— University of Mosul —

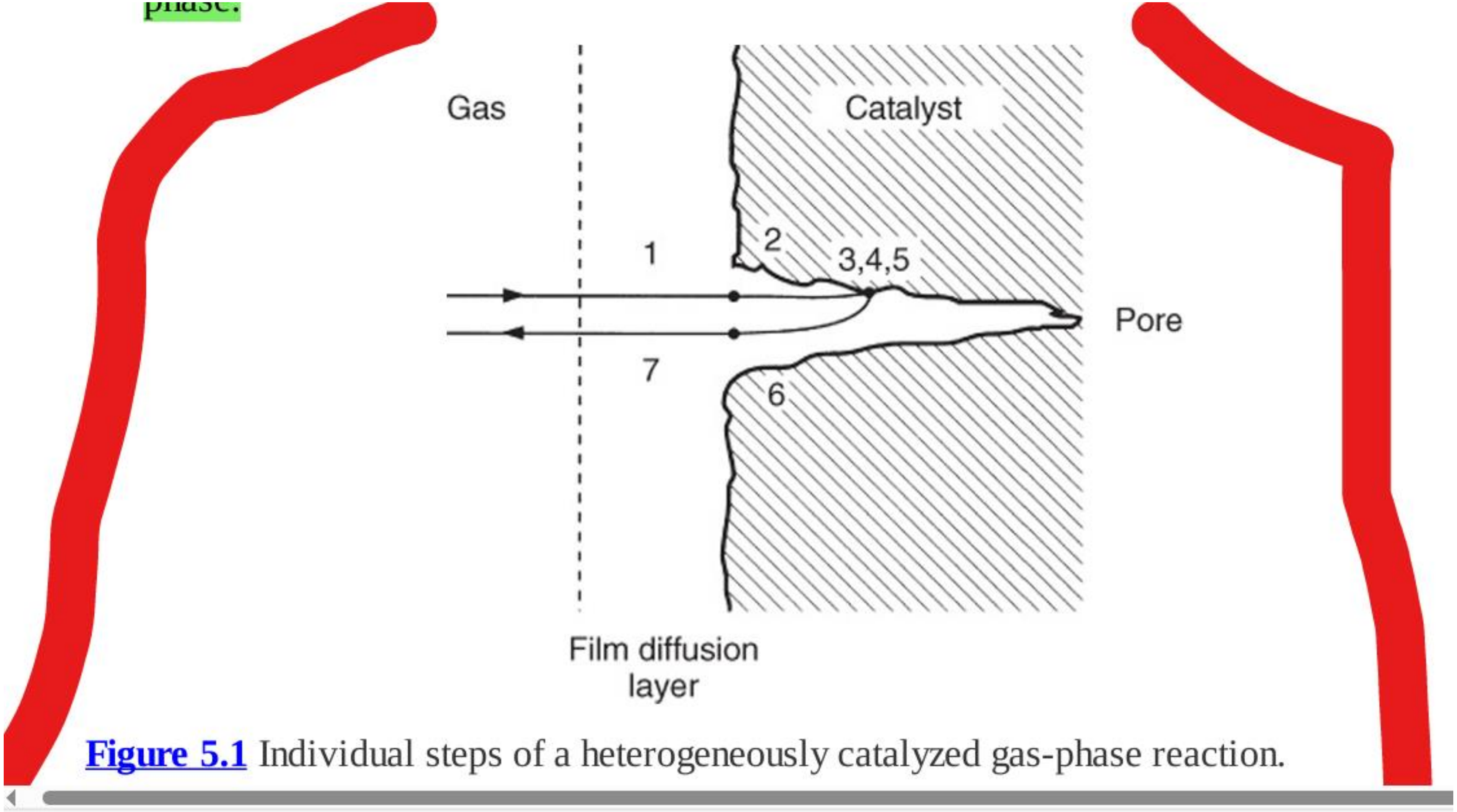
College of Petroleum & Mining Engineering

Industrial Chemistry

Lecture …(2)….

Petroleum and Refining Engineering Department

Heterogeneous Catalysis: Fundamentals



phase:

Figure 5.1 Individual steps of a heterogeneously catalyzed gas-phase reaction.

Catalysis Kinetics: Rate Laws and Activation Energy

- • Reaction Rate: $r = -d[A]/dt = k \cdot f(cA)$
- • Arrhenius Equation: $k = k_0 \cdot \exp(-Ea / RT)$

- Where:
- k = rate constant
- Ea = activation energy
- R = gas constant
- T = temperature (Kelvin)

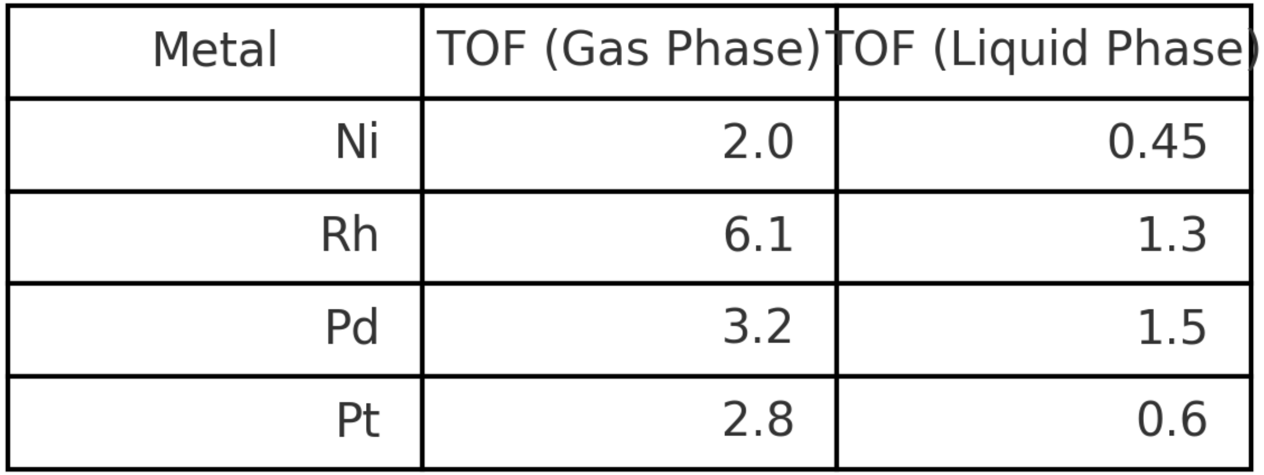
Heterogeneous Catalysis: Fundamentals

We will now consider the simplest case of a catalytic gas reaction on a porous catalyst. The following reaction steps can be expected (Figure 5.1) [1, 2]:

1. Diffusion of the starting materials through the boundary layer to the catalyst surface.
2. Diffusion of the starting materials into the pores (pore diffusion).
3. Adsorption of the reactants on the inner surface of the pores.
4. Chemical reaction on the catalyst surface.
5. Desorption of the products from the catalyst surface.
6. Diffusion of the products out of the pores.
7. Diffusion of the products away from the catalyst through the boundary layer and into the gas phase.

Turnover Frequency (TOF) Comparison

- TOF indicates how many reactions each active site performs per



Metal	TOF (Gas Phase)	TOF (Liquid Phase)
Ni	2.0	0.45
Rh	6.1	1.3
Pd	3.2	1.5
Pt	2.8	0.6

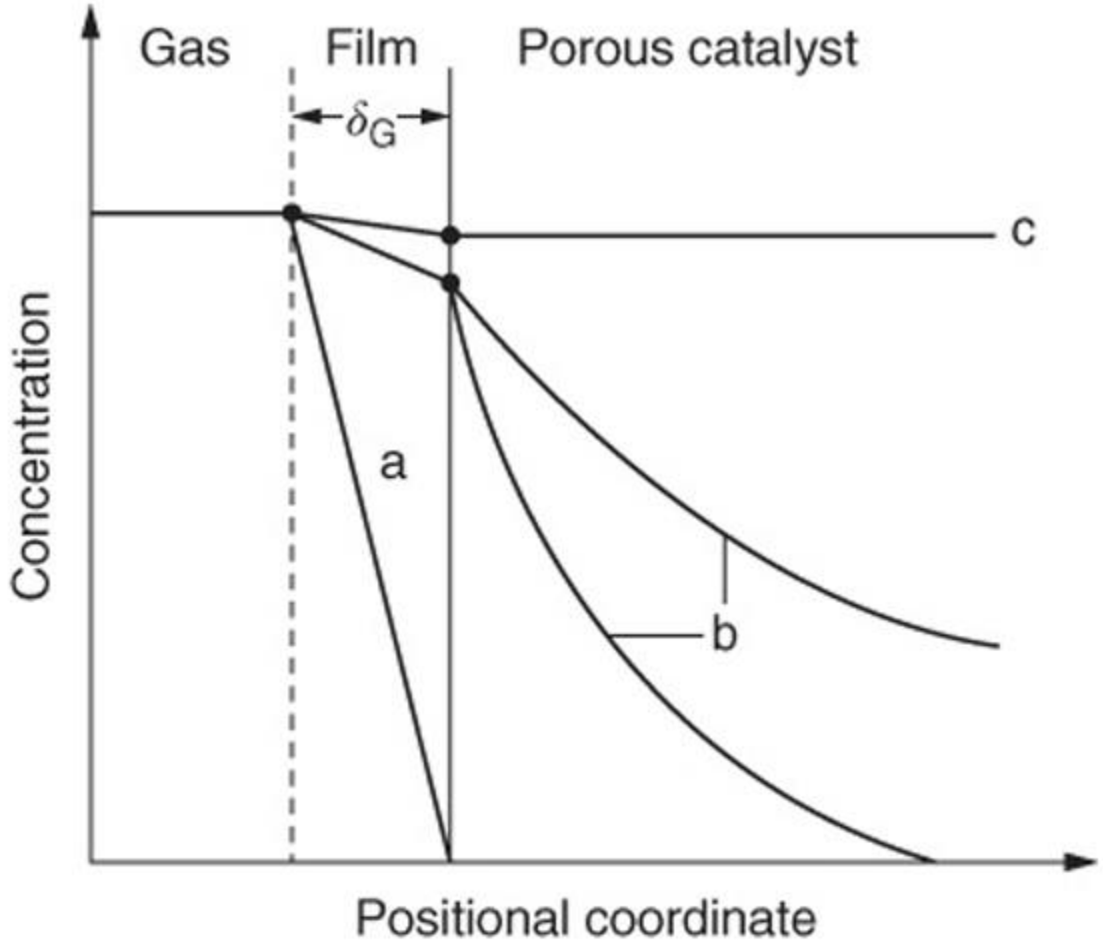


Figure 5.2 Concentration–position curves in the film diffusion region (a), the pore diffusion region (b), and the kinetic region (c).

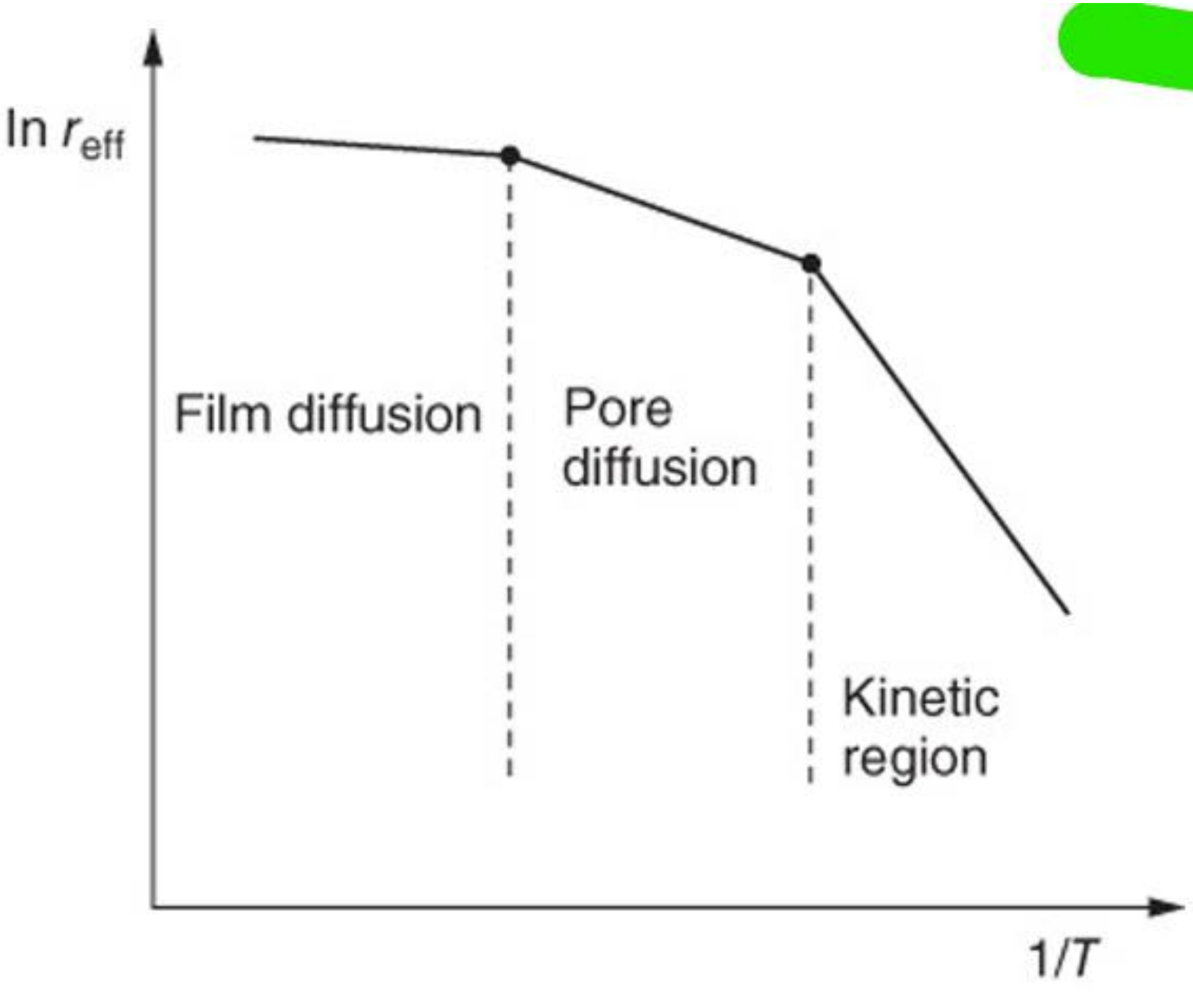


Figure 5.3 Dependence of effective reaction rate on temperature.

Example

The methanol synthesis in a laboratory reactor is carried out at 80 bar and 250 °C with the addition of inert gas nitrogen. Under these conditions, the conversion of CO is 30%.

$$CO + 2\,H_2 \rightarrow CH_3OH$$

The feed of the reactor consists of 1 mol/h CO, 2 mol h^{-1} H_2, and 3 mol h^{-1} N_2. In the condenser, it results in 9.2 g h^{-1} liquid methanol.

a. Calculate the composition of the gas phase at the reactor outlet (mol%).
b. Calculate the volume flow rates at the reactor outlet.
c. Which amount of liquid methanol/h should be obtained theoretically?

Solution

(a) At the end of the conversion, there should be obtained

Species	n_i	n_i (mol) gas	%	(b) flow rate (l h^{-1})
CO	$1 - X$	0.7	13.7	15.7
H_2	$2(1 - X)$	1.4	27.5	31.4
CH_3OH	X	—	—	—
N_2	3	3	58.8	67.2

(c) 0.3 mol methanol = 9.6 g CH_3OH/h.

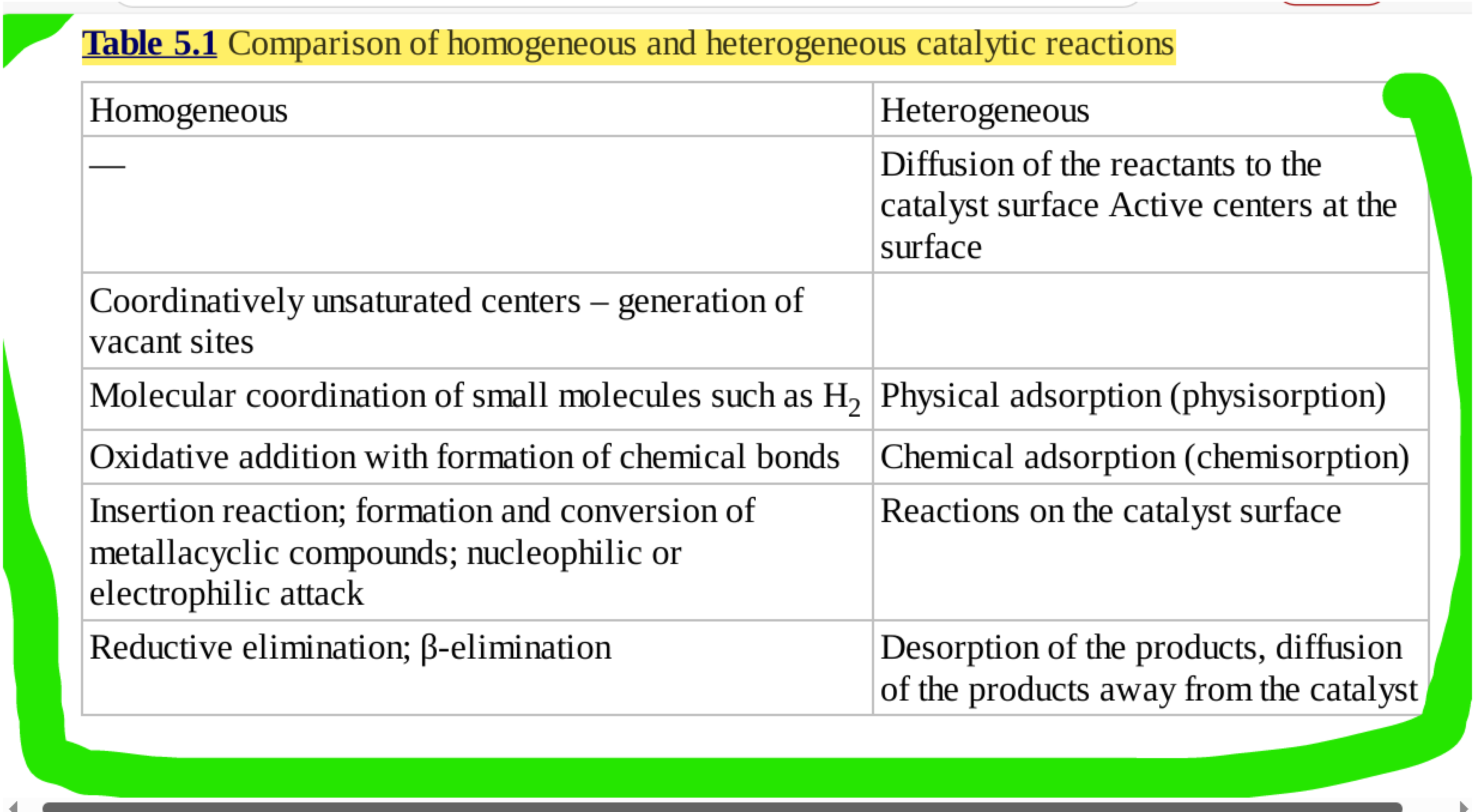


Table 5.1 Comparison of homogeneous and heterogeneous catalytic reactions

Homogeneous	Heterogeneous
—	Diffusion of the reactants to the catalyst surface Active centers at the surface
Coordinatively unsaturated centers – generation of vacant sites	
Molecular coordination of small molecules such as H_2	Physical adsorption (physisorption)
Oxidative addition with formation of chemical bonds	Chemical adsorption (chemisorption)
Insertion reaction; formation and conversion of metallacyclic compounds; nucleophilic or electrophilic attack	Reactions on the catalyst surface
Reductive elimination; β-elimination	Desorption of the products, diffusion of the products away from the catalyst

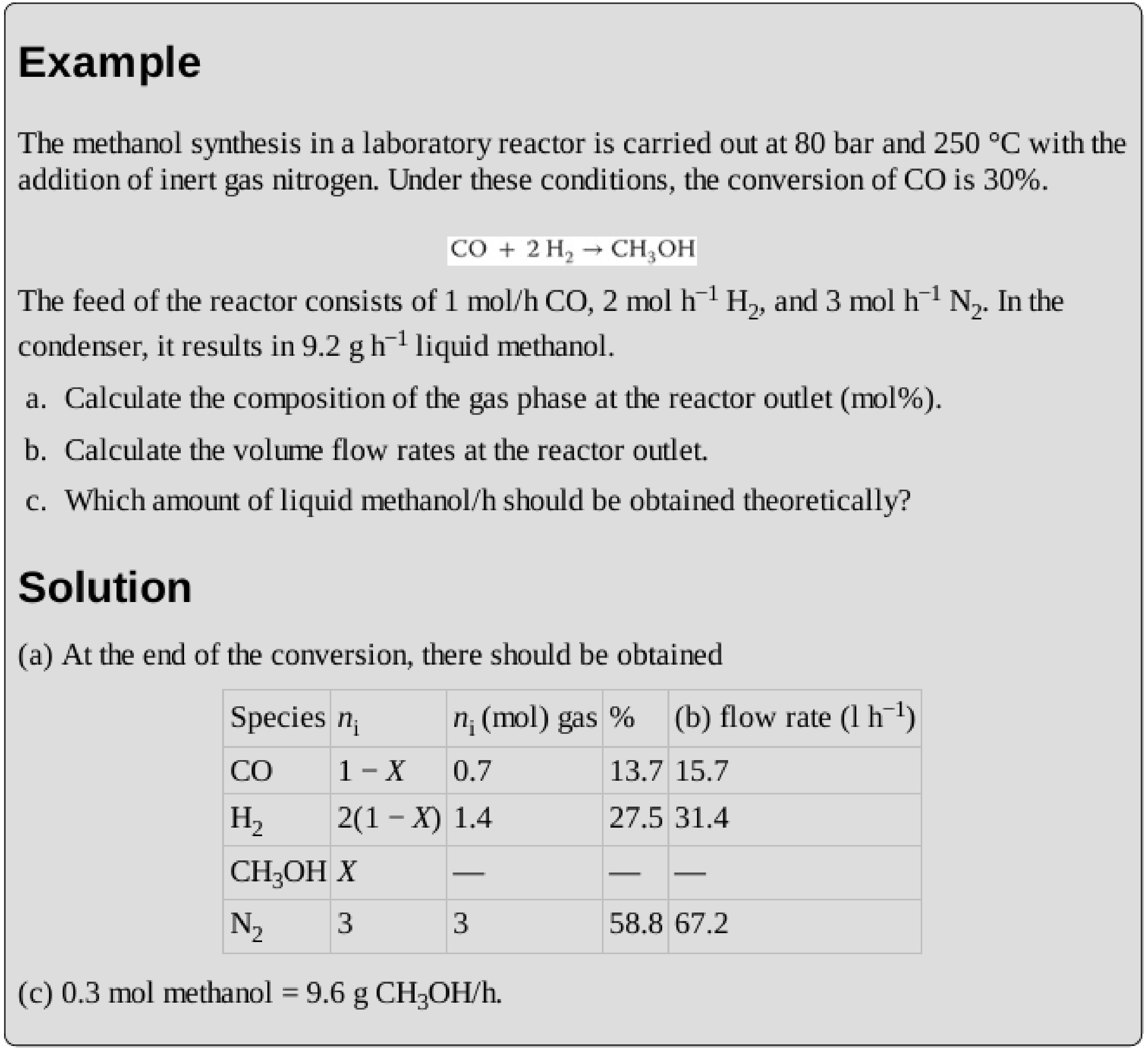


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Table 1.4 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Effectivity		
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problems	Practically absent	Present (mass-transfer-controlled reaction)
Reaction conditions	Mild (50–200 °C)	Severe (often >250 °C)
Applicability	Limited	Wide
Activity loss	Irreversible reaction with products (cluster formation); poisoning	Sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	Defined	Undefined
Modification possibilities	High	Low
Thermal stability	Low	High
Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed: unnecessary suspension: filtration
Catalyst recycling	Possible	Unnecessary (fixed-bed) or easy (suspension)
Cost of catalyst losses	High	Low

The major disadvantage of homogeneous transition metal catalysts is the difficulty of