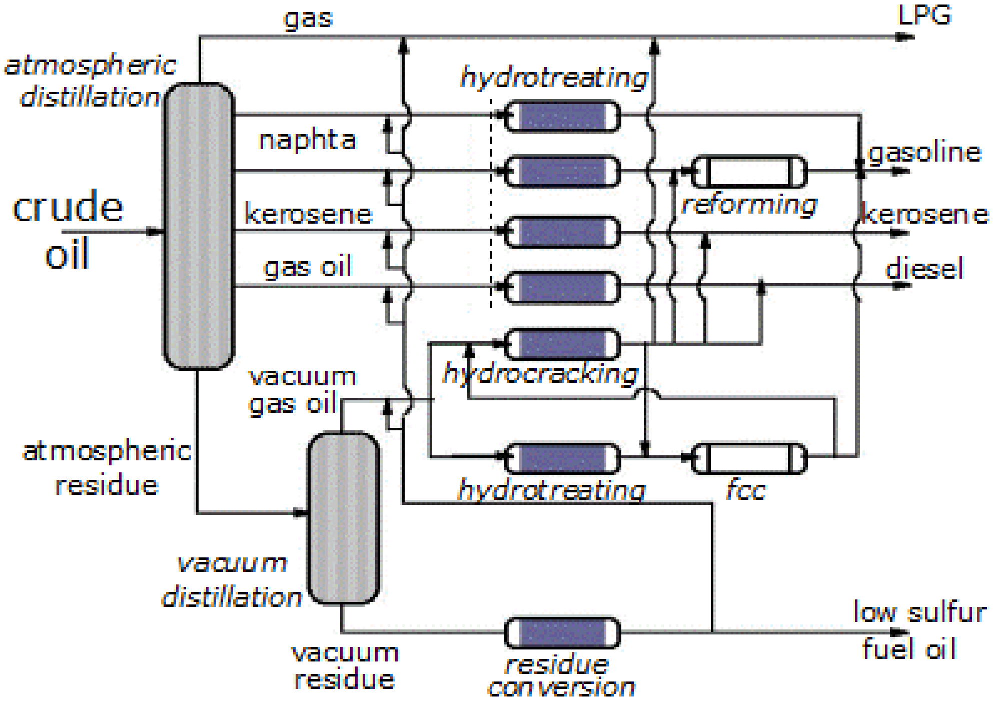
# Examination MSc Course Adsorption Kinetics and Catalysis
# April 11, 2017, 17.00 – 20.00 h, Educatorium-Gamma

- Use separate sheets of paper for parts **A**, **B,** and **C** of this examination.
- Turn off your mobile phone + display your ID card.
- We wish you success with the examination!

## Part A. Catalysis

### Question A-1 [40 points]

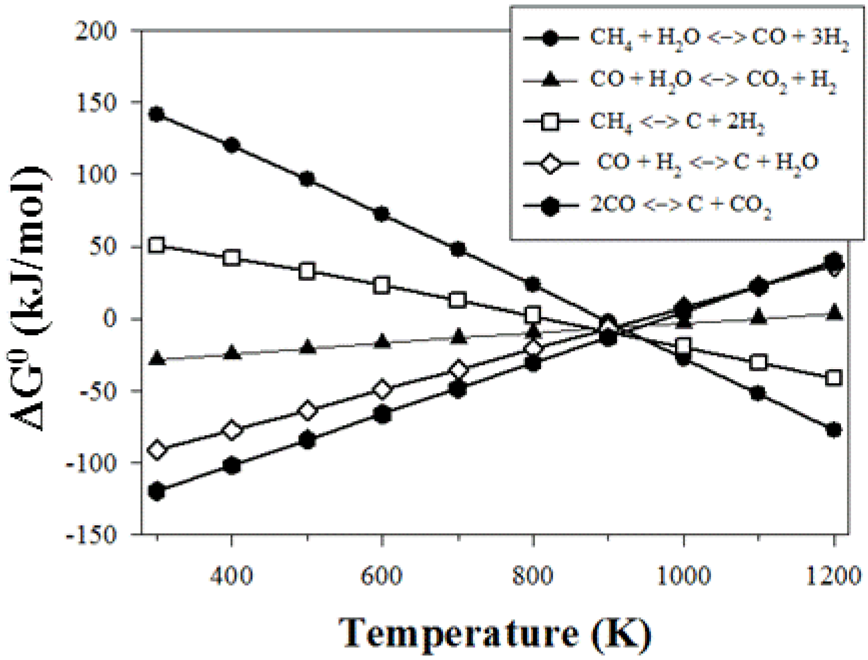
Oil refining consists of a number of distillation and catalytic processes. A processing scheme of an oil refinery is shown below. Answer the following questions.



a. What are the three main overall objectives of an oil refinery?
b. Mention one process that deliver gasoline as main product. Mention for this process: feedstock used; catalyst used; main catalytic reaction. Describe in detail how the main catalytic reaction contributes to the objective of the process.
c. The main product from the hydrocracking process is normally diesel. How can one operate the refinery (see scheme above) in such a way that also the hydrocracker will contribute substantially to the production of gasoline?

**Question A-2 [40 points]**

Methane can be reacted with steam to provide synthesis gas; the reaction is referred to as steam methane reforming (SMR). The reverse reaction of synthesis gas to methane is referred to as methanation. Relevant data on the thermodynamic equilibria for these main reactions and possible side reactions are shown below.



Please answer the following questions making use of the above data.

a. Which temperature range do you suggest for the steam methane reforming to proceed?
b. Which side reaction is a major threat during SMR. Provide the reaction equation of this side reaction. Provide also one proposal how to mitigate the risk that this side reaction will proceed.
c. The reaction of synthesis gas to form methane may become more important in the future to obtain synthetic natural gas from biomass. Which temperature range do you suggest for methanation?
d. What is a major threat for methanation as far as side reactions are concerned? Provide the reaction equations of these side reactions.

**Question A-3 [30 points]**

A carbon-supported palladium catalyst (Pd/C) is used for the hydrogenation of cyclohexene to cyclohexane in the liquid phase using hydrogen gas at a pressure of 1 bar. The reaction is first-order with respect to hydrogen that dissolves in the liquid phase. The solubility of hydrogen at 1 bar is $C_{H2} = 1.0$ mol.m$^{-3}$ and the effective diffusion coefficient of dissolved hydrogen is $D_e = 3.0*10^{-9}$ m$^2$.s$^{-1}$. The reaction rate does not depend on the cyclohexene concentration and is equal to $r = -20$ mol.m$^{-3}{}_{cat}$.s$^{-1}$.

a. In order to calculate whether or not internal diffusion limitation takes place we use the Thiele modulus ($\phi$). Write down the formula for the Thiele modulus for a spherical (!) particle and explain the meaning of all symbols including the units used.
b. Calculate the value of the Thiele modulus ($\phi$) and the effectiveness factor ($\eta$) for the spherical catalyst particles with a diameter of 0.10 cm on the basis of the data provided. What is your conclusion with respect to diffusion limitation?
c. Propose two fundamentally different experimental actions to reduce internal mass transfer limitation for this catalytic reaction. Describe briefly how you would carry out this action in a laboratory experiment.

## Part B. Kinetics, Transition State Theory, Chemisorption

**Question B-1: [30 points]**

An atom A reacts with atom B to a molecule AB.
The associated rate constant is $k_1^+$ and the back-reaction has a rate constant $k_1^-$.
Molecule AB reacts with another atom B to the product $AB_2$ with rate constant $k_2^+$.
Assume that the rate constant $k_2^-$ of the backward reaction is zero and use the steady state approximation for the concentration of the molecules AB.

a. Give the equation for the reaction rate $d[AB_2]/dt$ as a function of the concentrations of the atoms A and B.
b. What orders of the reaction in the concentrations of A and B are possible? Explain.

**Question B-2: [40 points]**

Consider the adsorption of molecule A to a transition state (#) that is completely immobile over a flat surface. The rate of adsorption can be described with transition state theory.

a. Give all possible degrees of freedom of a free molecule. Which of these degrees of freedom play a role in the determination of the rate of adsorption.

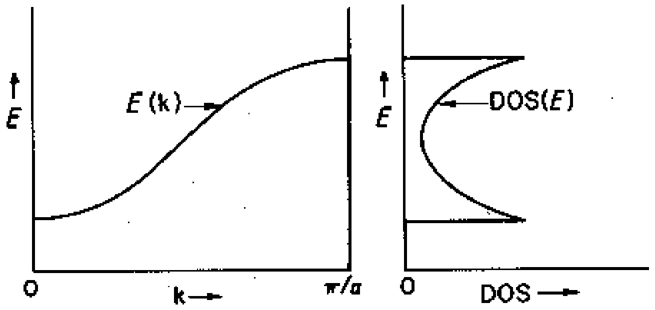
The resulting rate of adsorption can be given with this expression:

$$\frac{d\theta_{A^*}}{dt} = \frac{S_0(T)}{N_0\sqrt{2\pi m k_B T}}\, p_A$$

b. Explain the origin of the denominator $\sqrt{2\pi m k_b T}$.
c. Explain the meaning of the parameter $S_0(T)$;
d. What is a typical value of $S_0(T)$ in case of an immobile transition state for molecular adsorption.

**Question B-3: [30 points]**

Consider a one-dimensional chain of equally distanced carbon atoms that are positioned on the x-axis. The figure shows the band structure of the carbon 2s orbitals.



a) Describe the figure. Explain the meaning of the parameter ‘k’ and explain the shape of the density of states (DOS). If you give additional explanations of the figure you can obtain extra points.
b) If you consider the 2p orbitals, what aspects of their band structure is different than the 2s orbitals? Describe separately the 2p orbitals in the x-, y- and z- direction.

# Part C. Physisorption

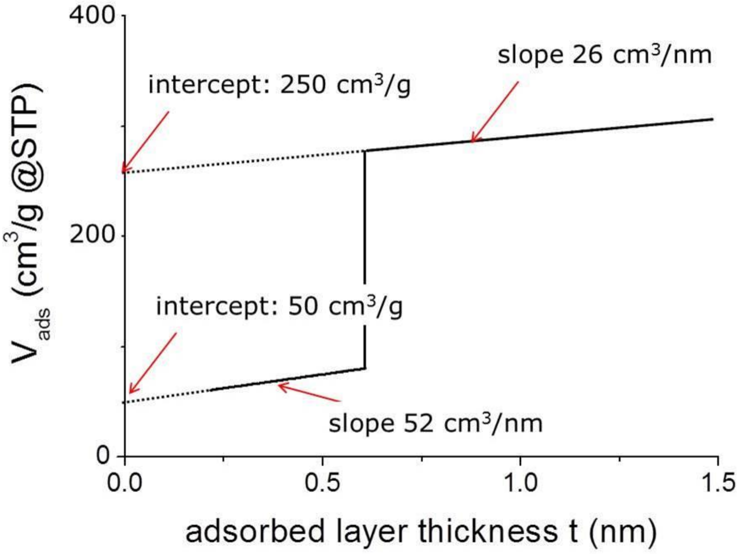
## Question C-1 (see additional information on page 6)

Consider Langmuir-type adsorption.

a. What are the four assumptions regarding the equilibrium between molecules in the gas phase and molecules adsorbed at the surface of a solid that form the basis for the Langmuir isotherm description?

b. Does the fractional coverage of the solid surface with adsorbed gas molecules at a given gas pressure change with temperature or not? If it changes, does the coverage increase or decrease with increasing temperature? Explain your answer.

Below is a t-plot, constructed using data from the experimental 77K $N_2$ physisorption isotherm (the adsorption branch) for a silica sample with unknown morphology, porosity and particle size. The solid black line indicates the experimental data. Also indicated are the fitting results to obtain the intercepts with the y-axis and the slopes of the plot in two designated regions. The t-plot has been constructed with the help of the Harkins-Jura-de Boer reference isotherm (see additional information at the end of the text).



c. Explain in maximum 5 sentences how a t-plot is constructed from an experimentally measured isotherm.

d. Does this sample contain micropores and/or mesopores? If not, explain why not. If there are pores, please give the micro- and mesopore volumes for this material.

e. At an adsorbed layer thickness t of 0.6 nm, a sudden jump in the plot is observed. Calculate the diameter of the pores causing this jump in the t-plot.

**Additional information:**

The volume of (ideal) gaseous $N_2$ at standard temperature (273 K) and pressure (1 atm) is 649 times that of liquid $N_2$ at 77 K.

Kelvin equation (mind the minus sign!): $-\dfrac{2v_l\gamma}{r} = RT\ln\dfrac{p}{p_0}$

With for $N_2$ at 77K:
$v_l$ = 30 cm$^3$/mol
$\gamma$ = 0.0085 J/m$^2$
R= 8.314 J/K mol

The BET model description of an isotherm is the following:

$$\frac{V_{\mathrm{ad}}}{V_{\mathrm{ml}}} = \frac{cp/p_0}{\left(1-p/p_0+cp/p_0\right)\left(1-p/p_0\right)}$$

The reference isotherm used is the Harkins-Jura-de Boer (HJdB) isotherm:

with $p_r=p/p_0$.

$$t[\mathrm{nm}] = \sqrt{\frac{0.1399}{0.034-\log p_r}}$$

Exam AKC, April 11, 2017
Utrecht University