COURSE: **Adsorption, Kinetics and Catalysis (COURSE CODE: SK-MAKC)**
EXAM: Final Exam
TIME: 08-11-2019 from 11.30 to 14.30 h
LENGTH: 3h00
PLACE: Educatorium - Megaron

IMPORTANT
- PLACE YOUR ID CARD (WITH PHOTO) ON THE TABLE
- WRITE YOUR NAME AND STUDENT NUMBER ON EVERY ANSWER SHEET
- USE A SEPARATE PAPER SHEET FOR PARTS A, B, C OF THE EXAM
- HAND IN YOUR EXAM (you may keep the question sheet)

EXAM SPECIFICS
- **ALWAYS EXPLAIN YOUR ANSWER!!!**
- This exam counts for 100% of the final grade.
- The minimum score of this exam needs to be at least 6.0 to prevent a re-exam. In order to be allowed to take a re-exam, the final grade for the course needs to be at least 4.0.
- Points per question are distributed as indicated at each question, part A contributes 25%, part B 37.5% and part C 37.5% to the final grade
- When answering the questions, please make sure that your writing is readable (if it takes us too much time to decipher, it will be consired as an incorrect answer). You can answer either in English or in Dutch (or a mixture if you prefer)

PERMITTED EQUIPMENT
Calculator (mobile phone and graphical calculator are not allowed).

We wish you much success!

Petra de Jongh
Frank de Groot
Eelco Vogt

GENERAL EXAMINATION RULES
- You are not allowed to leave the exam room before 13.00 (this is become online exams are running in parallel). Latecomers are allowed in up to 30 minutes after the start time.
- All electronic equipment needs to be switched off (including mobile phones), with the exception of electronic equipment allowed by the examiner.
- Your coat and closed bag are placed on the ground.
- Raise your hand when you need to go to the bathroom. 1 person at a time. Place your mobile phone visibly on your table just before you go.
- Raise your hand if you have a question about the exam, or need extra paper, etc.
- Not following the instructions of the surveillant (examiner) can lead to exclusion from the exam.
- When fraud is suspected the surveillant (examiner) will collect evidence of the fraud, will file a report of which you will receive a copy, and will allow you to finish your exam. The examiner will send the evidence, report and the exam to the Exam Committee within one working day and will inform the Education Manager of the suspicion of fraud. See also EER article 5.14.
- Upon receiving your result you can request the examiner for access to your graded exam.

Part A. Physisorption (de Jongh)
50 points = 25% of total grade

Question A-1 (first additional information, then the question itself)

Additional information:

Simplified form of the Kelvin equation: $$\ln\frac{p}{p_0} = -\frac{2v_l\gamma}{rRT}$$

For N_2 at 77K: $v_l = 30$ cm^3/mol, $\gamma = 0.0085$ J/m^2. R= 8.314 J K^{-1} mol^{-1}
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.

A monolayer of liquid N_2 on surface has a thickness of 0.354 nm.

The BET model description of an isotherm is the following:

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

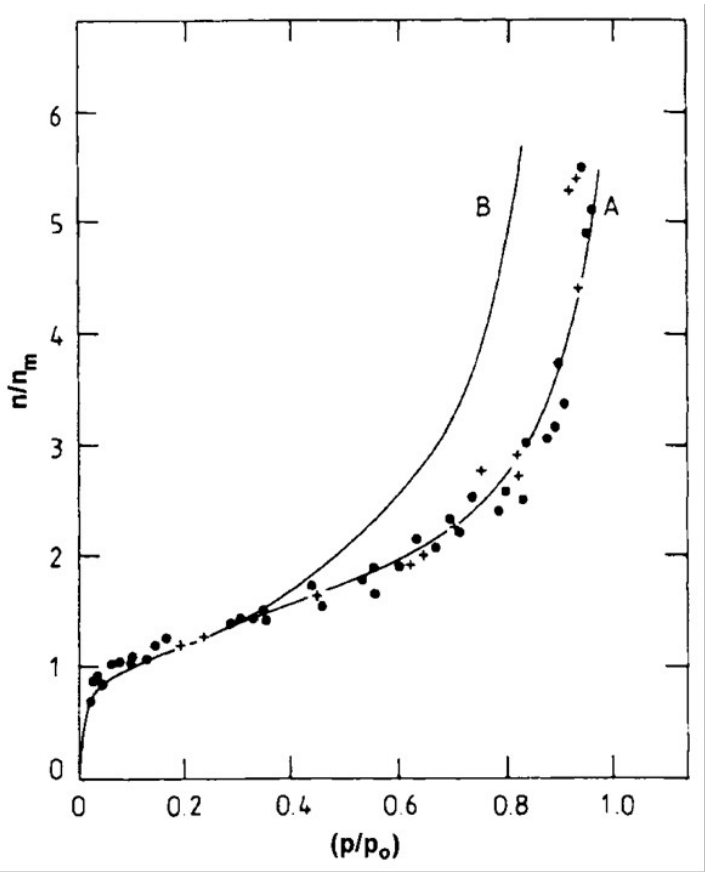
As a reference isotherm you can use the Harkins-Jura-de Boer (HJdB) isotherm:

with $p_r = p/p_0$.

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

Question A-1

The Figure on the right shows N_2 physisorption isotherms measured at 77 K for alumina and silica samples (experimental data fitted with line A) and a fit in the region around p/p_0=0.2 with the BET equation (from Lippens et al, *J. Catal.* **3** (1964) 32). The unit on the y-axis is the number of adsorbed molecules n divided by the number of molecules in a monolayer n_m.



N_2 on non-porous Al_2O_3 (+) and SiO_2 (•) experimental isotherm (A) and BET fit (B)

a) Name three reasons why N_2 is a very convenient adsorbens (compared to for instance Ar or H_2O) for this type of measurements that are meant to determine the structure of a sample. (6 points)

b) What is the more common variable and unit that is used on the y-axis of an N_2 isotherm? Explain its exact meaning (6 points).

c) Mention 7 assumptions that have been made to derive the BET equation (7 points).

d) At low pressures (p/p_0<0.2) the experimental adsorption is higher than predicted by he BET equation. Explain why - involve in your explanation one of the assumptions mentioned in c) (7 points).

e) At high pressures (p/p_0>0.4) the experimental adsorption is lower than predicted by the BET equation. Explain why - involve in your explanation one of the assumptions mentioned in c) (7 points).

f) Do these alumina and silica samples contain a significant amount of micropores? Explain your answer. With which method could you quantify the micropore volume from these experimental data? Describe the main principle of this method (max 5 lines, 7 points).

g) Make a sketch of what the experimental isotherm would look like if the silica and alumina materials additionally would contain 0.2 cm^3/g cylindrical mesopores (open at both ends) with a radius of 2 nm. Be as precise as possible, e.g. mind the exact numbers at the x, and y-axis at which you draw additional features. Explain the main features of the sketch. (10 points)

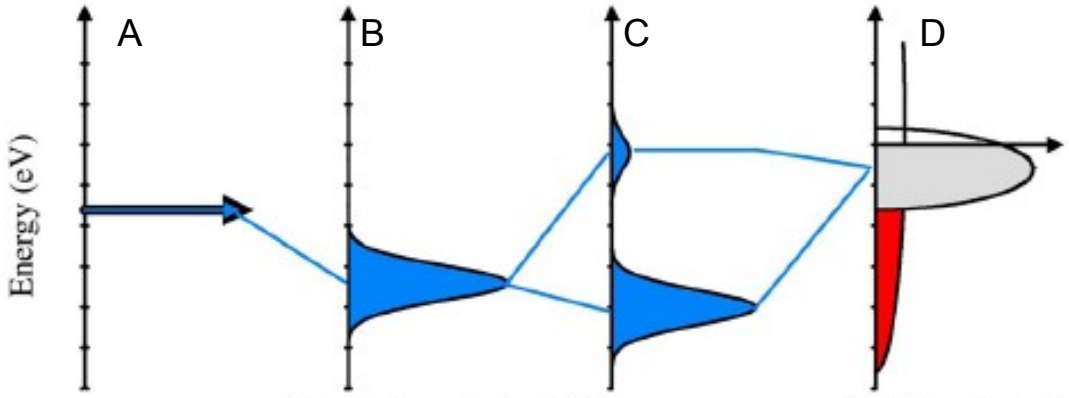
Part B. Kinetics and Chemisorptions (de Groot)
10 points for this part of the exam, which is 37.5% of the total grade

Question B-1

a) Make a drawing of the 1-dimensional band structure of a chain of $2p_x$ orbitals in an infinite chain of carbon atoms on the x-axis. Explain the drawing.
b) Make a drawing of the 1-dimensional band structure of a chain of $2p_z$ orbitals in an infinite chain of carbon atoms on the x-axis. Use the same scale as for question a. Explain the drawing.

Question B-2

The diagram below indicates the energy effects related to the orbital energy positions in the adsorption of an atom (diagram A) on a metal surface (diagram D). In diagrams B and C the energy effects are indicated if the atom approaches the surface of the metal.



a) Explain the shape of the density of states indicated in image D?
b) What (type of) metal does image D relate to? Explain.
c) What interaction is the reason for the energy effect as indicated in panel B? Explain.
d) What interaction is the reason for the energy effect as indicated in panel C? Explain.
e) What is wrongly (or incompletely) indicated in these images? Explain.

Question B-3

a) Derive Langmuir adsorption isotherm for the dissociative adsorption of H_2.

Suppose the catalytic formation of methanol from CO and H_2 occurs through a mechanism in which the surface reaction between adsorbed CO and the first H-atom determines the rate (the reverse reaction may be ignored), while all subsequent reaction steps are fast.
The first three reaction steps are:

$CO + * \leftrightarrow CO^*$ (equilibrium)
$H_2 + 2^* \leftrightarrow 2H^*$ (equilibrium)
$CO^* + H^* \rightarrow COH^* + *$

b) Why can the subsequent reaction steps be ignored?
c) Derive an expression for the rate of the reaction, using the Langmuir-Hinshelwood mechanism.
d) Discuss the range of values that the orders in H_2 and CO can have.

Part C. Catalysis (Vogt, 30 points = 37.5% of total grade)

1. Ammonia synthesis (10 points)

The synthesis of ammonia from the elements is exothermic.

a. Provide the reaction equation. (1 pt)
b. What happens to the equilibrium at increasing temperature? What conditions will favor the formation of ammonia? (3pts)
c. Describe the key reaction steps that are required for this process. (2 pts)
d. Describe which element is most suited for this reaction, and why (2 pts)
e. Why is the production of Ammonia one of the largest emitters of CO_2? (2pts)

2. KLM-Shell syn fuels (10 points)

The following press release was published on February 8, 2021:

World first in the Netherlands by KLM, Shell and Dutch ministry for Infrastructure and Water Management: first passenger flight performed with sustainable synthetic kerosene
For the first time worldwide, a passenger flight partly flown on sustainably produced synthetic kerosene, was carried out in The Netherlands. This was announced today during the international conference on Synthetic Sustainable Aviation Fuels (SAF) in The Hague. Shell, producer of the sustainable kerosene and KLM, operating the flight, presented this showcase during the meeting initiated by Cora van Nieuwenhuizen, Dutch Minister for Infrastructure and Water Management. European politicians, policymakers, representatives from the business community, the (aviation) industry and NGOs participated at the conference. The parties stated that 500 liters of synthetic fuel was delivered, refueled and used on a flight from Amsterdam to Madrid. The synthetic fuel was made from CO_2 and green hydrogen.

a. Provide the combination of processes required (at least four are required) to go from CO_2 in air to jet-fuel molecules (4 pts)
b. The reaction of CO_2 to hydrocarbons requires hydrogen. Give at least two processes to make hydrogen, of which one should be carbon-neutral. (2 pts)
c. Describe the key reaction steps that are required on the catalyst surface for the main synthesis process involving C-C-coupling reactions. Describe which metals are good catalysts for this reaction, why they are good catalysts, and what are the main differences between the metals with respect to the process. (4 pts)

Mind that there is another question on the next page…

3. **Ideal plug flow reactor (10 points)**

This is the result of a set of catalyst test measurements at 350°C. You have measured the concentration of reactant A at the inlet (C_{in}) and the outlet (C_{out}) of your ideal tubular plug flow reactor. You have varied the flowrate (Gas Flow) and the Catalyst volume. You have determined that the reaction is first order in reactant A.

	Test 1	*Test 2*	*Test 3*	*Test 4*
Gas flow (ml/s)	9.0	6.7	4.8	2.5
Catalyst volume (ml)	29.7	22.2	15.8	8.3
C_{in} (g/ml)	327.0	326.0	327.0	328.0
C_{out} (g/ml)	297.5	297.0	297.3	313.1

A. Calculate the conversion for each test (2 pts)
B. Calculate the reaction rate constant K for these measurements (3 pts)
C. Does this set of experiment indicate any problems with mass transfer? If so, what is the problem, and how can it be prevented? (3 pts)
D. Is this a differential or integral reactor? (2 pts)