

Written Exam Problems for PET 635

Autumn 2018

P 1

The initial reaction rate for the elementary reaction $2A + B \rightarrow 4C$ was measured as a function of temperature when the concentration of A was 2 M and that of B was 1.5 M.

$-r_A(\text{mol/dm}^3\cdot\text{s})$	0,002	0,046	0,72	8,33
T(K)	300	320	340	360

- What is the activation energy?
- What is the frequency factor?
- What is the rate constant as a function of temperature using $T=300\text{K}$ as the base case?

P 2

For the reaction $2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}$ with a rate law $= k[\text{NO}_2][\text{F}_2]$

- Write the steps for a bimolecular elementary process.
- Identify which elementary process is the rate determining and which one is the fast reaction.

P 3

For a zero-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of $-k$;

for a first-order reaction, a plot of the logarithm of the concentration of a reactant versus time is a straight line with a slope of $-k$;

for a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of k .

Please deduct the above linear relationship for the zero, first, and second order reactions.

P 4

Please calculate the half-life of the zero, first, and second order reactions.

P 5

The rate law for the reaction $2A + B \rightarrow C$ is $-r_A = k_A C_A^2 C_B$ with $k_A = 25(\text{dm}^3/\text{mol})^2/\text{s}$. What are k_B and k_C ?

P 6

The decomposition of NO_2 at 300°C is described by the equation



and yields these data:

Time (s)	[NO ₂], M
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Determine the reaction order of NO₂.

P 7

Consider the reaction: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$; ΔG° at 25 °C is -33 kJ/mol, and at 250 °C is 12 kJ/mol.

1. Write the expression of the equilibrium constant K_p .
2. What is the value of ΔG at standard conditions.
3. What is the value of ΔG at 250 °C, with $P_{\text{N}_2} = 5.0$ atm, $P_{\text{H}_2} = 15$ atm, and $P_{\text{NH}_3} = 5.0$ atm.

P 8

1. Find the activation energy (in kJ/mol) of the reaction if the rate constant at 600 K is $3.4 \text{ M}^{-1}\text{s}^{-1}$ and 31.0 at 750 K.
2. Find the temperature if the rate constant at that temperature is $15 \text{ M}^{-1}\text{s}^{-1}$ while at temperature of 389 K the rate constant is $7 \text{ M}^{-1}\text{s}^{-1}$, the activation energy is 600 kJ/mol.

P 9

For a first-order reaction, the following rate coefficients were found:

Temperature, °C	k, h ⁻¹
38.5	0.044
53.1	0.301
77.9	1.665

Determine the activation energy of the reaction in kJ/mol.

P 10

For the reaction

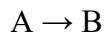


The equilibrium constant $K = 2.5 \times 10^{-25}$ at 298 K, $\Delta H^\circ(\text{SO}_2) = -296.83 \text{ kJ/mol}$, $\Delta H^\circ(\text{SO}_3) = -395.72 \text{ kJ/mol}$.

1. What is the value of K at 500 K?
2. Explain how the calculated equilibrium constant is consistent with Le Châtelier's principle.

P 11

Consider a reaction which can be symbolically written as

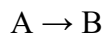


This is a first order reaction carried out in a tubular reactor in which the volumetric flow rate, v , is constant, i.e., $v = v_0$

1. Sketch the concentration profile.
2. Derive an equation relating the reactor volume to the entering and exiting concentration of A, the rate constant k , and the volumetric flow rate v .
3. Determine the reactor volume necessary to reduce the exiting concentration to 10% of the entering concentration when the volumetric flow rate is $10 \text{ dm}^3/\text{min}$ and the specific reaction rate, k , is 0.23 min^{-1} .

P 12

Consider a reaction which can be symbolically written as



This is a first order liquid phase reaction carried out in a CSTR reactor. The volumetric flow rate, v , is constant at $10 \text{ dm}^3/\text{min}$, i.e., $v = v_0$. What is the CSTR volume necessary to reduce the exit concentration to 10% of the entering concentration. The specific reaction rate, k , is 0.23 min^{-1} .

P 13

The reaction $A \rightarrow B$ is to be carried out isothermally in a continuous-flow reactor. The entering molar flow rate is 5 mol/h ; the entering volumetric flow rate is $10 \text{ dm}^3/\text{h}$ and is constant. If the reaction is a second order reaction ($-r_A = kC_A^2$) with $k = 3 \text{ dm}^3/\text{mol}\cdot\text{h}$.

1. Calculate both the CSTR and PFR reactor volumes necessary to convert 99% of A (i.e., $C_A = 0.01 C_{A0}$).
2. Calculate the time necessary to consume 99.9% of species A in a 1000 dm^3 constant volume batch reactor with $C_{A0} = 0.5 \text{ mol/dm}^3$.

P 14

The exothermic reaction $A \rightarrow B + C$ is to be carried out adiabatically and the following data recorded:

X	0.0	0.2	0.4	0.45	0.5	0.6	0.8	0.9
$-r_A(\text{mol/dm}^3\cdot\text{min})$	1.0	1.67	5.0	5.0	5.0	5.0	1.25	0.91

The entering molar flow rate of A was 300 mol/min .

1. What are the PFR and CSTR volumes necessary to achieve 40% conversion?
 2. Over what range of conversions would the CSTR and PFR reactor volumes be identical?
- Hint: Simpson's three-point formula is needed to calculate the PFR volume.

P 15

Consider the isothermal gas-phase isomerization reaction $A \rightarrow B$. The laboratory measurement have obtained the reaction rates as a function of conversion as shown the table below. The entering molar flow rate is $F_{A0} = 0.4 \text{ mol/s}$.

X	0.0	0.1	0.2	0.4	0.6	0.7	0.8
$-r_A(\text{mol/m}^3.\text{s})$	0.45	0.37	0.30	0.195	0.113	0.079	0.05

Assume two CSTRs in series are used, and 40% conversion is achieved in the first reactor.

1. What is the volume of each of the two CSTR reactors necessary to achieve 80% overall conversion of the entering species A?
2. What is the volume of one CSTR reactor necessary to achieve 80% conversion?

P 16

Consider the isothermal gas-phase isomerization reaction $A \rightarrow B$. The laboratory measurement have obtained the reaction rates as a function of conversion as shown in the table below. The entering molar flow rate is $F_{A0} = 0.4 \text{ mol/s}$.

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$-r_A(\text{mol/m}^3.\text{s})$	0.45	0.37	0.30	0.195	0.113	0.079	0.05

Assume two PFRs in series are used, and 40% conversion is achieved in the first reactor.

1. What is the volume of each of the two PFR reactors necessary to achieve 80% overall conversion of the entering species A?
2. What is the volume of one PFR reactor necessary to achieve 80% conversion?

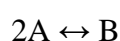
P 17

A number of small, equal-volume CSTRs in series will achieve the same conversion as one big PFR whose volume is equal to the sum of the CSTR volumes.

Use Levenspile plot and relevant reactor design equations, explain qualitatively why the CSTR reactors in series will approximate a big PFR reactor.

P 18

Consider the following elementary gas phase reaction

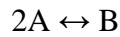


with equilibrium constant $K_C = 20 \text{ dm}^3/\text{mol}$ and entering concentration at $C_{A0} = 0.2 \text{ mol/dm}^3$. Assume the reaction is isothermal and isobaric.

Calculate the equilibrium conversion for a batch reactor, X_e .

P 19

Consider the following elementary gas phase reaction



with equilibrium constant $K_C = 20 \text{ dm}^3/\text{mol}$ and entering concentration $C_{A0} = 0.2 \text{ mol/dm}^3$. Assume the reaction is isothermal and isobaric.

Calculate the equilibrium conversion for a flow reactor, X_e .

P 20

Consider the following elementary gas phase reaction carried out in a flow reactor with no pressure drop.



Pure A enters at a temperature of 400 K and 10 atm. At this temperature, $K_C = 0.25 (\text{mol/dm}^3)^2$.

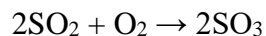
Calculate the equilibrium conversion and concentration.

P 21

Calculate the equilibrium conversion and concentration for the liquid-phase reaction $A + B \leftrightarrow C$ with $C_{A0} = C_{B0} = 2 \text{ mol/dm}^3$ and $K_C = 10 \text{ dm}^3/\text{mol}$.

P 22

A mixture of 28% SO_2 and 72% air is charged to a flow reactor in which SO_2 is oxidized.



1. Setup a stoichiometric table using only the symbols (i.e., Θ_i , F_i)
2. Setup a second stoichiometric table evaluating numerically as many symbols as possible for the case when the total pressure is 1485 kPa and the temperature is constant at 500 K.

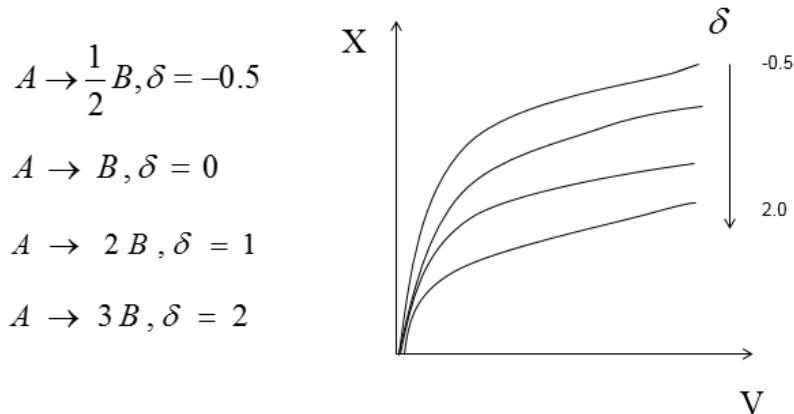
P 23

The gas phase reaction $1/2\text{N}_2 + 3/2\text{H}_2 \leftrightarrow \text{NH}_3$ is to be carried out isothermally. The molar feed is 50% H_2 and 50% N_2 , at a pressure of 16.4 atm and temperature of 227 °C.

1. Construct a complete stoichiometric table.
2. What are C_{A0} , δ , and ϵ ? Calculate the concentrations of ammonia and hydrogen when the conversion of H_2 is 60%.
3. Suppose by chance the reaction is elementary with $k_{N_2}=40 \text{ dm}^3/\text{mol}\cdot\text{s}$. Write the rate of reaction solely as a function of conversion for (1) a flow system and (2) a constant volume batch system.

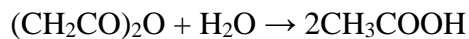
P 24

Please explain qualitatively the effect of changes in moles for the gas phase reaction on conversion for a plug flow reactor. Assume the reactions are carried out at constant temperature and pressure.



P 25

Consider the liquid phase reaction which is carried out in a CSTR reactor with a volume of 1 dm^3 :

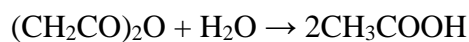


The entering volumetric flow rate v_0 is $0.0033 \text{ dm}^3/\text{s}$; the entering concentration of acetic anhydride is 1 M , and the remaining is water at 51.2 M . The reaction is elementary with a reaction rate constant k of $1.95 \times 10^{-4} \text{ dm}^3/(\text{mol}\cdot\text{s})$.

Please calculate the conversion achieved in the CSTR reactor.

P 26

Consider the liquid phase reaction which is carried out in a PFR reactor with a volume of 0.311 dm^3 :



The entering volumetric flow rate v_0 is $0.0033 \text{ dm}^3/\text{s}$; the entering concentration of acetic anhydride is 1 M , and the remaining is water at 51.2 M . The reaction is elementary with a reaction rate constant k of $1.95 \times 10^{-4} \text{ dm}^3/(\text{mol}\cdot\text{s})$.

Please calculate the conversion achieved in the PFR reactor.

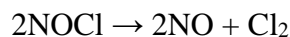
P 27

The liquid-phase reaction $A + B \rightarrow C$ follows an elementary rate law and is carried out isothermally in a batch reactor. The concentration of the A and B feed streams are 2 M before mixing, and the entering temperature is 300 K. The streams are mixed immediately before entering. $K = 0.07 \text{ dm}^3/\text{mol}\cdot\text{min}$ at 300 K and $E = 20 \text{ kcal/mol}$.

1. How long would it take to achieve 90% conversion in a 200 dm^3 batch reactor with $C_{A0} = C_{B0} = 1 \text{ M}$ after mixing at a temperature of $77 \text{ }^\circ\text{C}$?
2. What would your answer be if the reactor were cooled to $0 \text{ }^\circ\text{C}$?

P 28

Consider the following gas phase reaction carried out in a PFR:

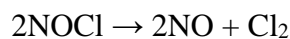


The entering reactant is pure NOCl fed with $C_{\text{NOCl},0} = 0.2 \text{ mol/dm}^3$, and the entering volumetric flow rate v_0 is $10 \text{ dm}^3/\text{s}$. The reaction follows an elementary rate law with $k = 0.29 \text{ dm}^3/(\text{mol}\cdot\text{s})$. If 90% conversion is to be achieved in the PFR

1. Please find the space time, τ
2. Please find the reactor volume, V

P 29

Consider the following gas phase reaction carried out in a constant volume batch reactor:



The entering reactant is pure NOCl fed with $C_{\text{NOCl},0} = 0.2 \text{ mol/dm}^3$, and the entering volumetric flow rate v_0 is $10 \text{ dm}^3/\text{s}$. The reaction follows an elementary rate law with $k = 0.29 \text{ dm}^3/(\text{mol}\cdot\text{s})$

Please find the time, t , necessary to achieve 90% conversion.

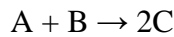
P 30

A second order reaction is carried out in a packed bed reactor, and assume no changes in the total molar of gases in the reaction. Please use equations and then sketch qualitative figures to illustrate the effect of pressure drop on the following important parameters in the PBR carried out isothermally:

1. Concentration profile
2. Reaction rate
3. Conversion
4. Volumetric flow rate

P 31

Consider the gas phase reaction in a PBR fed with equimolar feed of A and B, i.e., $C_{A0} = C_{B0} = 0.2 \text{ mol/dm}^3$



The entering molar flow rate of A is 2 mol/min; the reaction rate constant k_A is 1.5 dm⁶/mol/kg/min; the pressure drop term α is 0.0099 kg⁻¹. Assume 100 kg catalyst is used in the PBR.

1. Find the conversion X .
2. Assume there is no pressure drop (i.e., $\alpha = 0$), please calculate the conversion.
3. Compare and comment on the results from a and b.

P 32

The reversible isomerization *meta*-Xylene ↔ *para*-Xylene follows an elementary rate law. If X_e is the equilibrium conversion:

Show for a batch reactor and a PFR: $t = \tau_{PFR} = \frac{X_e}{k} \ln \frac{X_e}{X_e - X}$

P 33

The reversible isomerization *meta*-Xylene ↔ *para*-Xylene follows an elementary rate law. If X_e is the equilibrium conversion:

Show for a CSTR: $\tau_{CSTR} = \frac{X_e}{k} \frac{X}{X_e - X}$

P 34

1. Explain what is meant by homogeneous and heterogeneous as applied to catalysis.
2. What are some of the purposes of using a catalyst? State, in general terms, how a catalyst works.
3. Please name the important components of a heterogeneous catalyst, and list at least three most common examples of each component.
4. What is the advantage of supported catalysts? Why is a support used instead of just finely divided metal powder?

P 35

1. State and explain the effect of a catalyst on the rate and on the equilibrium yield in a reversible reaction.
2. Explain the terms heterogeneous and active sites as applied to a catalyst.
3. Define the following terms:
Turnover frequency; Catalyst selectivity; Sintering.

P 36

1. What is the difference between structure sensitive and structure insensitive reactions. Give one example of each.
2. Transition elements and their compounds are often used as catalysts.

- ✓ Explain why catalysts do not affect the position of an equilibrium.
 - ✓ Write an equation for one large-scale industrial process in which a transition element is used as a catalyst. State the catalyst used.
3. Addition of molybdenum enhances the catalytic activity of iron in the Haber's process for the manufacture of ammonia. What are the substances like molybdenum called?
 4. Very small amounts of impurity in mixtures of reactants can drastically reduce catalytic activity. Give one example of this effect and explain why this happens.

P 37

1. Please describe at least three causes of catalyst deactivation.
2. Explain the different shape selectivities of zeolite or molecular sieve catalysts.
3. Consider a platinum catalyzed reaction. You can run the reaction on the wire, or take the wire and smash it with a hammer and then run the reaction. Will you get higher rate on the smashed wire? why?
4. What are promoters and poisons? Give one example of each.
5. Suggest different measures that can be taken to maximise the efficiency and minimise the costs associated with a very expensive heterogeneous catalyst.
6. Catalysts are important in many industrial processes.
 - ✓ State a chemical equation for a reaction in an industrial process that uses a heterogeneous catalyst and name the catalyst used.
 - ✓ Explain one advantage and one disadvantage of using a heterogeneous catalyst as opposed to a homogeneous catalyst.

P 38

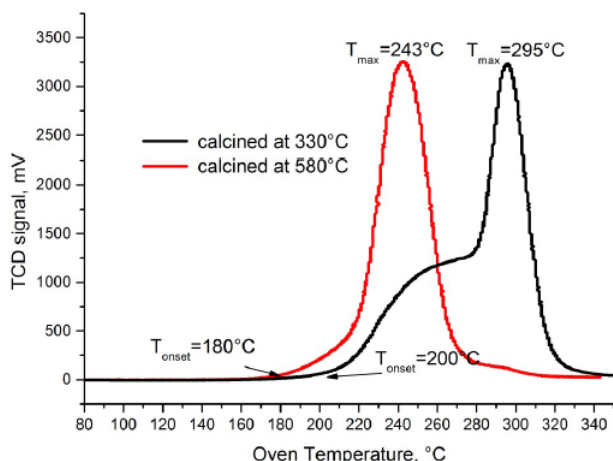
1. Impregnation is one of the simplest but most often used method for catalyst preparation. Explain the difference between incipient wetness impregnation and wet impregnation.
2. Describe the difference in co-precipitation and deposition-precipitation.
3. What is the principle behind the co-precipitation preparation method?
4. What is catalyst activation?

P 39

1. Name two surface characterization methods and two bulk characterization methods mentioned in the lecture.
2. How are physisorption and chemisorption measurement applied for different purposes? What parameters can be obtained for a catalyst from physisorption and chemisorption analyses?
3. Give a short description of the interaction on which the BET method is founded and describe which area is being measured by this method.

P 40

1. The following figure was obtained from a TPR study of Cu based catalysts for methanol synthesis. The methanol synthesis activity tests showed that the activity for the catalyst calcined at 330 °C was 90 μ mol/min/gcat, while for the catalyst calcined at 580 °C was 240 μ mol/min/gcat, under otherwise same reaction conditions. Explain the activity difference based on the TPR analyses.



- Describe how XRD, TEM, and chemisorption can be used to determine the catalyst particle sizes.
- Explain the main difference in TEM and SEM characterization.

P 41

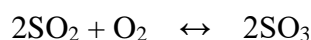
- State three essential steps in the mechanism of heterogeneous catalysis.
- The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its activity as a heterogeneous catalyst.
 - ✓ Explain why transition metals which adsorb strongly are not usually good catalysts.
 - ✓ Explain why transition metals which adsorb weakly are not usually good catalysts.
- Silver and tungsten aren't very good catalysts, but platinum and nickel can be excellent catalysts. Explain why this is in terms of the strength of the adsorption of gases to their surfaces.
- Give a reason, other than strength of adsorption, why the adsorption of reactants onto a catalyst surface does not always result in a reaction.

P 42

- Distinguish between physisorption and chemisorption. How does extent of adsorption vary with temperature in case of physisorption and chemisorption?
- How do chemisorption promote chemical reactions? What types of chemisorption lead to the poisoning of a catalyst?
- Nickel catalyzes the hydrogenation of a carbon-carbon double bond. For example, with ethylene to form ethane. Draw a series of labelled diagrams to show the mechanism for this reaction, showing clearly the role of adsorption.

P 43

Although the equilibrium constant, K_p , for the reaction



is $4 \times 10^{22} \text{ kPa}^{-1}$ at 298 K, SO_2 does not react readily with oxygen at this temperature.

- Explain why this reaction does not occur readily.

2. The reaction between sulphur dioxide and oxygen is catalysed by nitrogen dioxide, NO₂. The mechanism involves the formation of nitrogen monoxide, NO. Suggest two equations to show how NO₂ could be involved as a catalyst in this reaction.

P 44

For the following reaction: A(g) + B(g) → C(g)

1. Derive the rate equations of the reactions using the Langmuir-Hinshelwood model. Clearly state any assumptions.
2. Derive the rate equations of the reactions using the Eley-Rideal model. Clearly state any assumptions.
3. Explain how you would experimentally determine which of the two models actually operates for the reaction.

P 45

1. Deduct the Langmuir adsorption isotherm

$$\theta = \frac{C_{A \cdot S}}{C_t} = \frac{K_A P_A}{1 + K_A P_A}$$

Where $C_{A \cdot S}$ is the occupied sites by A, C_t is the total number of sites, thus θ is the site coverage of A; K_A is the adsorption equilibrium constant for A, P_A is the partial pressure of A.

2. What is the essential assumptions for Langmuir adsorption isotherm?

P 46

Show the adsorption isotherm in the presence of adsorbate A and B is given by the relationship

$$\theta = \frac{C_{A \cdot S}}{C_t} = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}$$

Where $C_{A \cdot S}$ is the occupied sites by A, C_t is the total number of sites, thus θ is the site coverage of A; K_A is the adsorption equilibrium constant for A, P_A is the partial pressure of A; K_B is the adsorption equilibrium constant for B, P_B is the partial pressure of B.

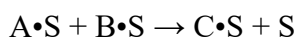
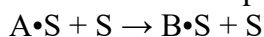
P 47

Deduct the adsorption isotherm for $A_2 + 2S \leftrightarrow 2A \cdot S$

Assume θ is the site coverage, K_A is the adsorption equilibrium constant, P_A is the partial pressure of the A.

P 48

Deduct the rate expression for the following dual site reaction



By assuming the surface reaction is the rate-determining step and irreversible, and explain qualitatively in the general LHHW rate expression.

P 49

- Given the reaction $2A \leftrightarrow B+C$, the rate law has been found to be $-r_A = \frac{kP_A^2}{(1+K_A P_A + K_C P_C)^2}$
Propose two possible mechanism for this reaction.
- Given the reaction $A \leftrightarrow B+C$, the rate law has been found to be $-r_A = \frac{kP_A}{1+K_A P_A + K_C P_C}$
Propose the possible mechanism for this reaction.

P 50

Given the reaction $2A \leftrightarrow B+C$, Where the adsorption equilibrium constant for reactant A is $K_A = 4 \text{ atm}^{-1}$ and for reactant C is $K_C = 6 \text{ atm}^{-1}$

- What is the ratio of sites with A adsorbed to those sites with C adsorbed when the conversion is 50%?
- What is the conversion when the sites with A adsorbed are equal to those with C adsorbed?

P 51

The rate law for the hydrogenation (H) of ethylene (E) to form ethane (A) over a cobalt-molybdenum catalyst is

$$-r'_E = \frac{kP_E P_H}{1+K_E P_E}$$

Suggest a mechanism and rate-limiting step consistent with the rate law.

P 52

The main reaction to produce hydrogen in industry in the steam methane reforming (SMR) using a supported Ni catalyst.

- Write down the reaction equation for the main reaction of SMR.
- Which side reactions can bring about carbon formation on the catalyst?
- Why extended carbon deposition can lead to hot spots?
- Describe briefly two independent methods to reduce carbon formation on the nickel catalyst during SMR.

P 53

Syngas produced by autothermal reforming has a lower H_2/CO ratio than syngas produced by steam reforming.

- Write the possible reactions occurring in the autothermal reformer.
- What is the reason for the lower H_2/CO ratio compared with steam reforming?
- Why would there be so much interest in catalyzing the oxidation reactions occurring in autothermal reforming?

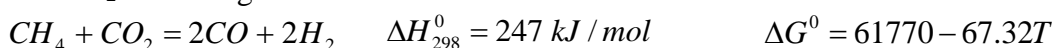
P 54

The steam reforming reactions are preferred thermodynamically at low pressure and high temperatures.

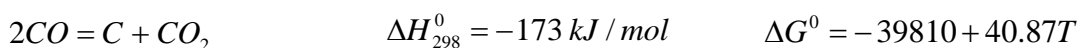
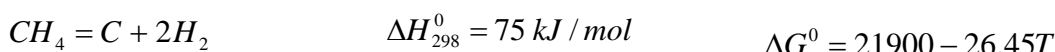
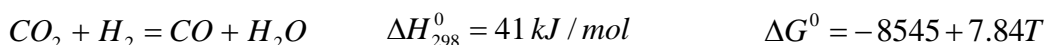
1. Why in practice they are always performed at high pressures?
2. What is the molar H_2/CO ratios resulting from steam reforming and partial oxidation?
3. The structure of the available metal surface strongly influences the catalyst activity for steam reforming. For instance, the close-packed (111) surface of nickel is less active than the more open (110) surface. What is this phenomenon named in catalysis? Could you please give another example of this phenomenon?

P 55

The CO_2 reforming reaction is described as



The side reactions are



Indicate in what temperature range each of the reactions will occur and discuss what is the desired operating temperature range for the DRM reaction to take place while avoid carbon formation.

P 56

Although the Fischer-Tropsch reaction has been known for a long time, there is still debate on its reaction mechanism.

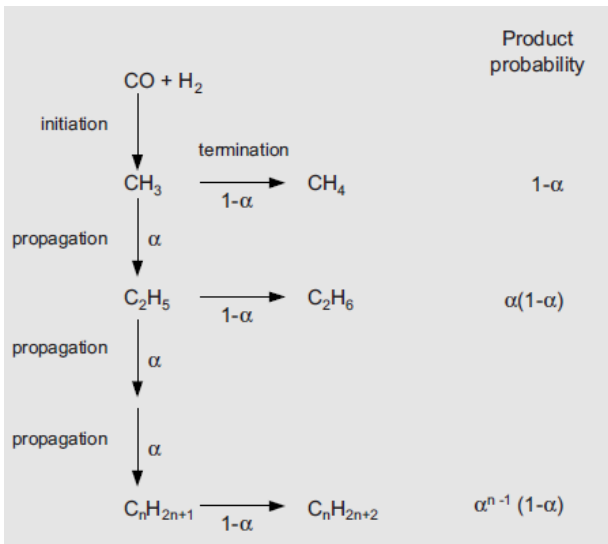
1. Propose one possible mechanisms.
2. Please illustrate the main difference between low temperature and high temperature Fischer-Tropsch synthesis (catalysts, reactors, reaction condition, and products, etc).
3. Explain the main difference over the Co based catalysts and Fe based catalysts for low temperature Fischer-Tropsch synthesis.

P 57

The CO methanation reaction was studied using a commercial 0.5 wt% Ru on $\gamma\text{-Al}_2\text{O}_3$. The catalyst dispersion percentage of atoms exposed, determined from hydrogen chemisorption, was found to be 49%. At a pressure of 988 kPa and a temperature of 475 K, a turnover frequency, TOF_{CH_4} , of 0.044 s^{-1} was reported for methane. What is the rate of formation of methane, r_M , in $\text{mol/s}\cdot\text{g}$ of catalyst?

P 58

The chain growth mechanism for Fischer-Tropsch synthesis can be described by the Anderson-Flory-Schulz kinetics, and can be schematically shown below.



Based on this model scheme:

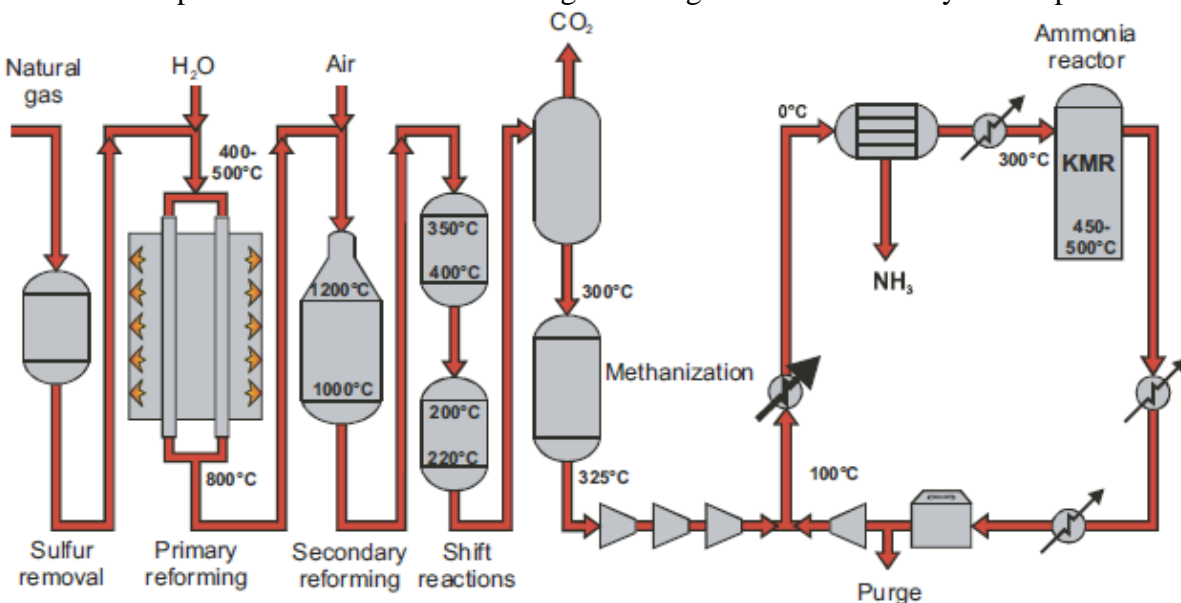
1. What would be the effect of an increase in the H₂/CO ratio in the feed on the average chain length of the produced hydrocarbons?
2. Would the products be mainly linear or branched? What is desired for gasoline and diesel fuel, respectively, and why?
3. Why is much more gasoline produced in fluidized bed reactors than in a fixed bed or slurry-phase reactor?

P 59

Explain the main difference between the Sasol GTL process and the Shell Middle Distillate Synthesis (SMDS) process.

P 60

Below is a simplified flow scheme of an integrated single-train ammonia synthesis plant:



1. Which reactions take place in the reactors (primary reforming, secondary reforming, shift reaction, methanation, ammonia reactor), please give reaction equations?
2. Why would carbon oxides be poisonous to the iron catalyst in the ammonia reactor?
3. Why would a methanation step be preferred over additional water-gas shift conversion in preparing for ammonia production?
4. Much more CO is converted in the HT shift reactor than in the LT shift reactor. Nevertheless, the catalyst volumes are approximately equal. What is the explanation?
5. What is the main difference between ammonia synthesis and methanol synthesis during the syngas preparation stage, if assume an autothermal reformer is used?

P 61

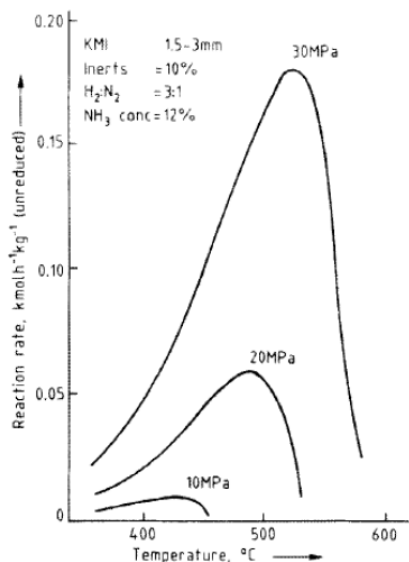
The most widely used NH_3 synthesis catalyst was the so-called BASF S6-10 catalyst, which is prepared from magnetite (Fe_3O_4), fused with a few percent of K_2O , Al_2O_3 and CaO and subsequently reduced. The table below shows the composition (atom %) of the catalyst in the bulk, and the Auger Electron Spectroscopy measurement of the surface composition of the catalyst before reduction and after reduction.

	Fe	K	Al	Ca	O
Bulk composition	40.5	0.35	2.0	1.7	53.2
AES					
Before reduction	8.6	36.1	10.7	4.7	40.0
After reduction	11.0	27.0	17.0	4.0	41.0

1. What is the dominant active component of the catalyst?
2. What are the different functions of K_2O , Al_2O_3 and CaO .
3. Why there is such a big difference in bulk composition and the surface composition, and the surface composition before and after reduction?
4. Please give a possible mechanism for the ammonia synthesis reaction over the Fe based catalyst.
5. One of the intriguing facts pertaining to ammonia synthesis is that catalysts that have been in continuous use industrially for 14 years exhibit essentially the same catalytic activity as the fresh catalysts. What characteristics of the catalysts have contributed to the long lifetime?

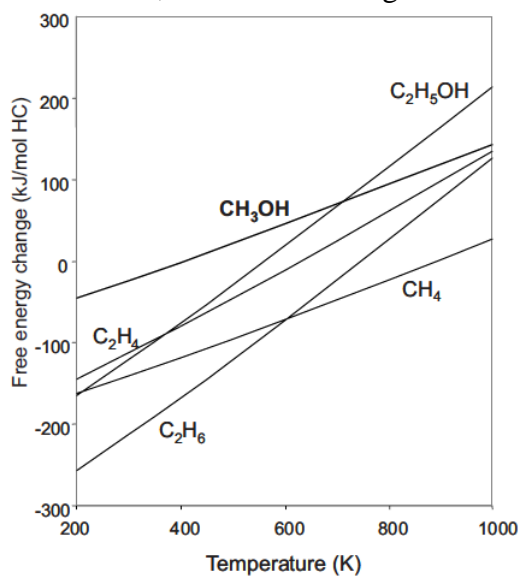
P 62

Explain the reaction rate curves for ammonia synthesis under different reaction conditions.



P 63

In view of the thermodynamic data for the formation of methanol and by-products from the reaction of CO and H₂, as show in the figure below.



1. What is important in terms of catalyst development? How is the catalyst development for methanol compared with that for ammonia synthesis?
2. Historically, both high temperature synthesis catalyst ($\text{ZnO}/\text{Cr}_2\text{O}_3$) and the low temperature catalyst ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$) have been used. Please indicate the typical working reaction conditions for the two different catalysts.
3. In view of the active component Cu and Zn, what is the main active component, Cu, Cu^I, Zn, or mixtures of them?
4. Exposing the partially deactivated $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst to a highly reducing mixture of CO₂-free synthesis gas for a short time restores the activity, why?

P 64

Methanol is not synthesized on the Cu/ZnO/Al₂O₃ catalysts since 1960s, with operating pressures of 60–100 bar, and temperatures of 220–270 °C.

1. The Cu based catalysts have been discovered much earlier than 1960s, why was it only applied industrially before that?
2. It has been widely accepted that CH₃OH is synthesized from CO₂ instead of CO, why the industrial processes do not synthesize CH₃OH directly from CO₂, and the CO₂ content in the syngas mixture has to be controlled to a small percentage?
3. Why air should not be used in the production of syngas during autothermal reforming for methanol production?
4. In the purification of syngas for methanol, would a methanation reactor be included? And a shift reactor?
5. What is the main advantage for direct conversion of methane to methanol instead of through the syngas process?

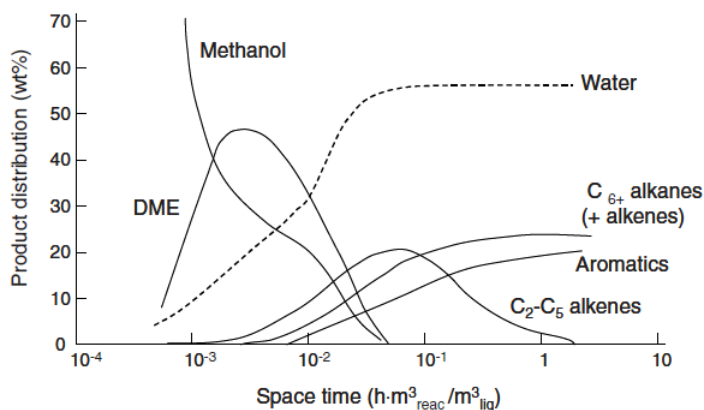
P 65

The following table is a typical product selectivity data for methanol to olefin (MTG) processes compared with the low temperature and high temperature Fischer-Tropsch processes, please comment on the product selectivity in terms of the catalysts used for the processes and the process conditions.

Selectivity (carbon atom basis), wt%	Low-temperature FT Co catalyst @ 470 K	High-temperature FT Fe catalyst @ 570 K	MTG
C ₂ - (fuel gas)	6	15	1
C ₃ -C ₄ (LPG)	6	23	10
C ₅ -C ₁₁ (gasoline)	19	36	89
C ₁₂ -C ₁₈ (diesel)	22	16	-
C ₁₉₊ (waxes)	46	5	-
Oxygenates	1	5	-

P 66

The following figure is the product selectivity as a function of the space time. Please explain why the product selectivity changes in this manner.



P 67

DME (dimethyl ether) can be produced by two different technologies, i.e, one-step process or two-step process.

1. Use reactions to describe the two different technologies.
2. What are the catalysts applied in the two different technologies?
3. Compare the two different technologies in terms of thermodynamic limits.

P 68

There are two different processes UOP/Hydro methanol to olefin (MTO) and Lurgi methanol to propylene (MTP) for the production of light alkenes from methanol. The following table compares the typical product composition of the two processes, together with the traditional naphtha cracking process for olefin production.

Product (wt%)	Naphtha cracker 1070 K, 2 bar	MTO 630 K, 2 bar	MTP 730 K, 1.5 bar
Light gases ^a	27	2	1
Ethene	29	39	—
Propene	16	42	72
Butenes	5	12	—
C ₅ +	23	5	27
Total	100	100	100

^aIncluding light alkanes.

1. Please comments on the product selectivity data for MTO and MTP. What is this particular type of selectivity named in catalysis, in relation to zeolite?
2. Name the catalysts used for the two processes.
3. What are the main differences between the two types of catalysts?
4. What are the main differences of reactors applied in the processes, and why?
5. Please briefly describe the UOP/Hydro MTO and Lurgi MTP processes.

P 69

1. What is the basic framework of zeolite?
2. Why zeolites are called molecular sieves?
3. Where does the acid sites in a zeolite structure originate?

P 70

1. In methanol conversion to olefins over zeolite catalyst with different pore sizes, explain why the product selectivity is different as exemplified in table below.
2. Explain why the different product selectivity at low conversion and high conversion as exemplified in table below.

Pore Size	Examples	Performance (low conversion)	Performance (high conversion)
Small	ERI ERI/OFF KFI	Light olefins	Paraffins
Medium	MFI FER MTT	Olefins	Paraffins Aromatics
Large	MOR FAU		Olefins Aromatics Paraffins