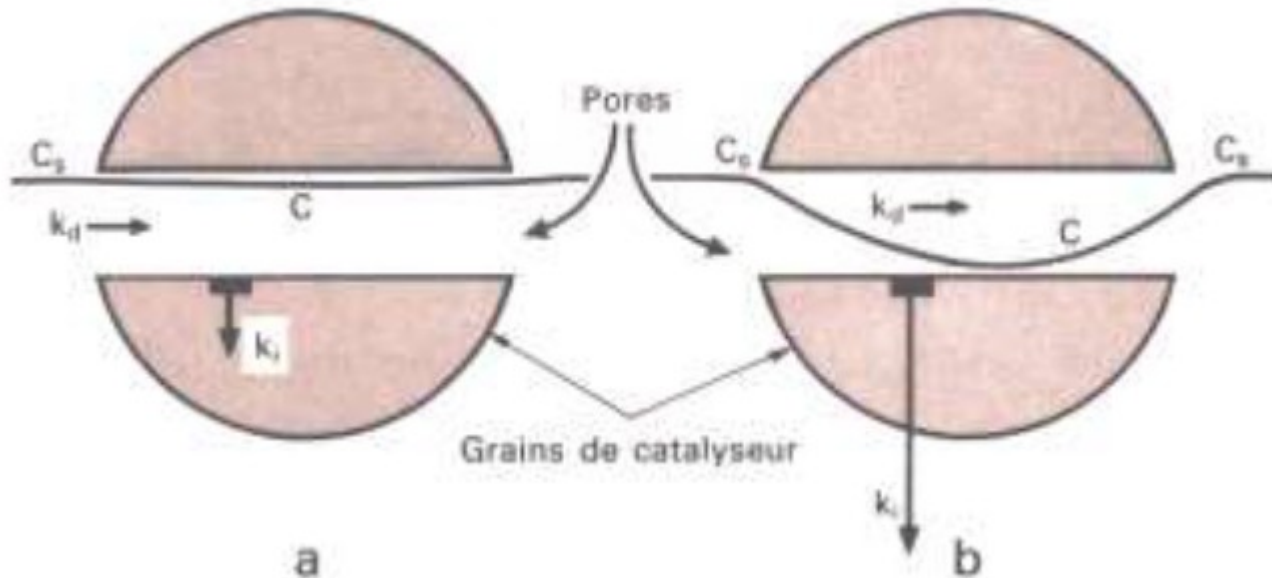 - E_{app} = E_a of the diffusion in the fluid film (**external diffusion**)

Rate determining step

- Intermediate temperature
  - Contribution of both chemistry and diffusion (diffusion in the pores, **internal diffusion**)
  - E_{app} = average of E_a of the reaction step and E_a of internal diffusion
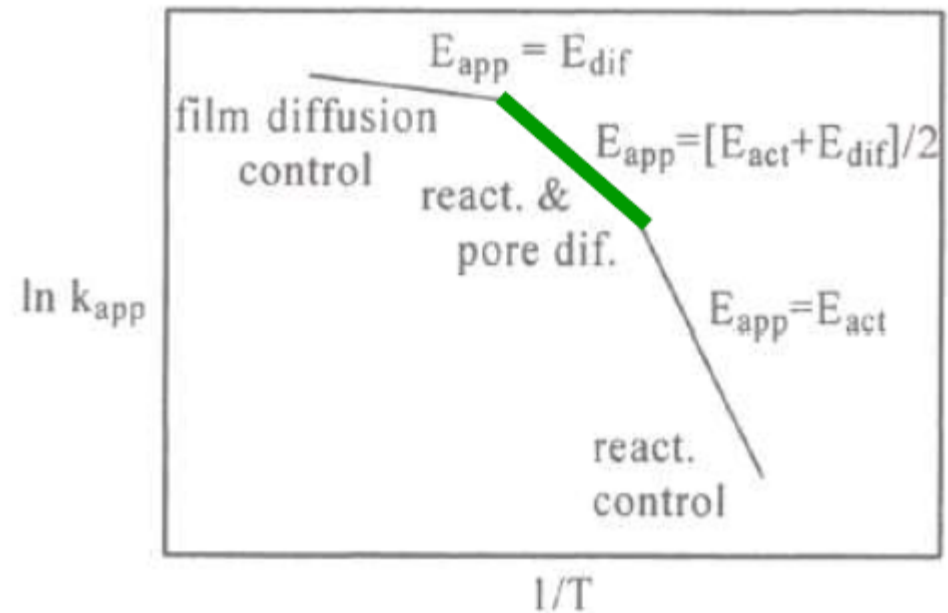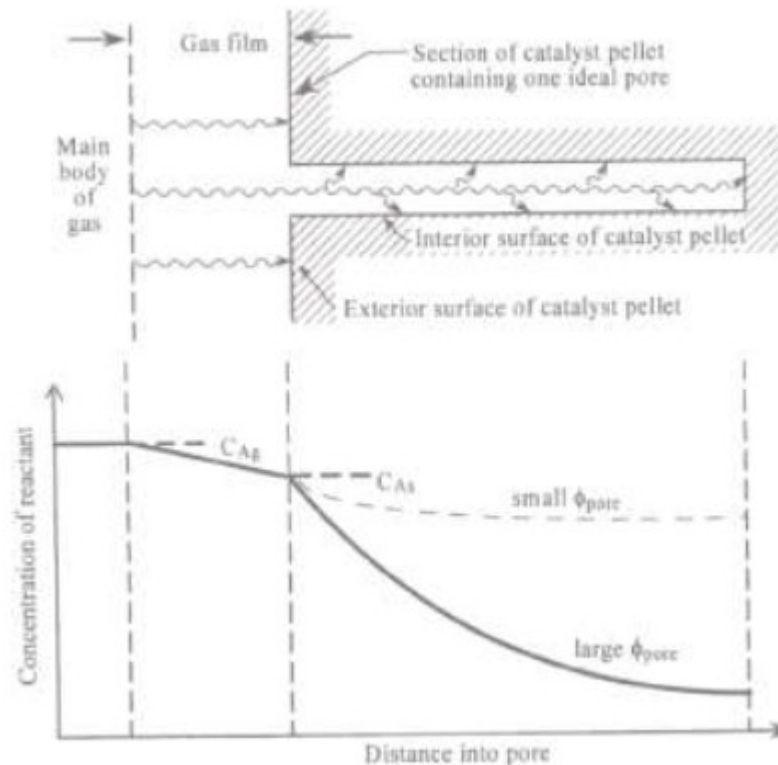
Diffusional limitation

k_d = diffusion constant; k_i = reaction rate constant per m^2 of catalysts; S = specific surface area

- k_d = $k_i \cdot$S; Surface is supplied with reactants; no diffusional limitation
- k_d << $k_i \cdot$S; Internal surface of the catalyst is not supplied with reactants; **Diffusional limitation**

Diffusional limitation

- Gradient of reactant concentration in
  - Fluid film of particle (External diffusion)
  - Inside the pore (Internal diffusion)

Diffusional limitation

- We want to use as many active sites as possible (even deep in the internal pore system)
- We want to avoid diffusional limitation

- **Effectivenes factor η** (observed reaction rate / maximal theoretical reaction rate) depends on Thiele modulus
- **Thiele modulus φ** describes the „quality" of catalyst grain in terms of **internal diffusion**:

$$\varphi = \frac{d_p}{2} \sqrt{\frac{k_i \cdot \rho_g \cdot S}{D_e}}$$

d_p = diameter of grain; k_i = reaction rate constant per m² of catalysts; S = specific surface area; ρ_g = density of the catalyst including pores; D_e = diffusion coefficient of the reactant in the pores

Diffusional limitation

- **Thiele modulus φ** describes the „quality" of catalyst grain in terms of internal diffusion:

$$\varphi = \frac{d_p}{2} \sqrt{\frac{k_i \cdot \rho_g \cdot S}{D_e}}$$

- The higher the Thiele modulus, the higher probability of diffusional limitations to occur

- Internal diffusional limitations occur always to some extent

Diffusional limitation

- **Thiele modulus φ** describes the „quality" of catalyst grain in terms of diffusion:

$$\varphi = \frac{d_p}{2}\sqrt{\frac{k_i \cdot \rho_g \cdot S}{D_e}}$$

- Let's decrease d_p = small catalyst grains
- Let's decrease ρ_g = higher pore volume
- Let's increase D_e = bigger pores

Catalyst synthesis, shaping, thermal treatment…

…in order to avoid the internal diffusional limitations as much as possible…

Diffusional limitation

- Gradient of reactant concentration in
  - Fluid film of particle (External diffusion)
    - Viscosity of vector gas
    - Linear velocity of vector gas
    - Size of the grains
    - Diffusion coeff of reactants
  - Inside the pore (Internal diffusion)
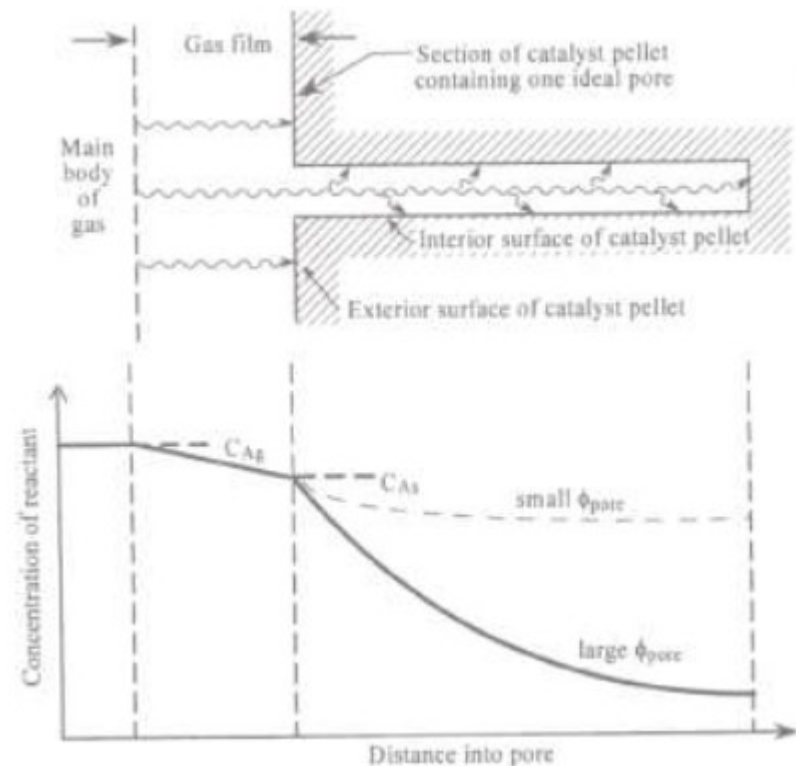
Diffusional limitations

- Note: Up to now we have discussed only diffusion of reactants

- Same applies for **heat diffusion**

- I.e. diffusional limitations can lead to important issues!
  - **Effectivenes factor η > 1**
  - **Hot spots**
  - **Sintering of catalysts**
  - **Shift/loss of selectivity**
  - **Explosion**

Industrial point of view

Diffusional limitations

- Internal diffusional limitations always present to some extent
  - We can diminish them **at the time of catalyst preparation** (pore volume, pore diameter, size of catalysts grains)
- External can be avoided **at the time of catalytic reaction**
  - Linear velocity of vector gas,…
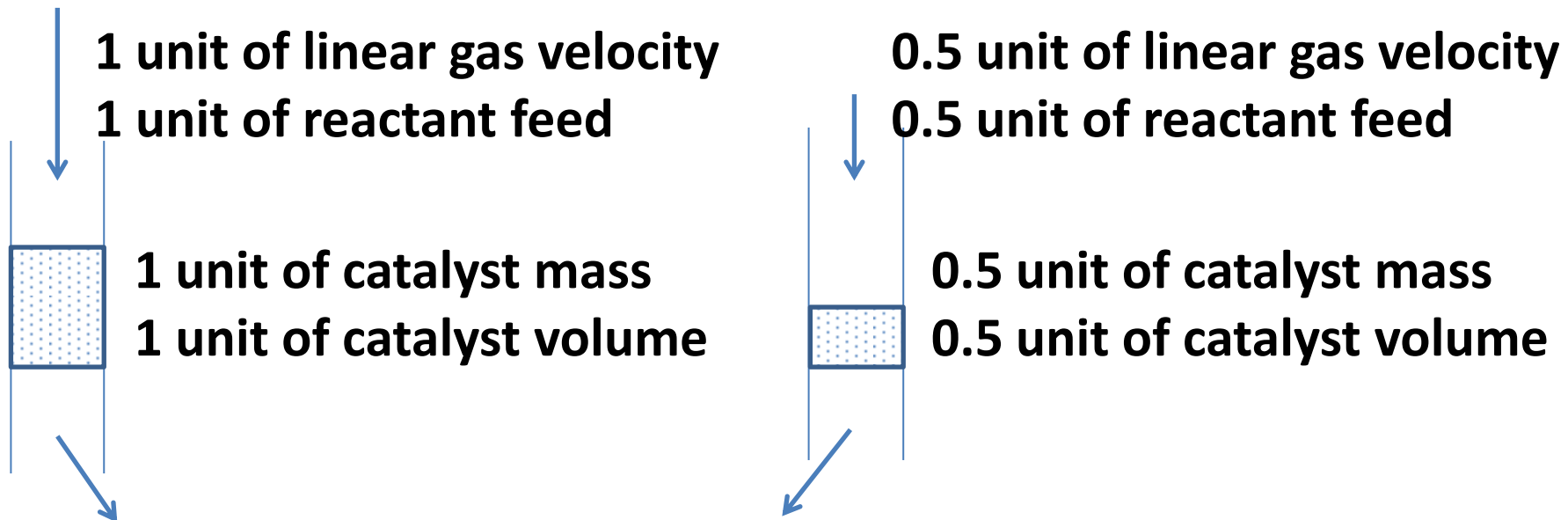- How to reveal external diffusional limitations?

Diffusional limitations

- How to reveal external diffusional limitations?

- Constant temperature and constant **contact time** (other parameters can vary) lead to constant conversion, selectivity, and yield

Diffusional limitations

- How to reveal external diffusional limitations?

- Contact time practically???

1 unit of linear gas velocity
1 unit of reactant feed

0.5 unit of linear gas velocity
0.5 unit of reactant feed

1 unit of catalyst mass
1 unit of catalyst volume

0.5 unit of catalyst mass
0.5 unit of catalyst volume

Conversion, yield, and selectivity are equal!
If not, then we encounter external diffusional limitations!

Space velocity and contact time

- Contact time = 1/space velocity

- Space velocity [h^{-1}]
  - Based on catalyst mass (WHSV, weight hourly space velocity)
    - weight of reactant per weight of catalyst per hour

  - Based on catalyst volume (GHSV or LHSV – gas/liquid...)
    - Volume of feed gas@STP (**reactant + gas vector**) per volume of **catalyst bed** per hour

Be careful, contact time can be based on WHSV, GHSV, or LHSV!
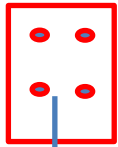
Space velocity and contact time

- Calculations with volumes always much less convenient than weight…

- So…Why is GHSV/LHSV important in heterogeneous catalysis??

1 unit of linear gas velocity
Feed of reactant constant

0.5 unit of linear gas velocity
Feed of reactant constant

1 unit of catalyst mass
1 unit of catalyst volume

1 unit of catalyst mass
1 unit of catalyst volume
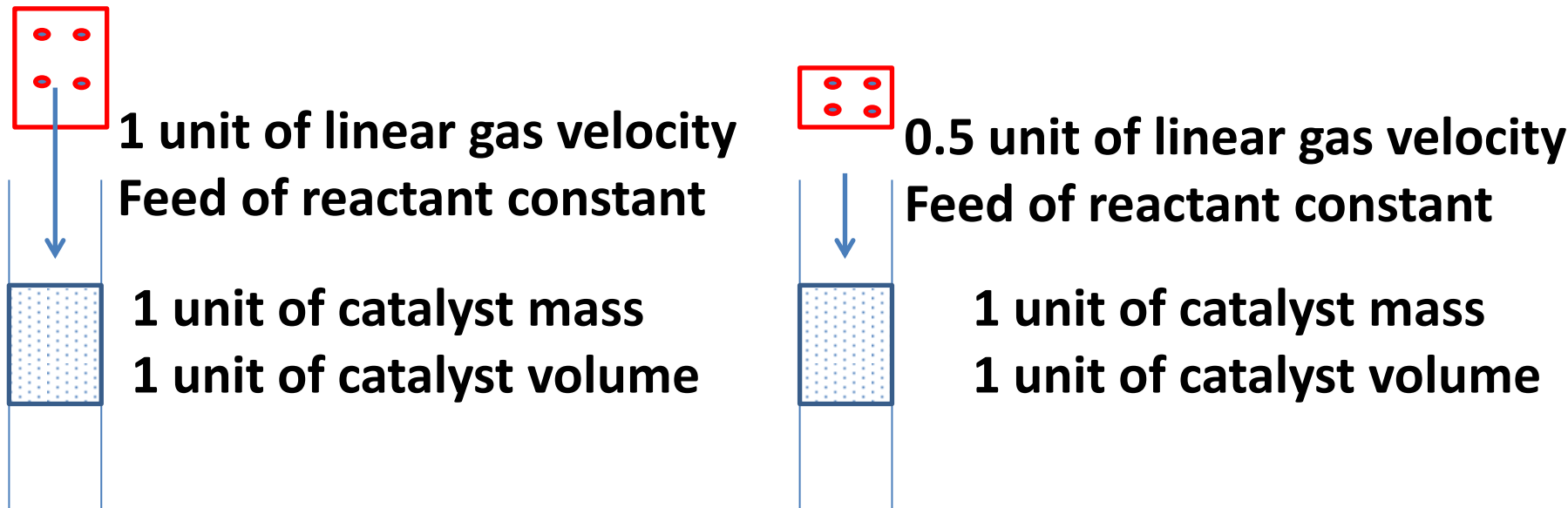
WHSV is constant. GHSV is different.
Conversion, yield, and selectivity are different!

Space velocity and contact time

1 unit of linear gas velocity [m^3 h^{-1}]
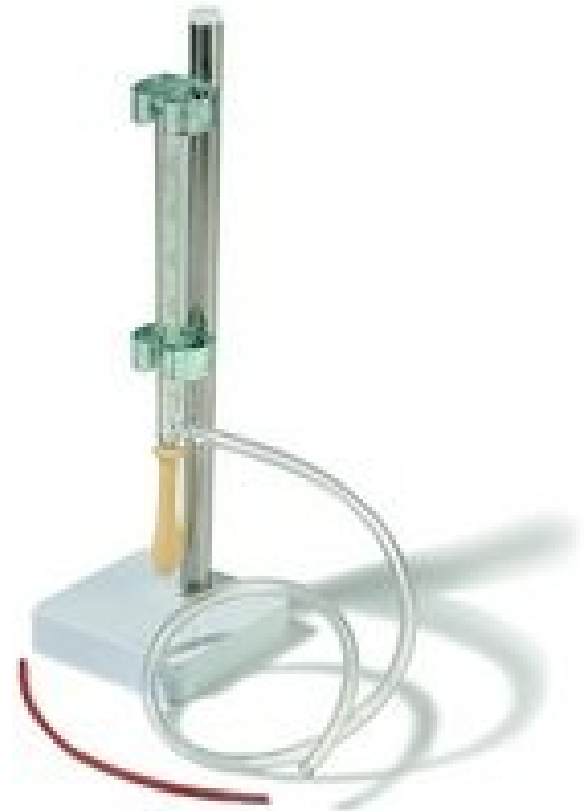1 unit of reactant feed
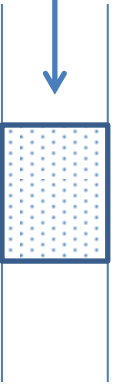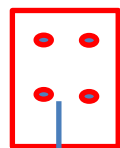
1 unit of catalyst mass
1 unit of catalyst volume

Mass flow controller

MF-1

FLOW

Soap bubble flow meter

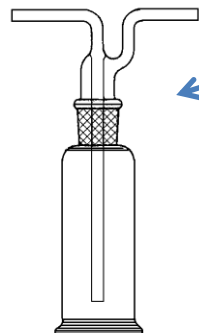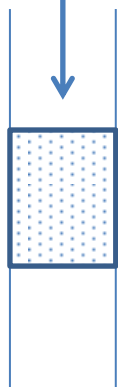# Space velocity and contact time

1 unit of linear gas velocity
1 unit of reactant feed [g or cm³ h⁻¹] → gas
(= mass flow control, soap…)
→ liquid

1 unit of catalyst mass
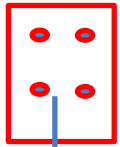1 unit of catalyst volume
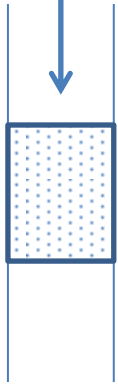
Vapor saturator (= bubbler)

Automatic syringe pump

Space velocity and contact time

1 unit of linear gas velocity
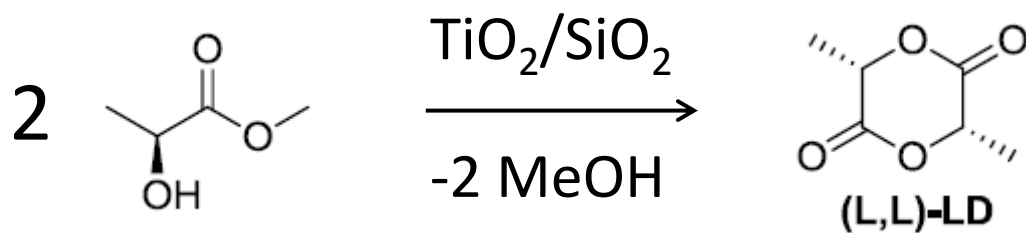1 unit of reactant feed

1 unit of catalyst mass [g]
1 unit of catalyst volume [cm³] → dilute with inert
material to
a constant volume

Remember,
GHSV important for catalyst comparison

Homework 2

2 [lactic acid methyl ester structure] $\xrightarrow[\text{-2 MeOH}]{\text{TiO}_2/\text{SiO}_2}$ [(L,L)-LD structure]

(L,L)-LD

- Gas phase transesterification
- Continuous flow fixed bed reactor

Temperature [°C]	Conversion sample 1 (4.2 wt% Ti) [%]	Conversion sample 2 (0.9 wt% Ti) [%]
220	39	8.6
230	48	9.6
240	59	13
250	82	17
260	93	21

Selectivity = 90 % in all cases; WHSV = 15.5 h^{-1}

ACS Catal. 2018, 8, 9, 8130–8139

- Create Arrhenius plots for both catalysts (plot ln k [mol$_{LD}$ g$_{cat}^{-1}$ h^{-1}] vs. 1000/T [K^{-1}]
- Estimate apparent E_a and A from Arrhenius equation
- What makes the difference between these two catalysts?