Heterogeneous catalysis (C9981)

0. Technical information
1. Basic principles, thermodynamics, and a little bit of kinetics
2. Active sites and catalyst evaluation

Technical information

Syllabus

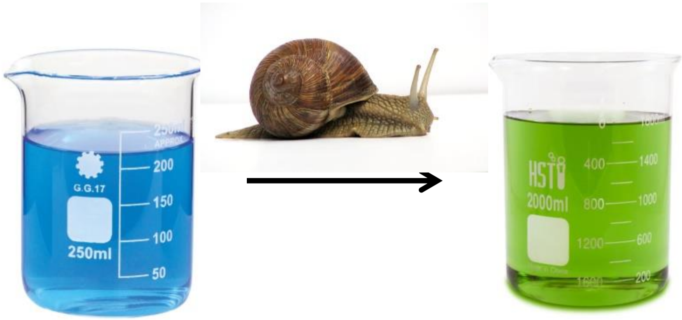
- Theory behind the heterogeneous catalysis: thermodynamics, kinetics, diffusion.
- Synthesis of heterogeneous and single-site catalysts
- Characterization
- **Your presentations**
- Examples of industrial catalytic processes: Haber-Bosch synthesis of ammonia; Three-way catalysts; Zeolites in oil refinement; Olefin metathesis.

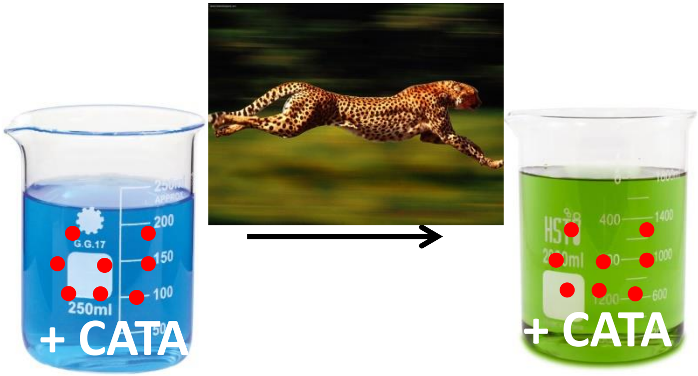
Homeworks

- Not mandatory
- **But** useful for the exam
- We will go through the homeworks in the lectures **only if** there are some homeworks to go through (uploaded in the information system)

Definition

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

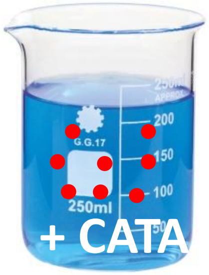




- We get our products
  - In shorter time; at lower rxn temperature; at lower pressure
  - **cheaper; economical; ecological**

Types of catalyst (based on phase)

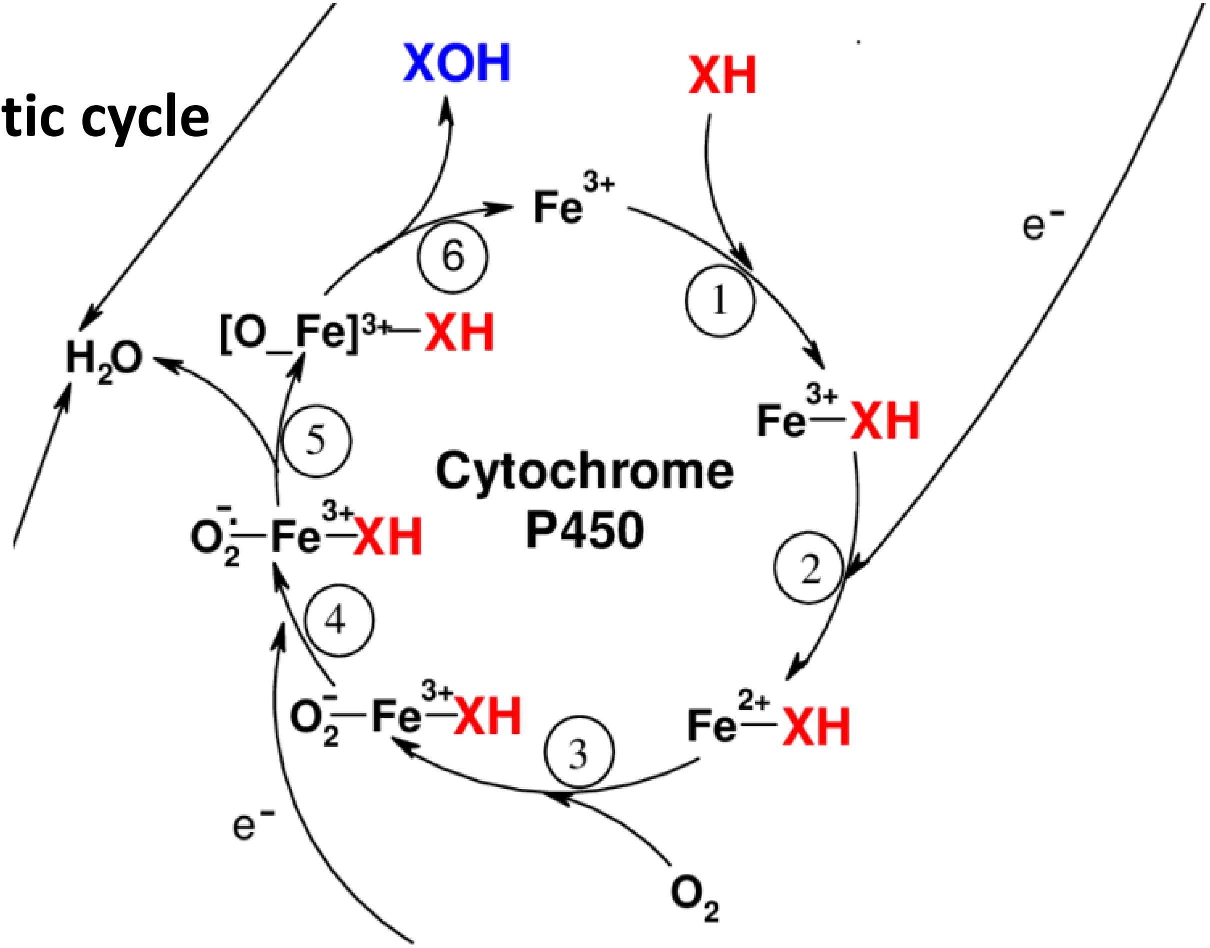
- Homogeneous
- Heterogeneous
- Enzymatic



Enzymatic catalysis

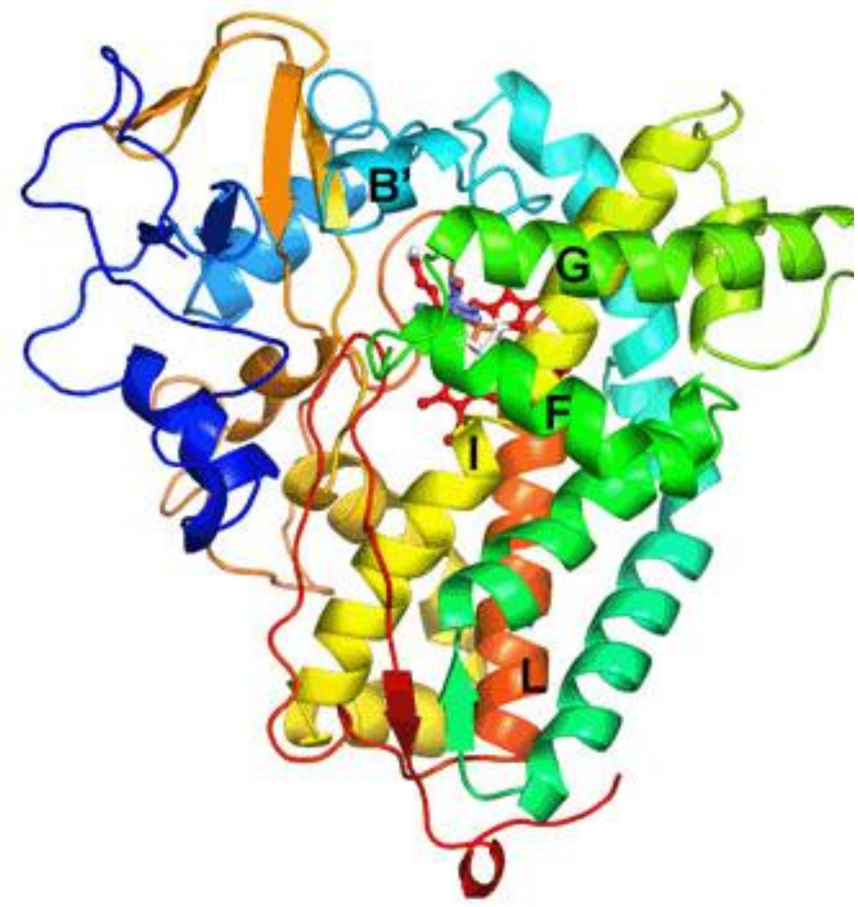
- Cytochrome P450

Catalytic cycle

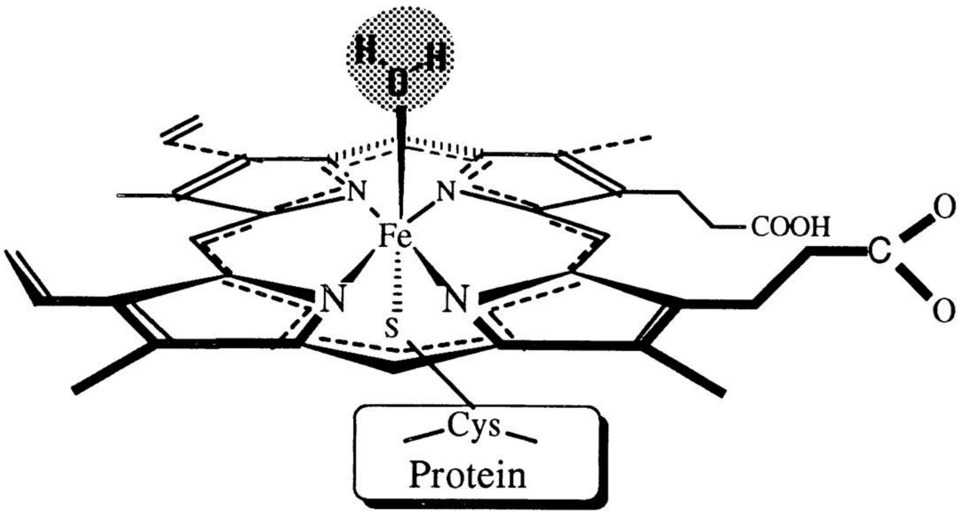


Enzymatic catalysis

- Cytochrome P450



Active site



Homogeneous catalysis

- A catalyst and rxn mixture in **one unique phase**
- Gas phase

1/

Cl + $O_3 \rightarrow ClO_3$

$ClO_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow$ **Cl** + O_2

Total:

$$\mathbf{O_3 + O \rightarrow 2\ O_2}$$

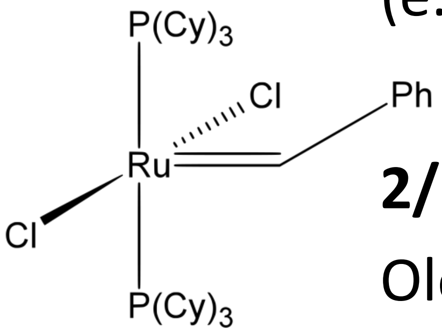
2/

Isomerization of hydrocarbons with **HF** (both in gaseous phase)

- Liquid phase

1/

Esterification of acids with alcohols catalyzed by **H^+** (e.g. **H_2SO_4, $H_3PW_{12}O_{40}$**)

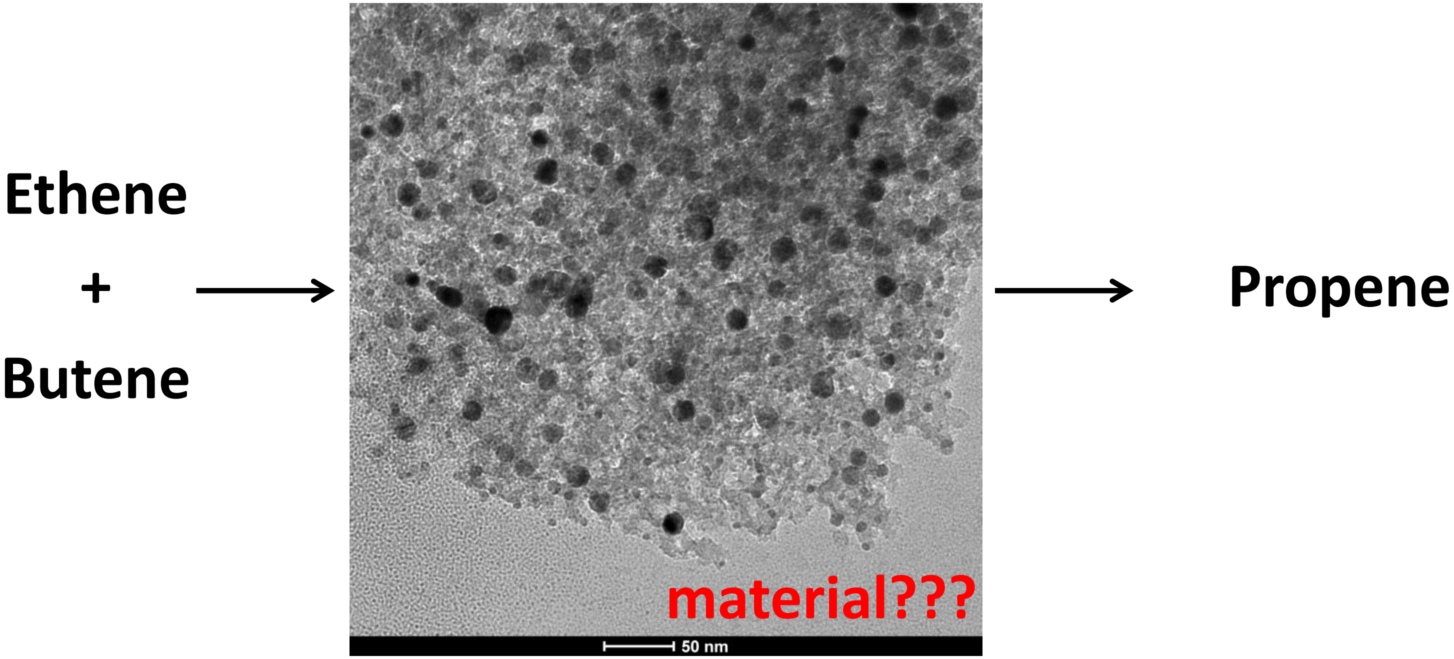


2/

Olefin metathesis over Grubbs catalyst (organometallics dissolved in liquid solvent along with precursors

Heterogeneous catalysis

- A catalyst is present in a **different, distinct phase** in contrary to the rxn mixture
- Gas phase rxn mixture over solid catalyst
  - Olefin metathesis



Ethene

+

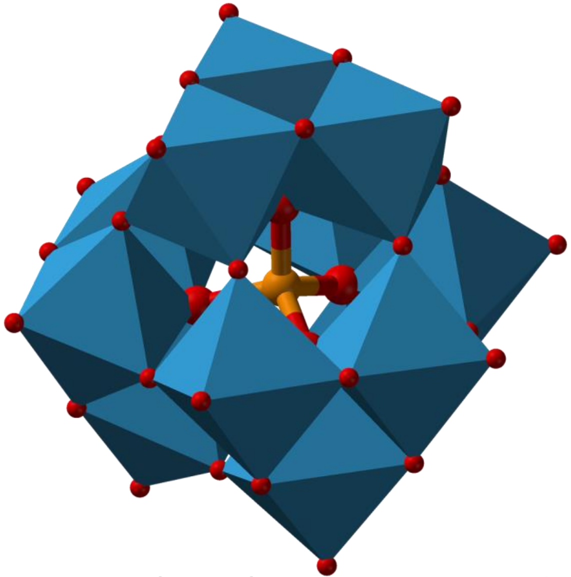
Butene

Propene

Heterogeneous catalysis

- A catalyst is present in a **different, distinct phase** in contrary to the rxn mixture
- Gas phase rxn mixture over solid catalyst
  - Alcohol dehydration

Methanol →

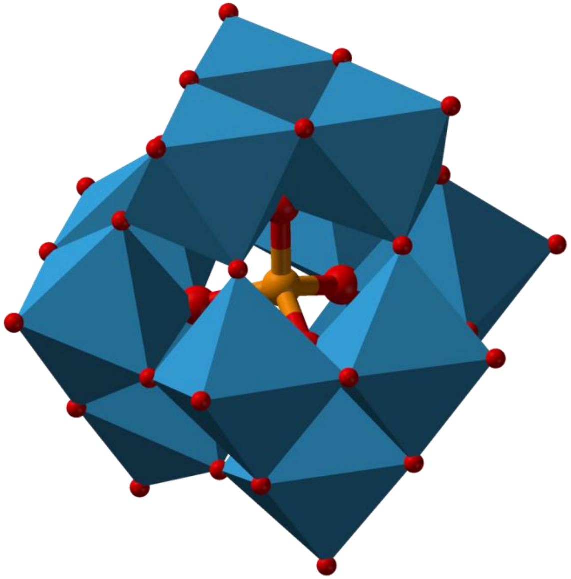


→ **Dimethylether**

$H_3PW_{12}O_{40}$; a molecular compound, not a material!

Heterogeneous catalysis

- A catalyst is present in a **different, distinct phase** in contrary to the rxn mixture
- Liquid phase rxn mixture over solid catalyst
  - Alcohol dehydration



Butanol ⟶ ⟶ **Dibutylether**

+

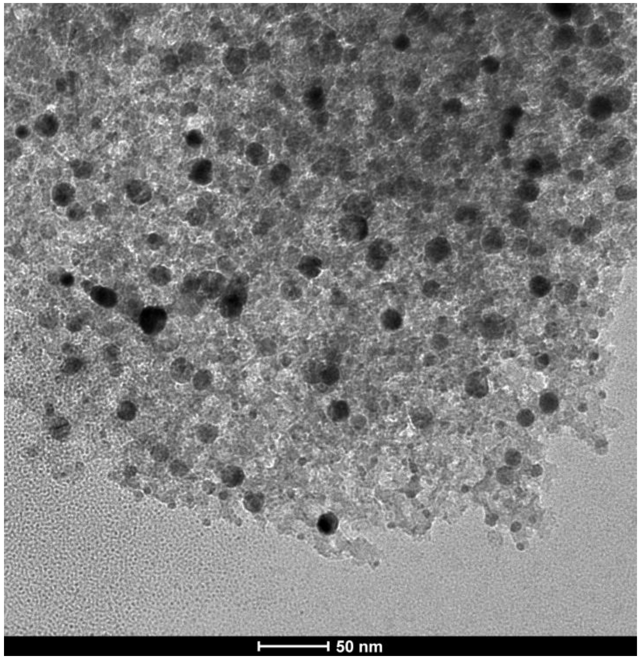
Butenes

$H_3PW_{12}O_{40}$; insoluble molecular compound

Heterogeneous catalysis

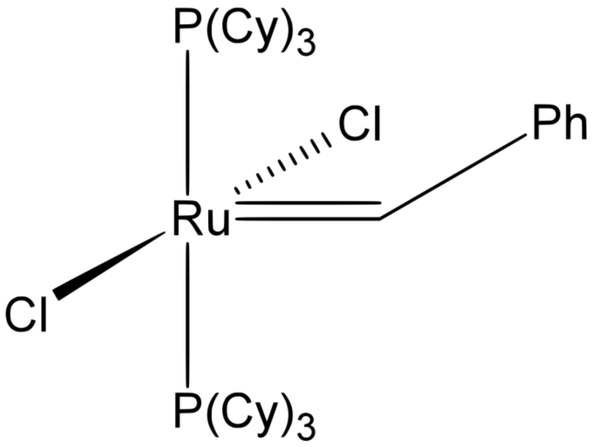
- A catalyst is present in a **different, distinct phase** in contrary to the rxn mixture
- Liquid phase rxn mixture over solid catalyst
  - Olefin metathesis

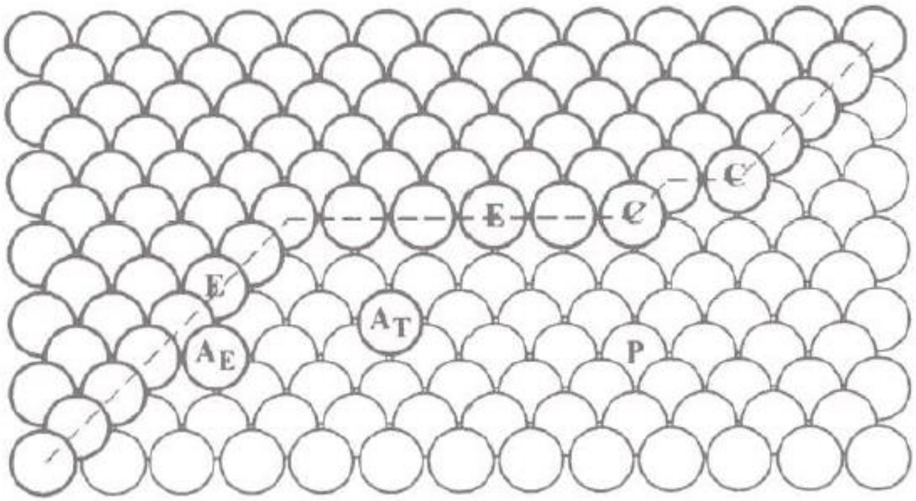
Longer olefins →



→ **Longer olefins**

Heterogeneous vs. Homogeneous catalysis

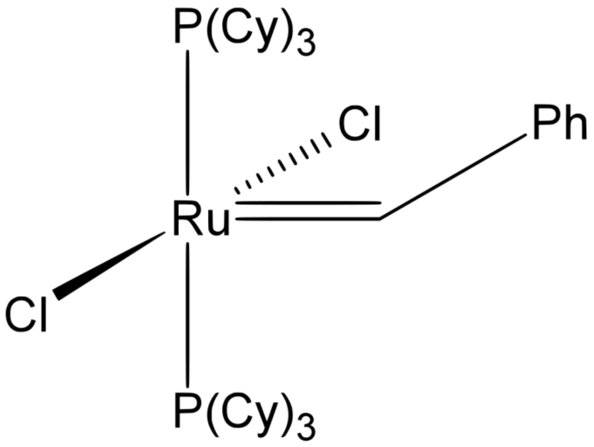


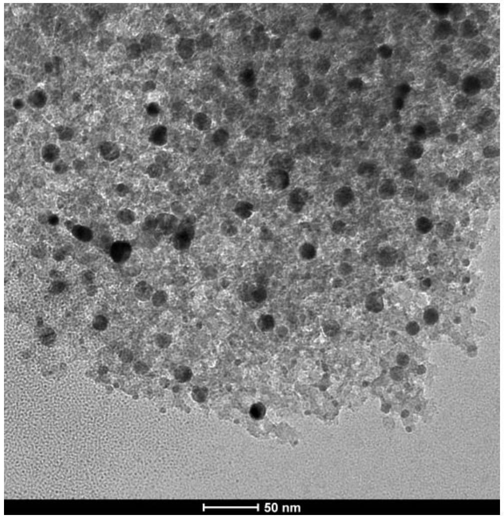


- **Well defined**
  = easier to characterize the active site, describe reactivity, and evaluate catalytic performance

- **Ill defined**
  = active site???
  = more than one type of active sites???
  = number of active sites???

Heterogeneous vs. Homogeneous catalysis

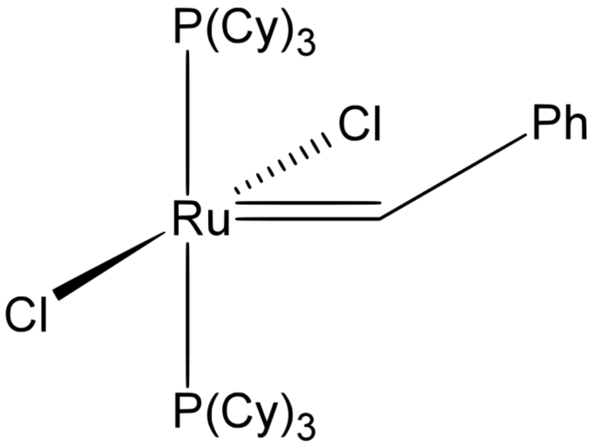


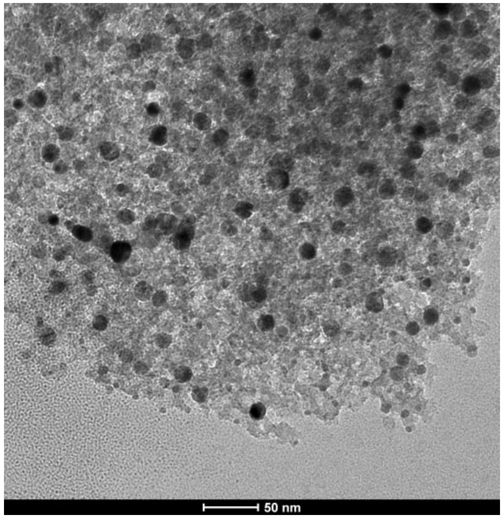


- **One phase with reactants**
  = higher probability that all necessary species meet and react☺

- **Distinct phase**
  = diffusion???
  = adsorption???
  = desorption???

Heterogeneous vs. Homogeneous catalysis

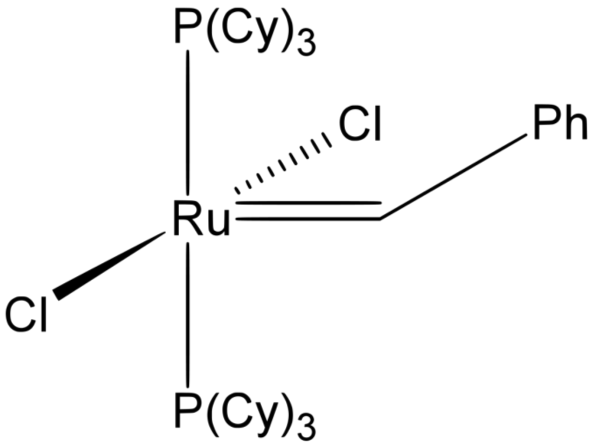


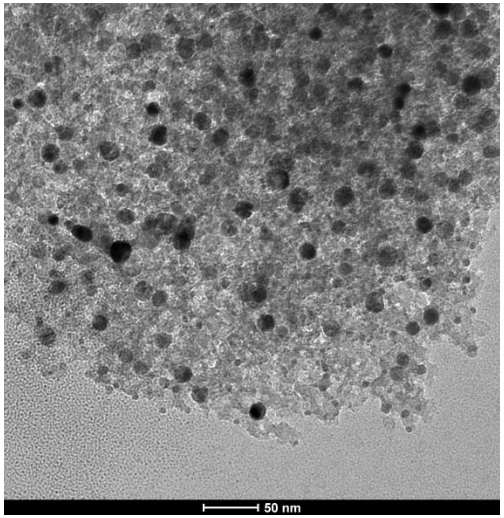


- **Separation???**
- **Reusability/Price???**
- **Toxicity???**
- **Batch rxns only???**

- **Distinct phase**
  = easy to separate
  = reusable/recyclable
  = clean products
  = continuous processes

Heterogeneous vs. Homogeneous catalysis



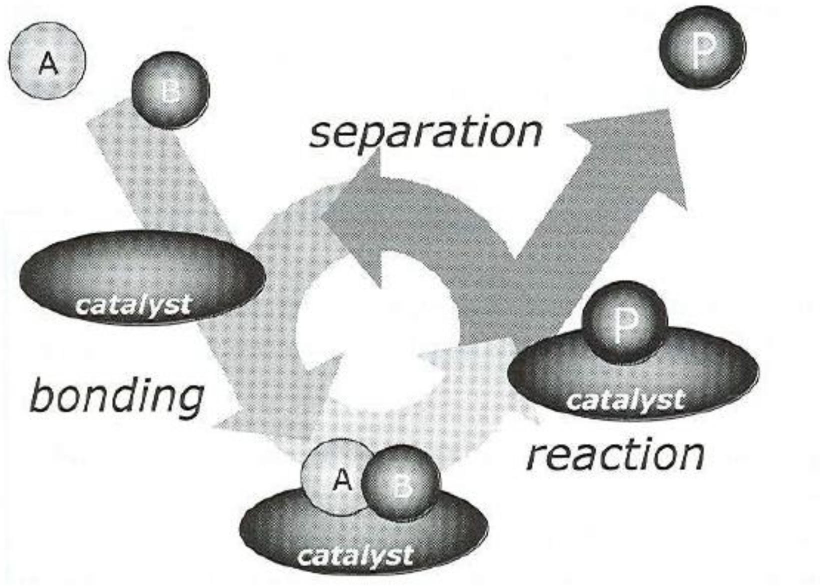


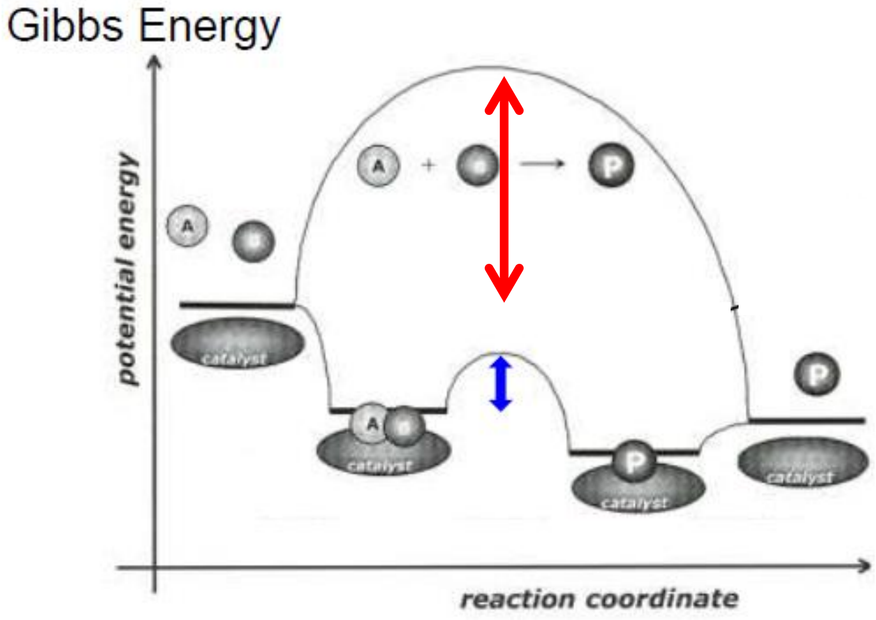
Homogeneous and Heterogeneous catalysis are complementary to each other

We choose either hetero or homo based on the rxn we want to catalyze (pros and cons)

Catalytic cycle

A + B → P





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

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

Thermodynamics vs. kinetics

- Addition of catalyst into the rxn mixture
  - **does** change „**k**“
  - **does not** change „**K**“

A → P, speeded up by addition of a catalyst

K = 1; ΔG = 0 kJ mol^{-1}; final rxn mixture: 1A + 1P

The catalyst is then **equally efficient** in catalysing **the opposite process**
P → A; final rxn mixture: 1A + 1P

Thermodynamics vs. kinetics

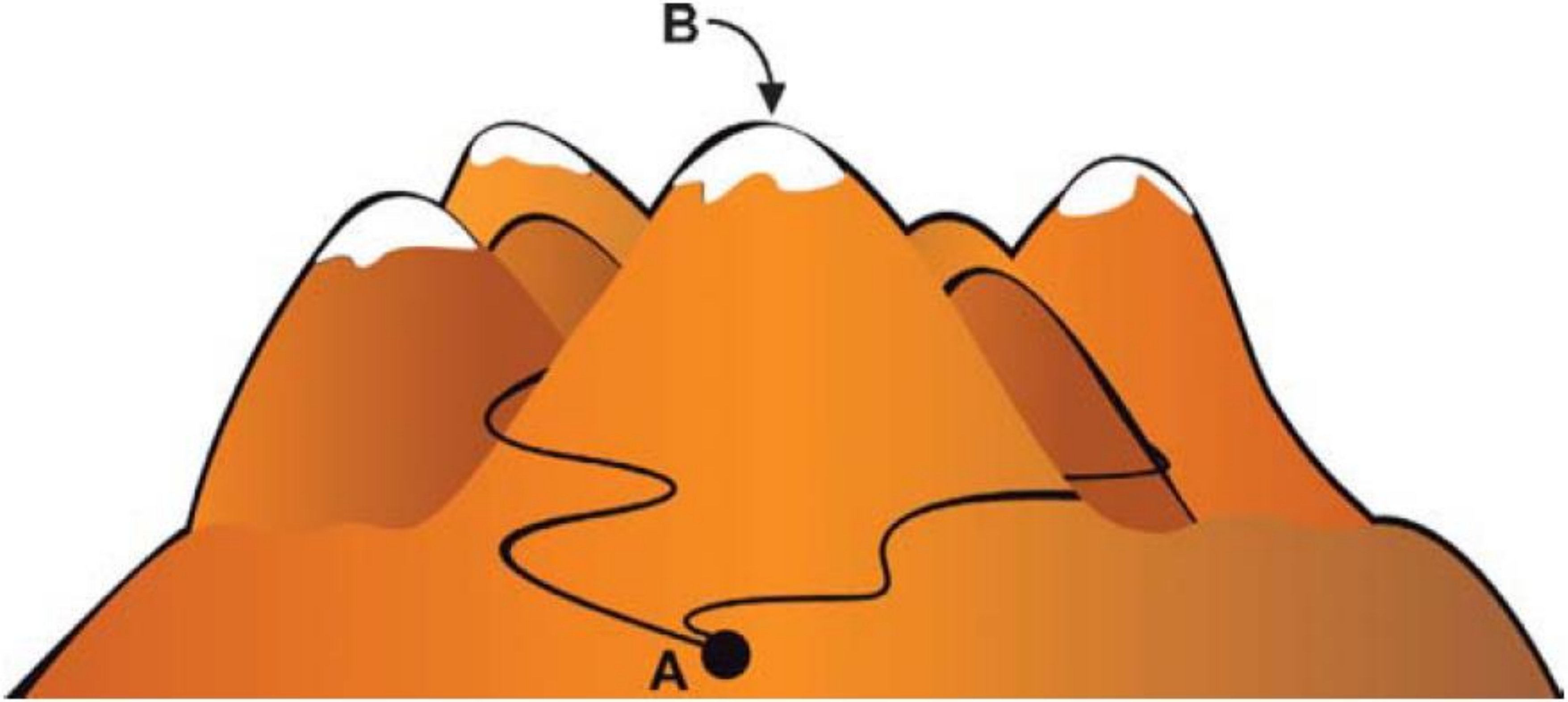
- If a catalyst is efficient in **dehydration**
  - then it can be possibly used in **hydration**
- If a catalyst is efficient in **hydrogenation**
  - then it can be possibly used in **dehydrogenation**

I.e.: It depends on **ΔG** of studied reaction, whether the **catalyst hydrogenates** or **dehydrogenates**.

We know how to shift equilibrium of chemical reaction☺ (#GenChem). This is not a job of the catalyst.

Thermodynamics vs. kinetics

- Reaction coordinate: A multidimensional problem



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Thermodynamics vs. kinetics

- Reaction coordinate: A multidimensional problem
  - e.g. selective oxidation reactions (Table 1)
    - We are not shooting for the most stable product (thermodynamically); **Difficult!**

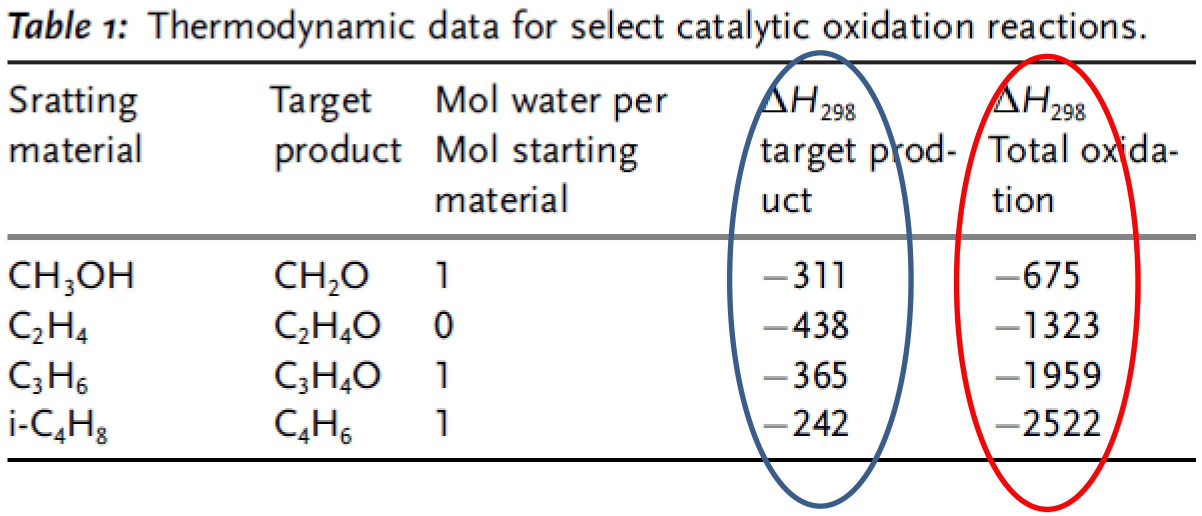

Table 1: Thermodynamic data for select catalytic oxidation reactions.

Sratting material	Target product	Mol water per Mol starting material	ΔH_{298} target product	ΔH_{298} Total oxidation
CH_3OH	CH_2O	1	−311	−675
C_2H_4	C_2H_4O	0	−438	−1323
C_3H_6	C_3H_4O	1	−365	−1959
i-C_4H_8	C_4H_6	1	−242	−2522

Mountain cottage

Spa resort

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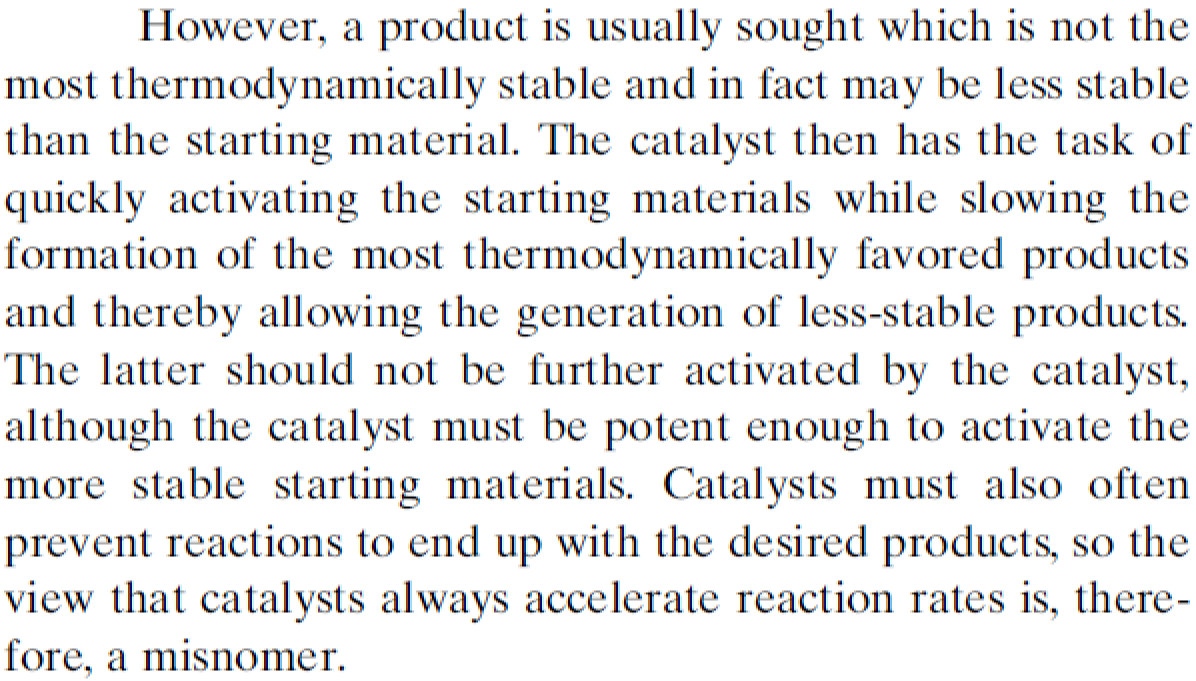
Thermodynamics vs. kinetics

- Reaction coordinate: A multidimensional problem
  - How is it possible that we sometimes end up in a mountain cottage and not in the spa resort???
  - We need a catalyst!
  - The catalyst will lower the activation energy of our way to the mountain cottage (beautiful views, crazy friends,…)
  - The catalyst will increase the activation energy of our way to the spa resort
  - E.g. The catalyst has to increase the rate of hiking (selective oxidation) and decrease the rate of hiking (total oxidation). What a difficult job!

Thermodynamics vs. kinetics

- Reaction coordinate: A multidimensional problem



However, a product is usually sought which is not the most thermodynamically stable and in fact may be less stable than the starting material. The catalyst then has the task of quickly activating the starting materials while slowing the formation of the most thermodynamically favored products and thereby allowing the generation of less-stable products. The latter should not be further activated by the catalyst, although the catalyst must be potent enough to activate the more stable starting materials. Catalysts must also often prevent reactions to end up with the desired products, so the view that catalysts always accelerate reaction rates is, therefore, a misnomer.

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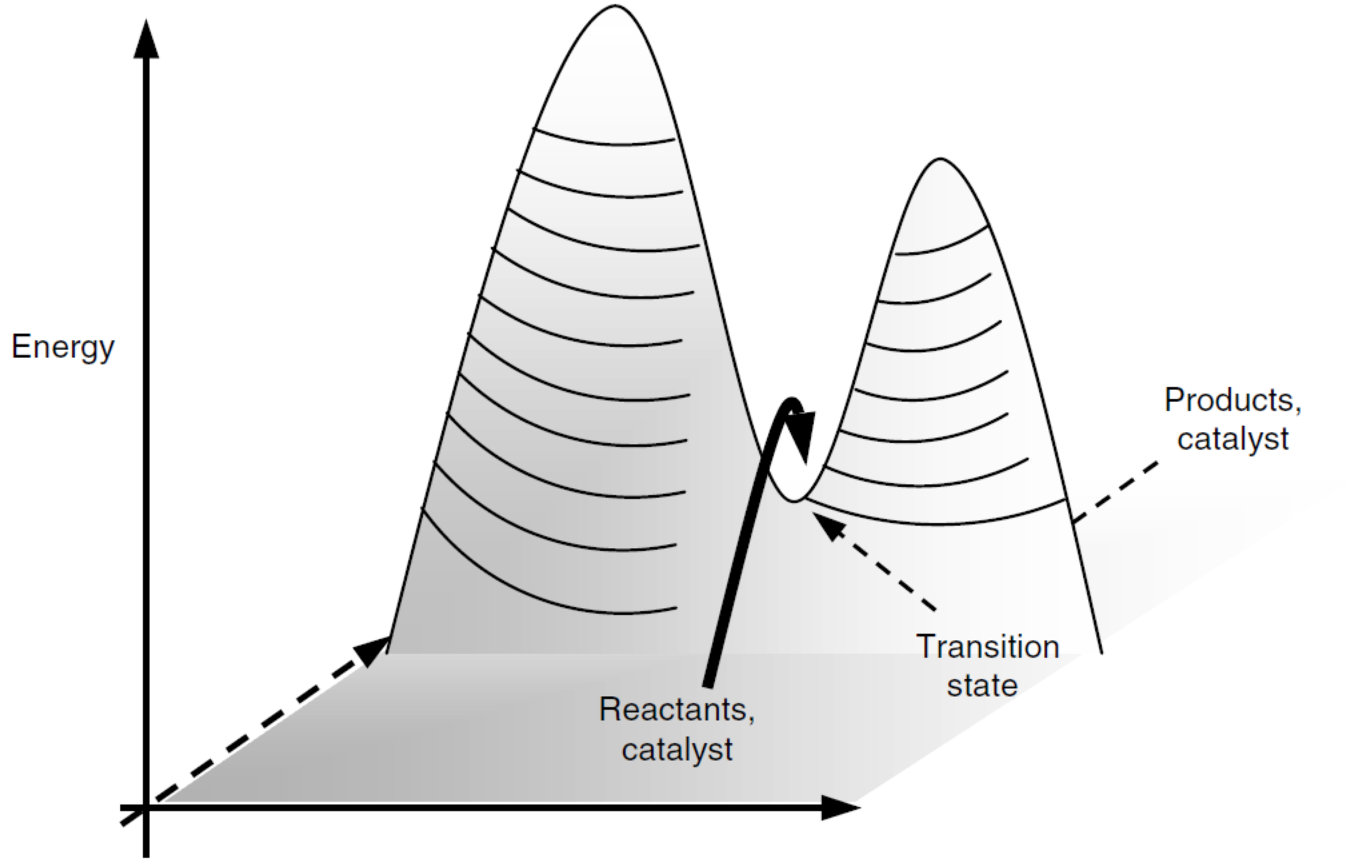
Thermodynamics vs. kinetics

- **Reaction coordinate:** From multidimensional to two-dimensional problem



Thermodynamics vs. kinetics

- Transitions state vs. Intermediate

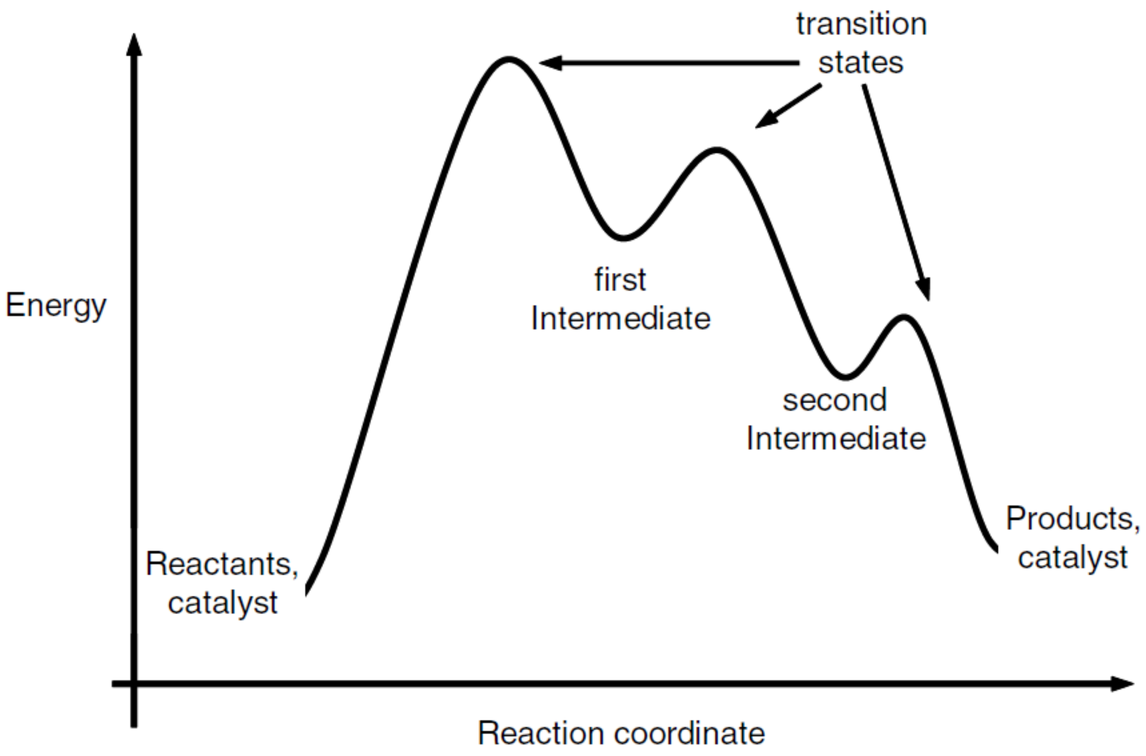
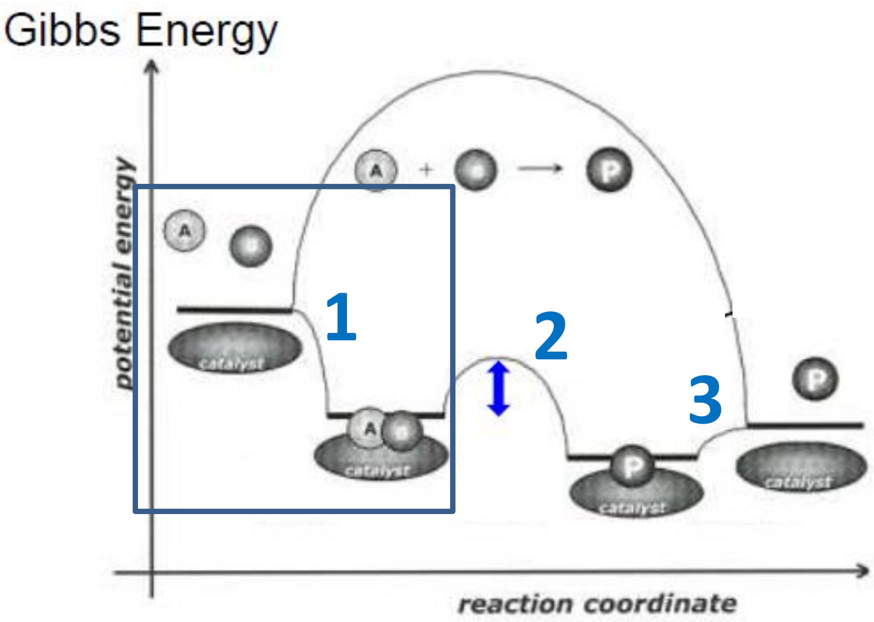


Figure 2.5 Energy/reaction coordinate diagram for a two-step reaction, with two catalytic intermediates and three transition states.

Thermodynamics – heterogeneous catalysis

A + B → P



1: Adsorption of reactants on catalyst surface (hetero) / Formation of reaction intermediate ABC (enzymes and homo)

In heterogeneous catalysis always thermodynamically favorable

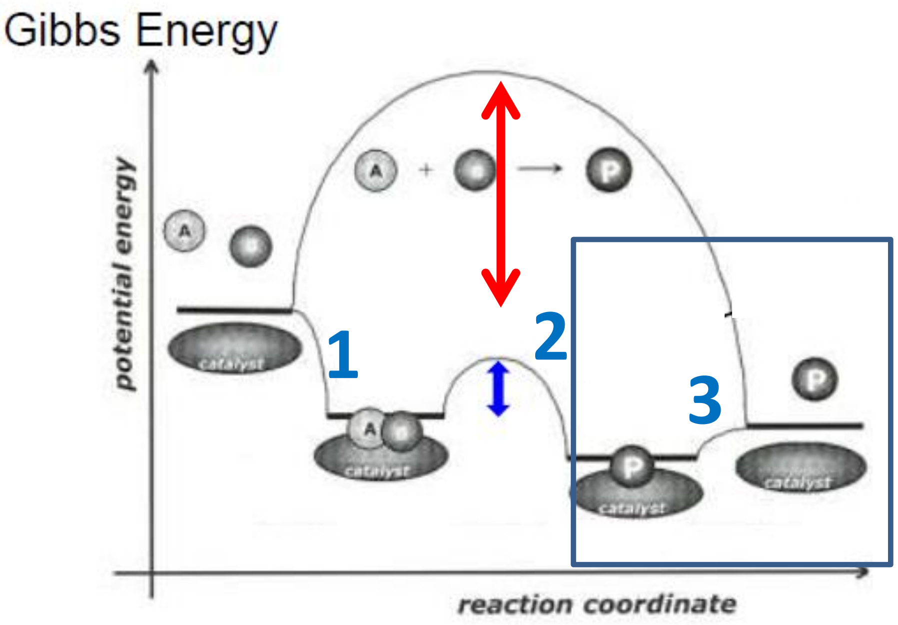
(coordinatively unsaturated surface + adsorbate)

Let‘s imagine weak interaction of A, B, and catalyst surface…???

Let‘s imagine very strong interaction of catalyst surface, A, and/or B…??

Thermodynamics

A + B → P

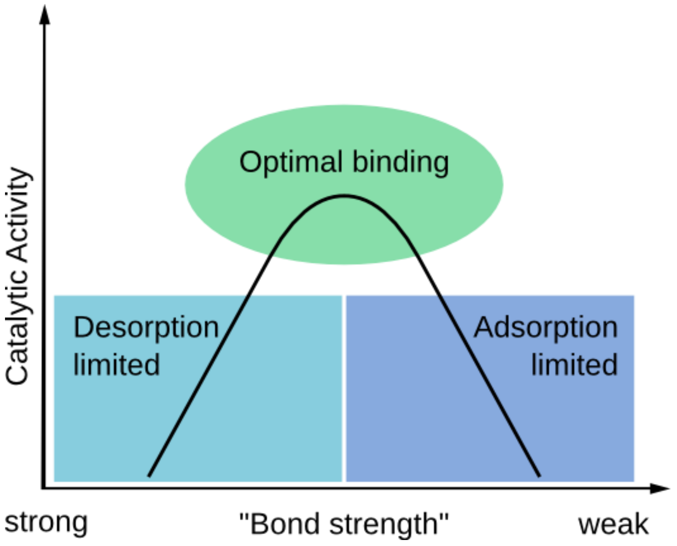


3: Desorption of products from catalyst surface (hetero) / Rupture of product intermediate PC (enzymes and homo)

Let‘s imagine very strong interaction of P with catalyst surface…???

Thermodynamics

- Interactions of A,B, and P with catalyst not too weak, not too strong
  (= physi/chemisorption on catalyst surface)



Sabatier‘s principle; Volcano plot

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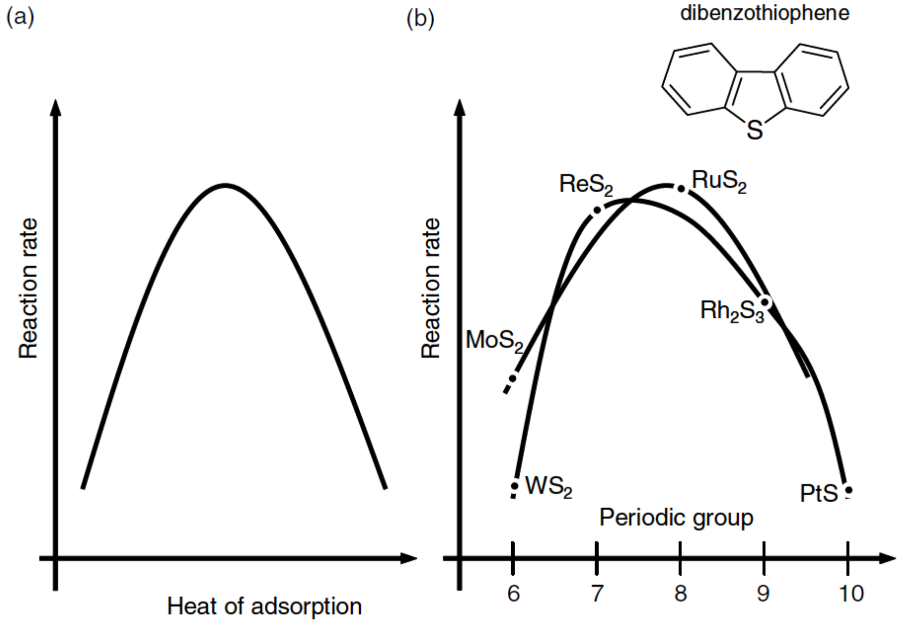
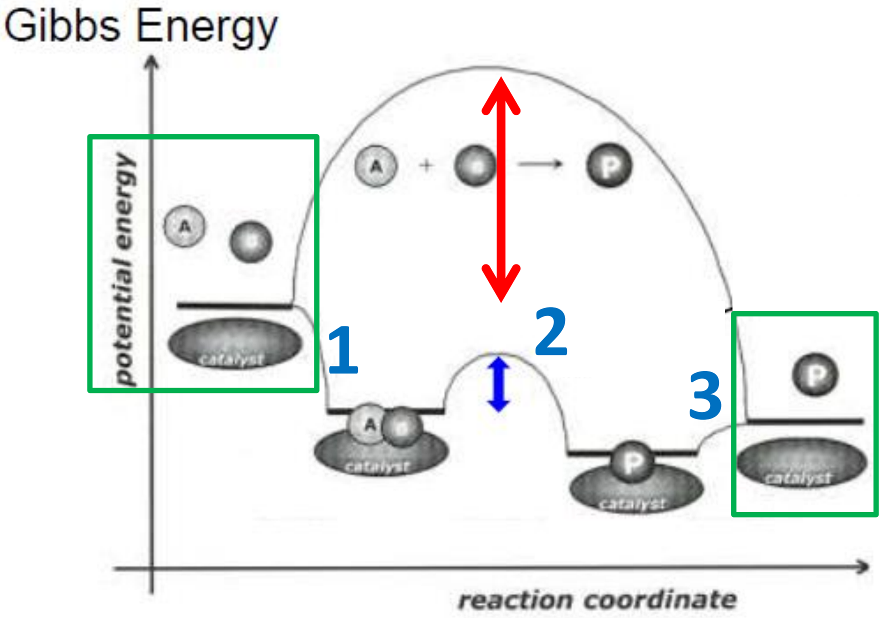


Figure 2.15 Examples of volcano plots, describing the reaction rate as a function of the heat of adsorption (*left*), and the activity of the second-row and third-row transition metal sulfides in the hydrodesulfurization of dibenzothiophene (*right*).

Thermodynamics vs. kinetics

A + B → P



Before going any further…

Steps 1 and 3 are equally important to step 2 in catalysis .

Adsorption and desorption of A, B, and P might have a significant effect on **E_a**.

In kinetic studies in heterogeneous catalysis we estimate only **apparent activation energy (E_{app})**, where all these contributions are included.

Thermodynamics vs. kinetics

- Importance of reactant adsorption and product desorption
  - Example: Ethylbenzene dehydrogenation to styrene

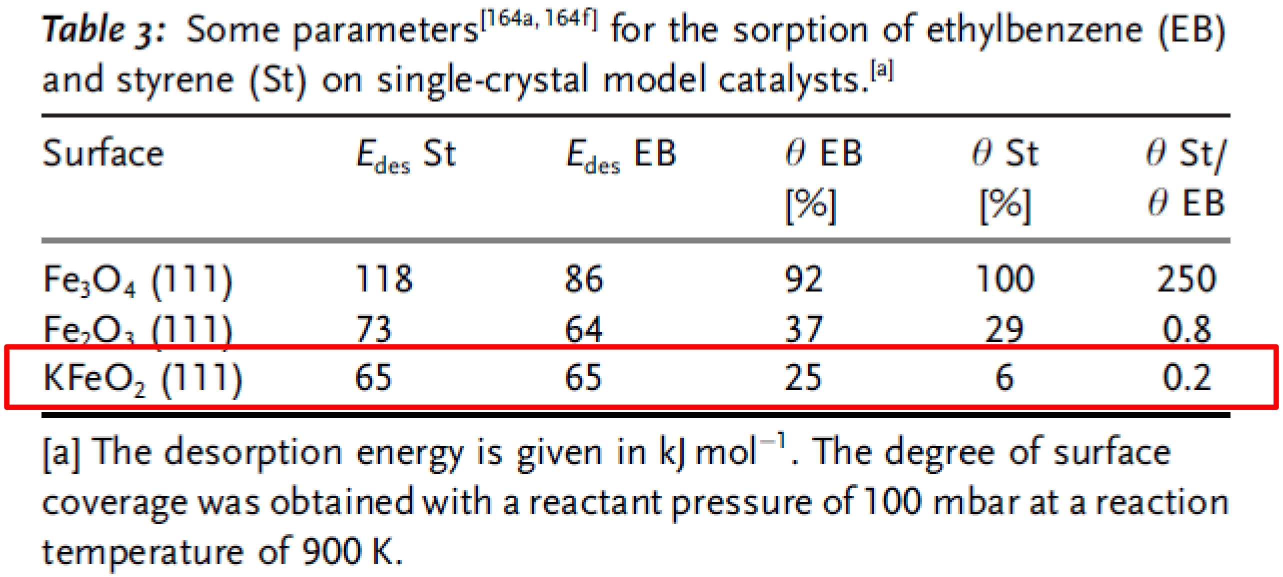


Table 3: Some parameters[164a, 164f] for the sorption of ethylbenzene (EB) and styrene (St) on single-crystal model catalysts.[a]

Surface	E_{des} St	E_{des} EB	θ EB [%]	θ St [%]	θ St/ θ EB
Fe_3O_4 (111)	118	86	92	100	250
Fe_2O_3 (111)	73	64	37	29	0.8
$KFeO_2$ (111)	65	65	25	6	0.2

[a] The desorption energy is given in kJ mol^{-1}. The degree of surface coverage was obtained with a reactant pressure of 100 mbar at a reaction temperature of 900 K.

The best catalyst

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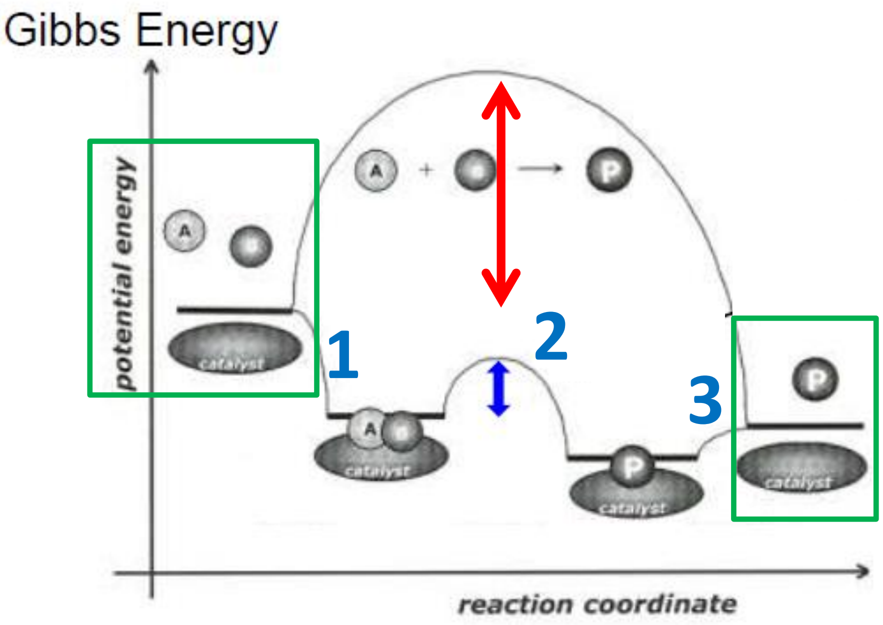
Thermodynamics vs. kinetics

$A + B \rightarrow P$



What is **preceding the step 1** and **following the step 3 ?**

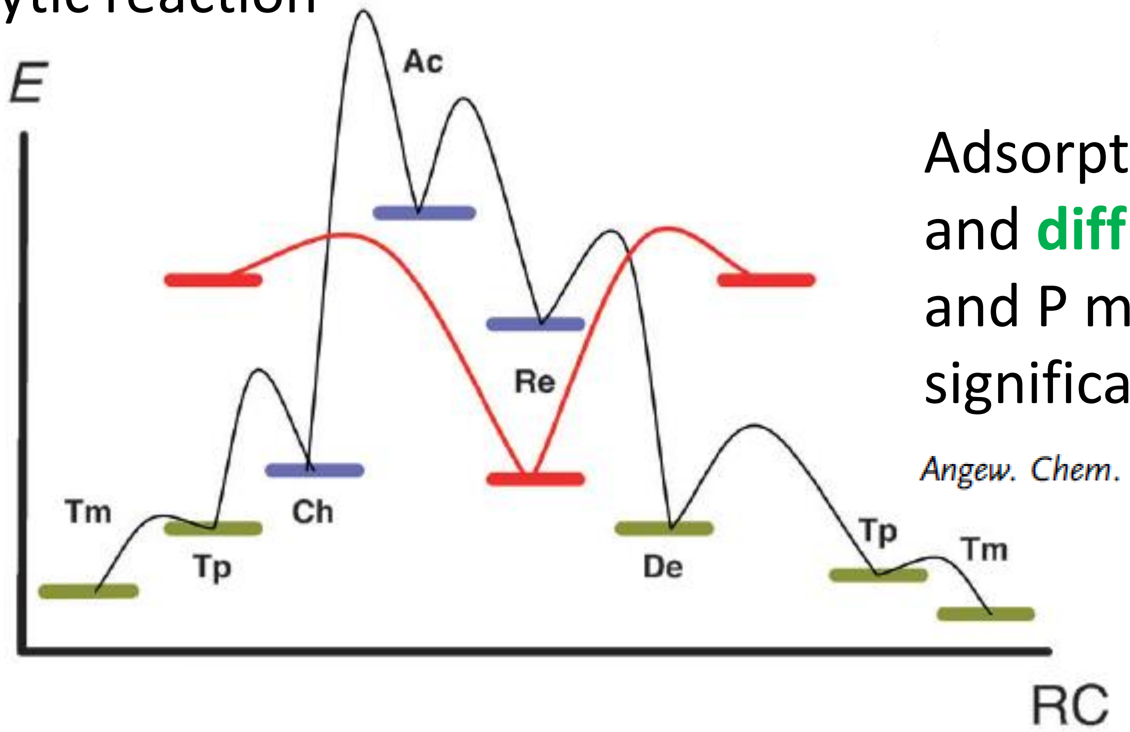
Diffusion!

Diffusion of A, B, and P might have a significant effect on E_a as well.

In kinetic studies in heterogeneous catalysis we estimate only **apparent activation energy (E_{app})**, where all these contributions are included.

Thermodynamics vs. kinetics

- Another representation of the complexity of heterogeneous catalytic reaction



Adsorption, desorption, and **diffusion** of A, B, and P might have a significant effect on **E_a**.

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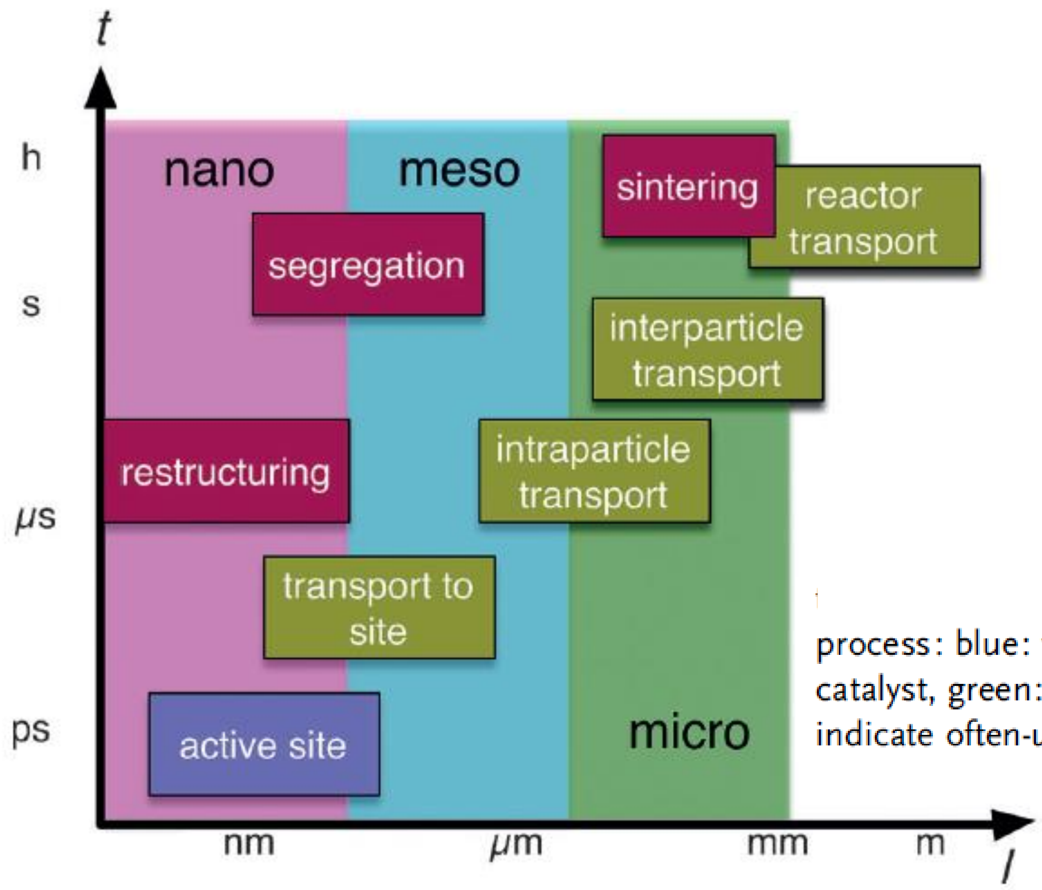
Figure 1. Dimensions in catalysis: A) Change in energy (*E*) of a catalytic system with respect to the reaction coordinate (RC) for the basic individual steps: Tm: transport macroscopic, Tp: transport in pores or solvation shells, Ch: chemisorption, AC: activation (dissociation), Re: reaction, De: desorption, dissociation. The energy changes in red denote the impact of the reaction on active centers

Thermodynamics vs. kinetics

- Another representation of the complexity of heterogeneous catalytic reaction



Adsorption, desorption, and **diffusion** of A, B, and P might have a significant effect on **E_a**.

Space–time scales for a heterogeneous catalytic process: blue: the molecular reaction, red: chemical dynamics on the catalyst, green: transport processes of the reactants. The vertical bars indicate often-used terms for the spacial dimensions.

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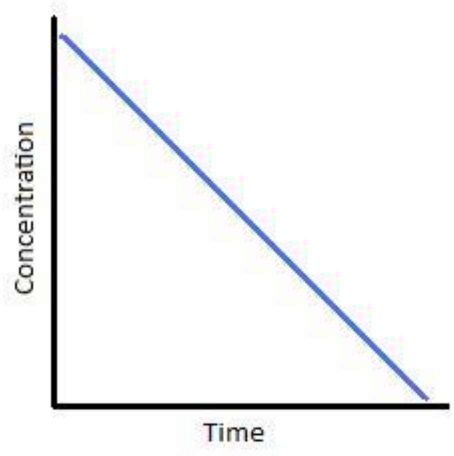
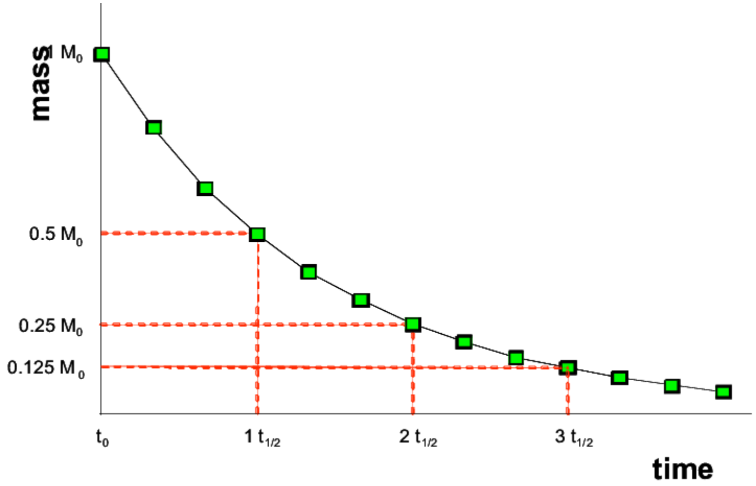
Kinetics

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

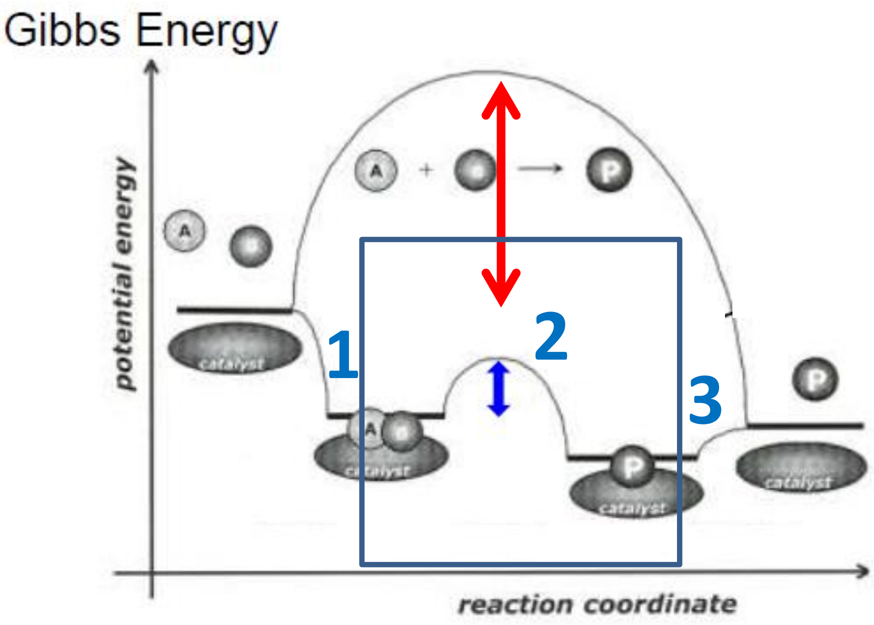




- But in catalysis also 0.39 order, –0.5 order… (many elementary rxns, fight for active site between reactants and products,…!)

Thermodynamics vs. kinetics

A + B → P

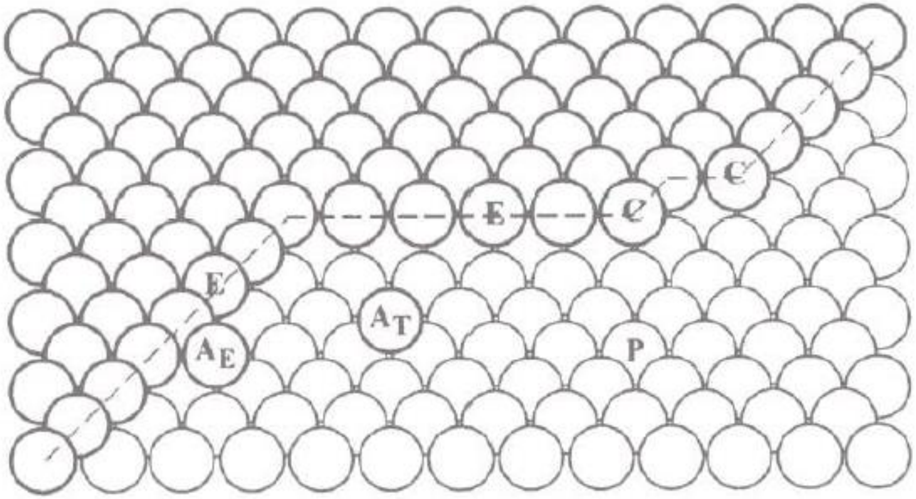


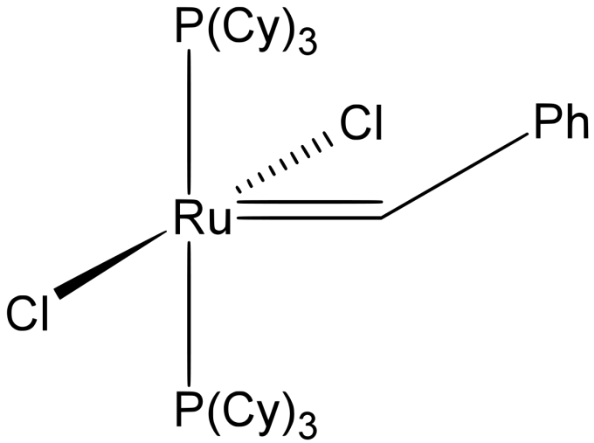
2: In order to decrease E_a for step 2 we need to **design** an **active site** of the catalyst **as good as possible**

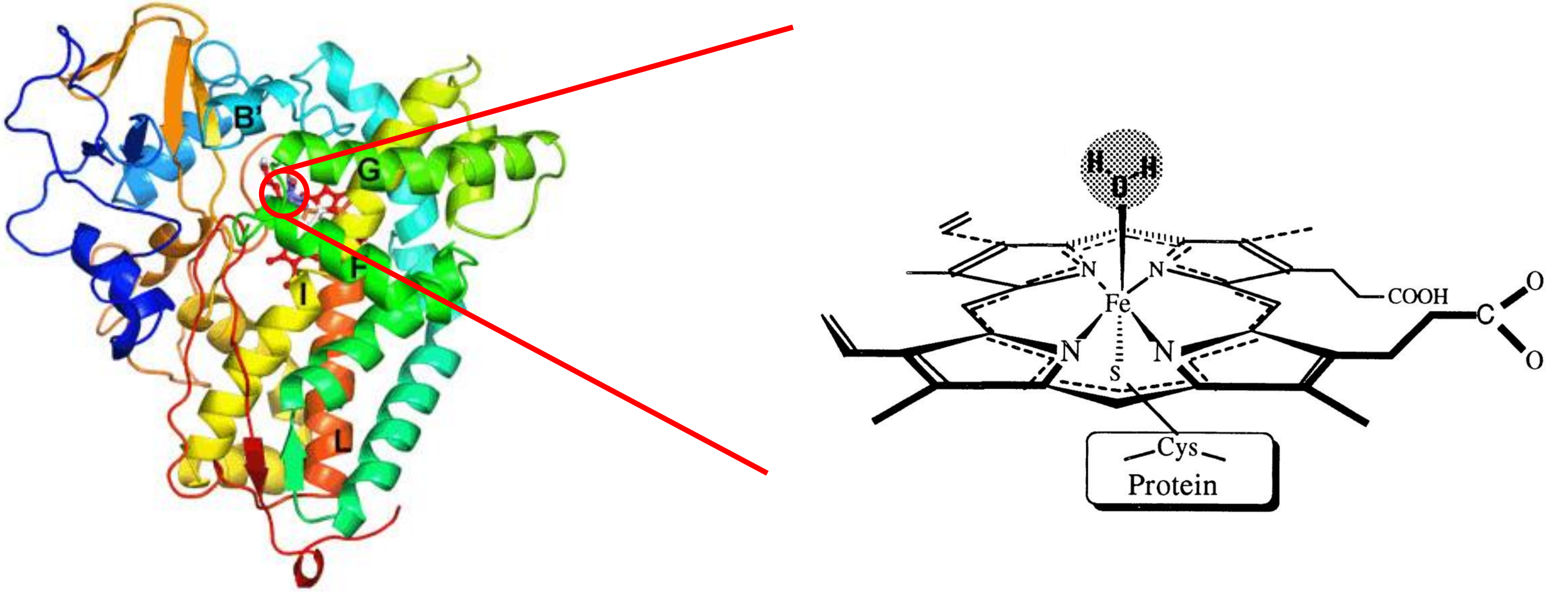
What is the **active site???**

How do we measure the **„goodness“** of the active site???

Active sites

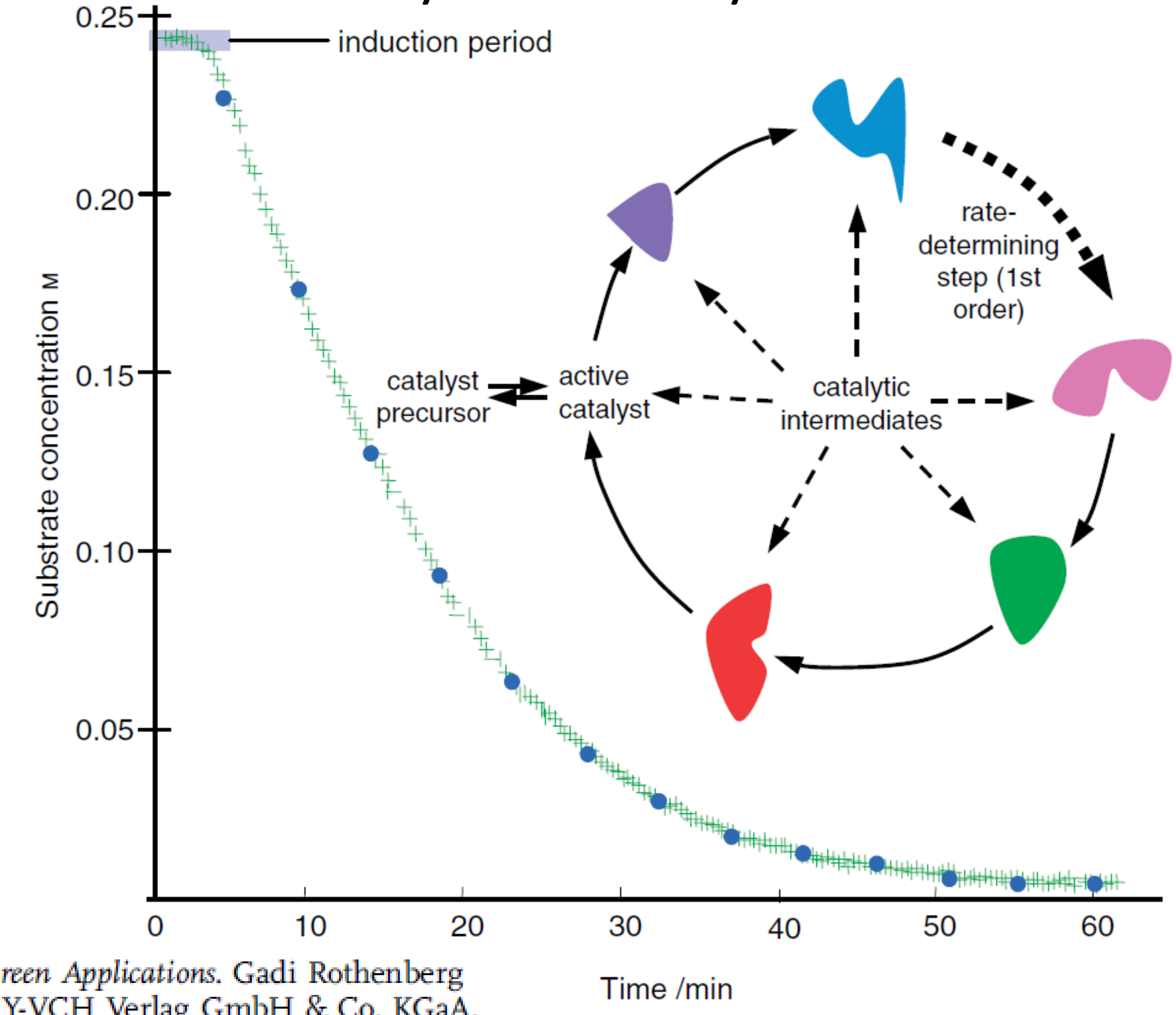






Active sites

- Active sites are often dynamic: They has to be created first!



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Active site/catalyst evaluation

- **Turn-over frequency** (TOF; [s^{-1}])
  = number of catalytic cycles performed by **1 active site** per time unit
- **Precise numbers for homogeneous and enzymatic catalysis**
- **Numbers for heterogeneous catalysis???**

	TOF [s^{-1}]
Hetero:	~1–100 s^{-1}
Homo:	~10–1000 s^{-1}
Enzymes:	~10000–1000000 s^{-1}

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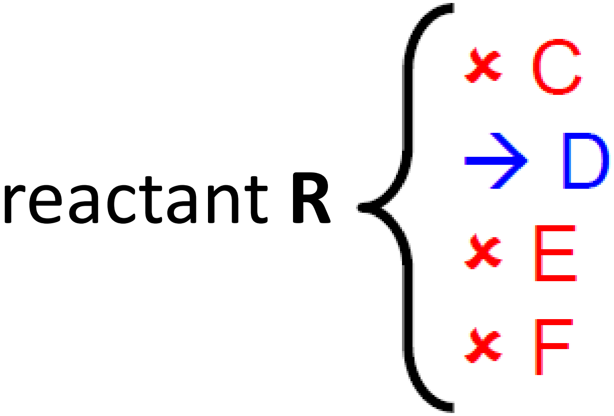
Active site/catalyst evaluation

- **Turn-over number** (TON; [-])
  = number of catalytic cycles performed by **1 active site** before deactivation (~lifetime)
- **Precise numbers for homogeneous and enzymatic catalysis**
- **Numbers for heterogeneous catalysis???**

Active site/catalyst evaluation

- **Selectivity** is ability of catalyst to form one product from a pool of products (possibly many)



- **Selectivity** (S; [%])
= number of D molecules produced / R molecules converted

Active site/catalyst evaluation

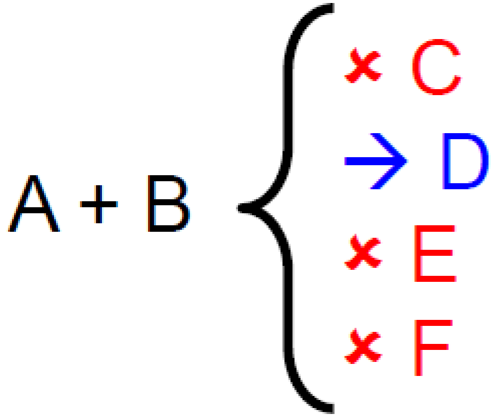
- **Enantiomeric enrichment** is ability of catalyst to form **selectively** one **enantiomer**
- **Enantiomeric enrichment** (ee; [%])
  = $S(P_R) – S(P_S)$
  (e.g. Final mixture consists of 90 % P_R and 10 % P_S
  ee = 80 %)

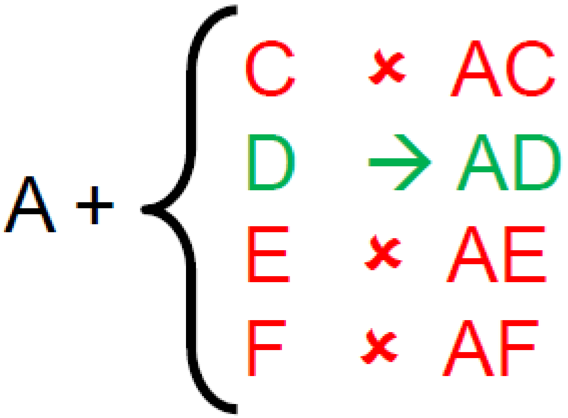
	S [%]	ee [%]
Hetero:	1–100	1–100
Homo:	> 90	> 70
Enzymes:	> 99.99	> 99.99

Active site/catalyst evaluation

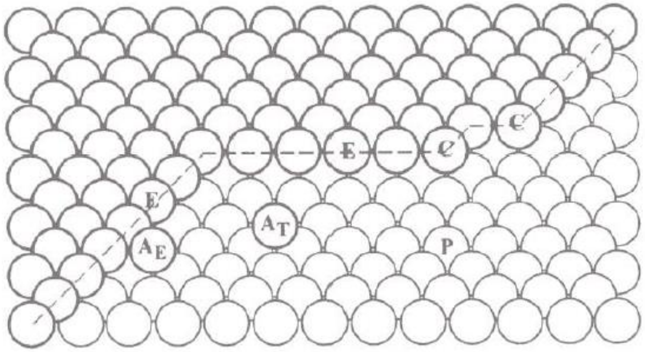
- Selectivity is ability of catalyst to form one product from a pool of products (possibly many)

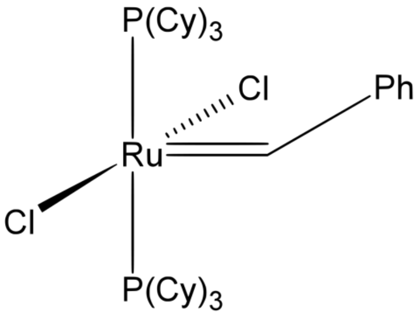
- **Specificity** is ability of catalyst to react with one reactant among many (similar) reactants

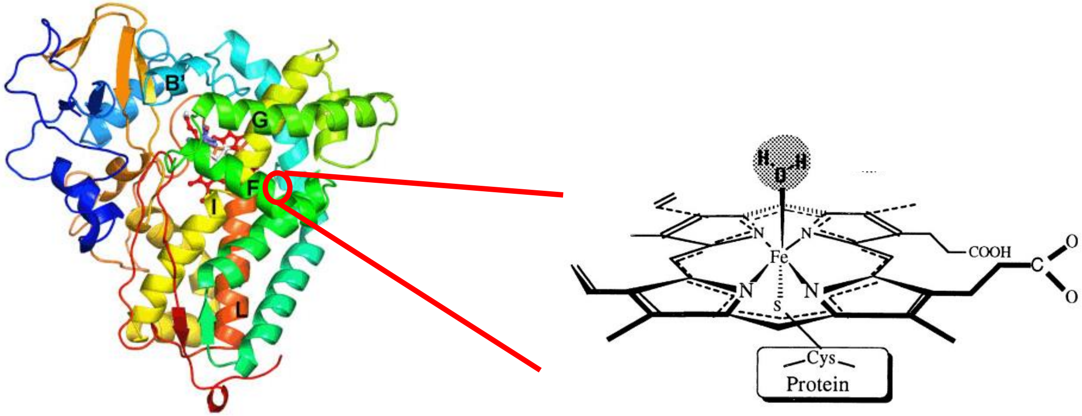




Active sites







Electronic and **steric** properties do play an important role! (TOF, TON, Selectivity, ee, specificity).

Catalyst evaluation

R → P + P‘

- **Conversion** (C; [%])
  = number of R molecules converted / number of R molecules introduced
- **Yield** (Y; [%])
  = number of P molecules produced / number of R molecules introduced
- **Selectivity** (S; [%])
  = number of P molecules converted / number of R molecules converted

$$\boxed{S = \frac{Y}{C}}$$

Catalyst evaluation

$R \rightarrow P + P'$

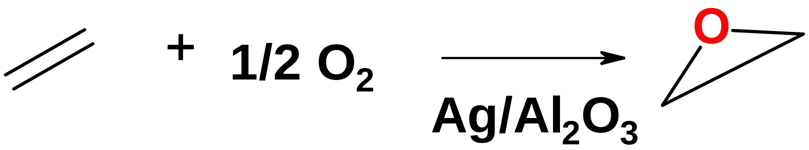
- **Productivity** (Site Time Yield, STY; [g g^{-1} s^{-1}])
  = amount of product P produced per unit of time and unit of catalyst mass
  = high conversion, high selectivity, low catalyst mass, high flow
  = industrial viewpoint

Catalyst evaluation

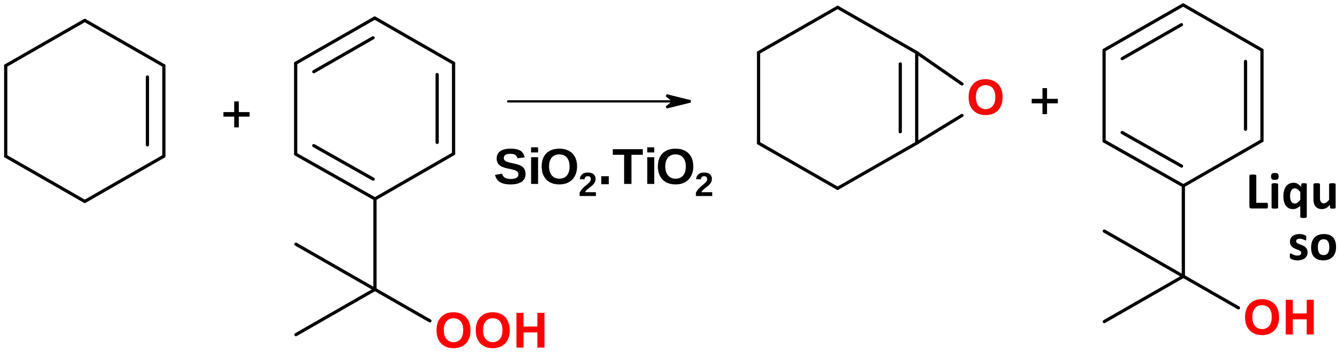
- Ecological point of view
- **Atom efficiency** [%]
  = mass of desired product / total mass of all products
- **E factor** [-]
  = mass of all wastes (solvents, gases, unreacted precursors, byproducts) / mass of desired products
- **EQ factor** [-]
  = E factor, mass of each waste multiplied by Q (environmental unfriendliness), e.g. Q = ~0 for water, ~ 1 for NaCl, and ~1000 for toluene…

Catalyst evaluation

- Ecological point of view
- **Atom efficiency** [%], **E factor** [-], **EQ factor** [-]

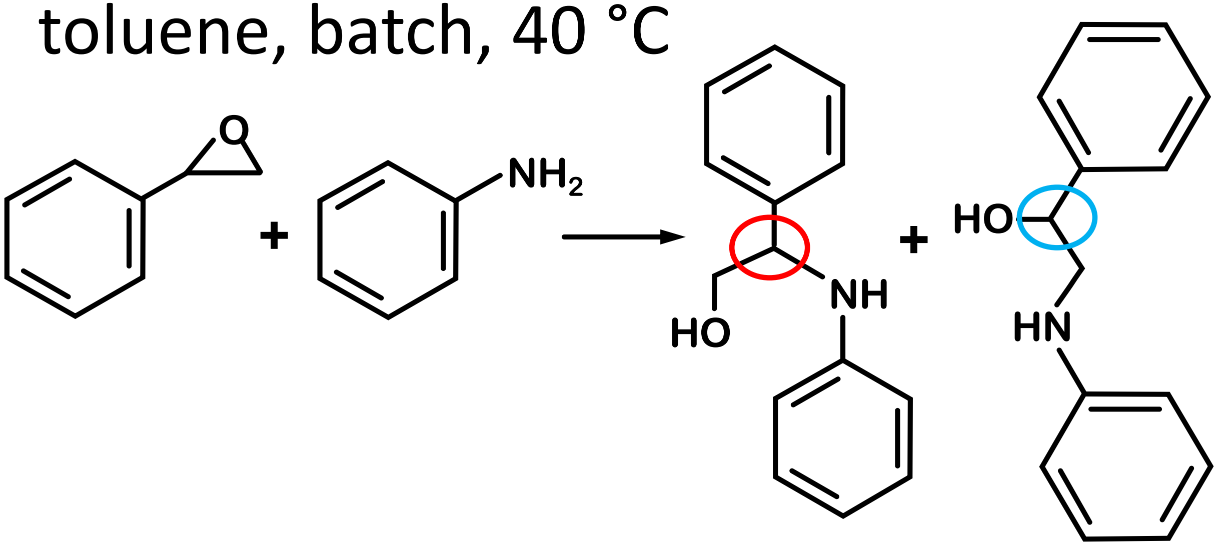


Gas phase, flow mode



Liquid phase, toluene as solvent, batch mode

HW1. Aminolysis of styrene oxide over Zr catalyst, in toluene, batch, 40 °C



Rxn mixture, time 0

1 Zr : 250 styrene oxide : 3000 toluene; aniline in excess

Rxn mixture, time = 10 min, ^{1}H NMR analysis – ratio of integrated areas, protons in red/blue circle

1 Product III : 0.01 Product IV : 19.4 styrene oxide : 777 toluene (CH_3 group integration)

Calculate conversion, TOF [h^{-1}], selectivity to product IV.

What is the fraction of the (by-)products we did not analyze?