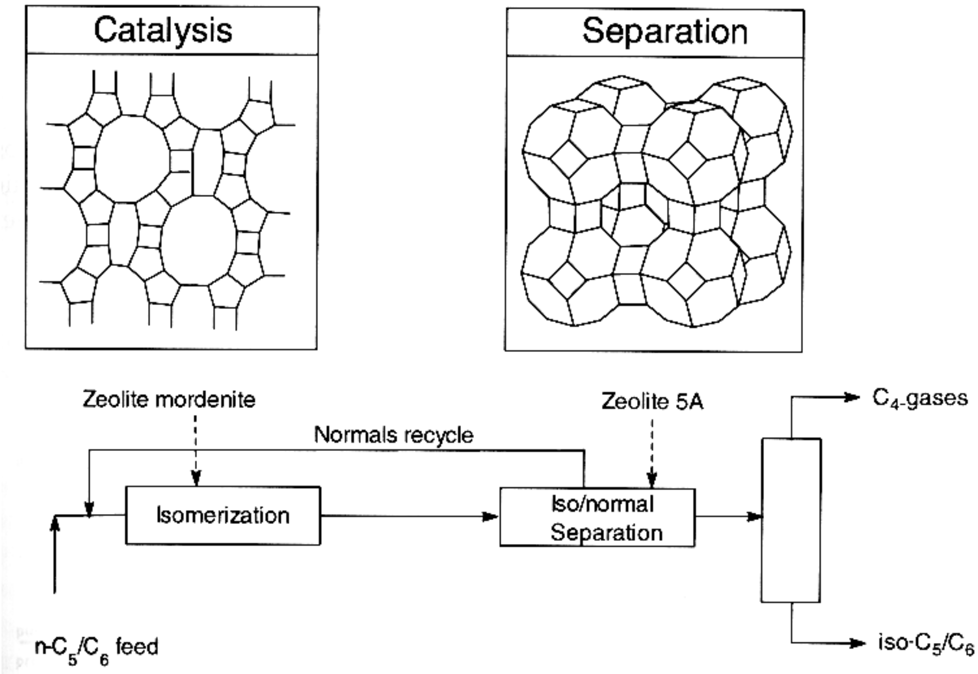
Examination MSc Course Adsorption Kinetics and Catalysis
April 11, 2016, 9.00 – 12.00 am
Location: BBL-083

Please use separate sheets of paper for parts **A**, **B,** and **C** of this examination.

A. Catalysis – general and diffusion

Question A.1

In oil refining hydro-isomerisation of C_5-C_6 normal alkanes to iso-alkanes is carried out according to the process lay-out shown below.



a. Why is hydro-isomerisation of C_5-C_6 normal alkanes relevant in an oil refinery? In your answer describe (i) in which refinery product the iso-alkanes will end up and (ii) discuss the product quality aspects (at least two) of the iso-alkanes that make these attractive molecules for the product in question.
b. Describe in in detail the role of the catalyst Pt/Mordenite. Explicitly mention the role of both Pt and H-MOR. In your answer give the equations of the reactions that proceed over Pt and over the acid sites of H-MOR. Also discuss the possible impact of the distance (intimacy) between metal and acid sites in the Pt/H-MOR catalyst.
c. What is the role of Zeolite 5A in the overall process? What is an important requirement of this zeolite to be effective in the process?

Question A.2

The oxidation of CO with O_2 is catalyzed by a metal oxide (MO) according to the Mars-Van Krevelen (MKV) mechanism.

a. Describe this mechanism by drawing schematically the surface of the metal oxide and showing clearly each elementary step of the oxidation of CO with O_2.
b. Draw a graph with on the x-axis the metal-oxygen (M-O) bond strength and on the y-axis the activity of the MO catalyst. In this graph draw the relationship between bond strength and activity of catalysts. Explain the shape of the curve by involving the relevance of the M-O bond strength for the elementary steps of the oxidation of CO with O_2.

Question A.3

A silica-supported nickel catalysts (spherical particles) is used for the hydrogenation of benzene to cyclo-hexane in the liquid phase. The hydrogen pressure used is 1 bar and at that pressure the solubility of hydrogen in the liquid phase is

$$C_{H2} = 5.0 \text{ mol.m}^{-3}.$$

The target rate of hydrogenation of benzene per unit volume of catalyst is

$$r = 1.0 \text{ mol.m}^{-3}\text{.s}^{-1}$$

The effective diffusion coefficient of hydrogen in the liquid phase under the prevailing conditions is

$$D_e = 1.0\text{x}10^{-9} \text{ m}^2\text{.s}^{-1}$$

The reaction is first-order with respect to hydrogen and zero-order with respect to benzene. It is also known that for diffusion limitation H_2 is the limiting reactant due to its low concentration in the liquid phase.

Calculate the maximum size of the catalyst spheres at which diffusion limitation is still absent. Describe the calculation in detail.

B- Kinetics, Transition State Theory, Chemisorption

Question B-1:

A wooden object is found that is believed to be ancient. With mass spectrometry one finds that the amount of carbon 14 is 75% of that of living trees. The half-life of carbon 14 is 6000 year

a) How old is the wooden object? **[1 point]**

b) Why is the amount of carbon 14 stable in living objects? **[0.5]**

Question B-2: [2.5 points]

a) Derive the Langmuir adsorption isotherm for the simultaneous adsorption of the two species A and B.

Question B-3:

Consider the atomic adsorption of atom A.

The rate of adsorption via a mobile transition state can be given with this expression:

$$\frac{d\theta_{A^*}}{dt} = \frac{1}{N_0 q_{1D}^*} p_A$$

Where N_0 are the adsorption sites per area.

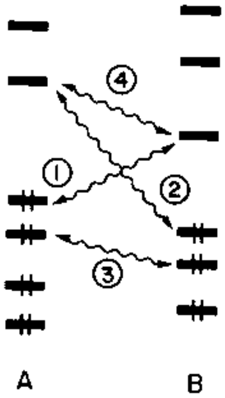
a) Explain the other two parameters q_{1D}^* and p_A. **[1]**

b) What is different in the equation for an immobile transition state? Explain **[1]**

c) Explain if a mobile or immobile transition state leads to the largest rate of adsorption. **[1]**

Question B-4:

The figure shows the bonding interactions between molecule A and molecule B, as described with the Frontier Orbital model.



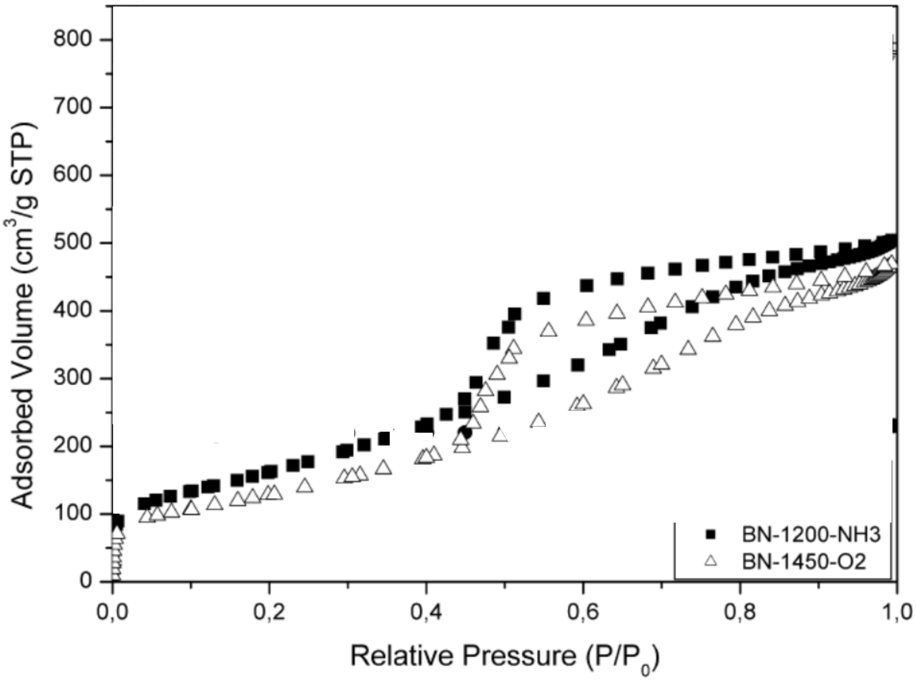
a) Describe the four interactions and explain their effect on the chemical bonding. **[1]**

b) Draw a similar figure describing the chemical bonding between an adsorbate and a metal surface and indicate the interactions. **[1]**

c) Describe all interactions and explain their effect on the chemical bonding, in particular the differences with the answer for question 4a). **[1]**

C. Physisorption (see additional information at the end of the text on page 5)

Below you see nitrogen physisorption isotherms that have been measured at 77 K. The picture is taken from a paper of Schlienger *et al* (Chem. Mater. 24 (2012), 88-96). The isotherm that we will discuss is labeled BN-1200-NH3 (filled squares). It is a boron nitride material that has been prepared by making a negative replica ("afdruk") of a porous carbon material.



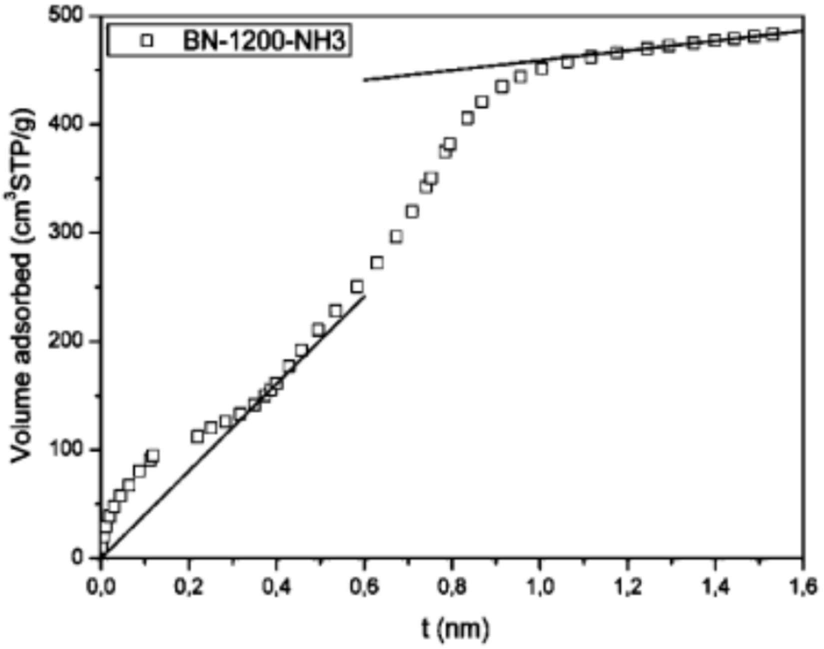
a. Give three reasons why in general experimental isotherms often do not have the exact shape as described by the BET model for multilayer adsorption (see additional information). Involve in your answer approximations/simplifications made to derive the BET model description of an isotherm.

b. In the specific isotherms shown above we observe hysteresis: a difference between the adsorption and desorption branches of the isotherm. Explain what the physical origin is of this hysteresis. Include in your explanation the concept "radius of curvature".

c. To learn more about the morphology and porosity of this material, the authors of the paper have constructed a socalled "t-plot", which is shown on the next page. Explain in maximum 5 lines how a t-plot can be constructured.

d. Give a rough estimate of the micropore volume and the mesopore volume of this material. Apart from those two pore volumes, which other two parameters can be derived from this t-plot?

e. Give a tentative explanation why at low pressures the experimental data lie above the straight line shown (that goes through the origin and is a fit to the data around 0.4 relative pressure)



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
γ = 0.0085 J/m^2
R= 8.314 J/K mol

The BET model description of an isotherm is the following:

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

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

with $p_r=p/p_0$.

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