



# **THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS**

## **Series 3**

**33<sup>rd</sup> – 37<sup>th</sup> IChOs  
2001 – 2005**

**Edited by Anton Sirota**

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**36<sup>th</sup>**



**International Chemistry Olympiad**

## **PREPARATORY PROBLEMS**

Edited by Anton Sirota

**34 theoretical problems  
6 practical problems**

**2004**

**THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS, Series 3**  
**The preparatory problems from the 33<sup>rd</sup> – 37<sup>th</sup> IChOs**

**Editor: Anton Sirota**

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# **Preparatory Problems and Worked Solutions**

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**PREPARATORY PROBLEMS**

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## PREPARATORY THEORETICAL PROBLEMS

### THEORETICAL PROBLEM 1

#### *Combustion Energy*

- 1.1 Write down the chemical equations for the total burning of propane and butane gas in air. Indicate whether the substances are liquid (l), gaseous (g), or solid (s) under standard conditions.
- 1.2 Calculate the combustion energies for the burning of 1 mol of propane and butane. It can be assumed that all reactants and products are obtained under standard conditions.
- 1.3 How much air (volume composition: 21 % of oxygen and 79 % of nitrogen) is used up in this process?  
Assume that oxygen and nitrogen behave like ideal gases.

The products are usually not obtained under standard conditions but at increased temperatures. Assume for the following that the products are produced at a temperature of 100 °C and at standard pressure, while the reactants react at standard conditions.

- 1.4 Calculate the combustion energies for the burning of 1 mol of propane and butane gas in air under these conditions.
- 1.5 What is the efficiency in % of the process in 1.4 compared to 1.2 and how is the energy difference stored?
- 1.6 Calculate the efficiency of the combustion process as a function of the temperature of the products between 25 °C and 300 °C. Assume that the water does not condense. Plot the efficiency as a function of the temperature (reactants still react at standard conditions).
- 1.7 Compare the combustion energy stored in a 1 liter bottle of propane and butane. Assume that the product temperature is 100 °C.  
The density of liquid propane is 0.493 g cm<sup>-3</sup>, while the density of liquid butane is 0.573 g cm<sup>-3</sup>.

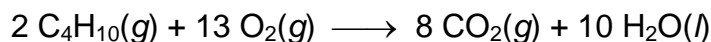
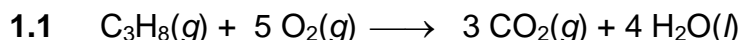


Thermochemical data:

Propane (g):	$\Delta_f H^\circ = -103.8 \text{ kJ mol}^{-1}$	$C_p = 73.6 \text{ J mol}^{-1} \text{ K}^{-1}$
Butane (g):	$\Delta_f H^\circ = -125.7 \text{ kJ mol}^{-1}$	$C_p = 140.6 \text{ J mol}^{-1} \text{ K}^{-1}$
CO <sub>2</sub> (g):	$\Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1}$	$C_p = 37.1 \text{ J mol}^{-1} \text{ K}^{-1}$
H <sub>2</sub> O (l):	$\Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1}$	$C_p = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$
H <sub>2</sub> O (g):	$\Delta_f H^\circ = -241.8 \text{ kJ mol}^{-1}$	$C_p = 33.6 \text{ J mol}^{-1} \text{ K}^{-1}$
O <sub>2</sub> (g):	$\Delta_f H^\circ = 0 \text{ kJ mol}^{-1}$	$C_p = 29.4 \text{ J mol}^{-1} \text{ K}^{-1}$
N <sub>2</sub> (g):	$\Delta_f H^\circ = 0 \text{ kJ mol}^{-1}$	$C_p = 29.1 \text{ J mol}^{-1} \text{ K}^{-1}$

---

## SOLUTION OF PREPARATORY PROBLEM 1



1.2 Combustion energy (reaction enthalpy):  $\Delta_c H^\circ = \sum_p \Delta_f H^\circ(\text{p}) - \sum_r \Delta_f H^\circ(\text{r})$

$$\Delta_c H^\circ(\text{propane}) = 3(-393.5 \text{ kJ mol}^{-1}) + 4(-285.8 \text{ kJ mol}^{-1}) - (-103.8 \text{ kJ mol}^{-1})$$

$$\Delta_c H^\circ(\text{propane}) = -2220 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\circ(\text{butane}) = 4(-393.5 \text{ kJ mol}^{-1}) + 5(-285.8 \text{ kJ mol}^{-1}) - (-125.7 \text{ kJ mol}^{-1})$$

$$\Delta_c H^\circ(\text{butane}) = -2877 \text{ kJ mol}^{-1}$$

1.3 On the assumption that oxygen and nitrogen behave like ideal gases, the volume is proportional to the amount of substance:

$$n_{\text{N}_2} = n_{\text{O}_2} \frac{V_{\text{N}_2}}{V_{\text{O}_2}} = n_{\text{O}_2} \times 3.76$$

5 mol of  $\text{O}_2$  and 18.8 mol of  $\text{N}_2$  are needed for the burning of 1 mol of propane.

6.5 mol of  $\text{O}_2$  and 24.4 mol of  $\text{N}_2$  are needed for the burning of 1 mol of butane.

When  $V = n R T p^{-1}$ , the volumes of air are:

$$\text{propane: } V_{\text{air}} = (5 + 18.8) \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times (1.013 \times 10^5 \text{ Pa})^{-1}$$

$$V_{\text{air}} = 0.582 \text{ m}^3$$

$$\text{butane: } V_{\text{air}} = (6.5 + 24.4) \text{ mol} \times 8.314 \text{ J (K mol)}^{-1} \times 298.15 \text{ K} \times (1.013 \times 10^5 \text{ Pa})^{-1}$$

$$V_{\text{air}} = 0.756 \text{ m}^3$$

1.4 Under these circumstances, water is no longer liquid but gaseous. The combustion energies change due to the enthalpy of vaporization of water and higher temperature of the products.

Energy of vaporization of water at 250 °C:

$$\Delta_v H^\circ(\text{H}_2\text{O}) = \Delta_f H^\circ(\text{H}_2\text{O}(\text{l})) - \Delta_f H^\circ(\text{H}_2\text{O}(\text{g})) = -285.8 \text{ kJ mol}^{-1} - (-241.8 \text{ kJ mol}^{-1})$$

$$\Delta_v H^\circ(\text{H}_2\text{O}) = 44 \text{ kJ mol}^{-1}$$

The energy needed to increase the temperature of the products up to 1000C is:

$$\Delta H(T) = (T - T_0) \sum n_i C_p(i)$$

The energy E released by burning of 1 mol of gas is:

$$E(\text{propane}, T) = (-2220 + 4 \times 44) \text{ kJ} + (T - T_0) (3 \times 37.1 + 4 \times 33.6 + 18.8 \text{ mol} \times 29.1) \text{ JK}^{-1}$$

$$E(\text{propane}, T) = -2044 \text{ kJ} + (T - T_0) \times 792.8 \text{ J K}^{-1} \quad (1)$$

$$E(\text{propane}, 373.15 \text{ K}) = -1984.5 \text{ kJ mol}^{-1}.$$

$$E(\text{butane}, T) = (-2877 + 5 \times 44) \text{ kJ} + (T - T_0) (4 \times 37.1 + 5 \times 33.6 + 24.4 \text{ mol} \times 29.1) \text{ JK}^{-1}$$

$$E(\text{butane}, T) = -2657 \text{ kJ} + (T - T_0) \times 1026.4 \text{ J K}^{-1} \quad (2)$$

$$E(\text{butane}, 373.15 \text{ K}) = -2580.0 \text{ kJ mol}^{-1}.$$

**1.5** Efficiency of propane:

$$\eta(\text{propane}) = \frac{E(\text{propane}, 373.15 \text{ K})}{\Delta_c H^0} = 1984.5 / 2220 = 89.4 \text{ \%}.$$

$$\eta(\text{butane}) = \frac{E(\text{butane}, 373.15 \text{ K})}{\Delta_c H^0} = 2580.0 / 2877 = 89.7 \text{ \%}.$$

The energy is stored in the thermal energies of the products.

**1.6** The combustion energies have been calculated in 1.4, equation (1), (2):

$$E(\text{propane}, T) = -2044 \text{ kJ} + (T - T_0) \times 792.8 \text{ J K}^{-1}$$

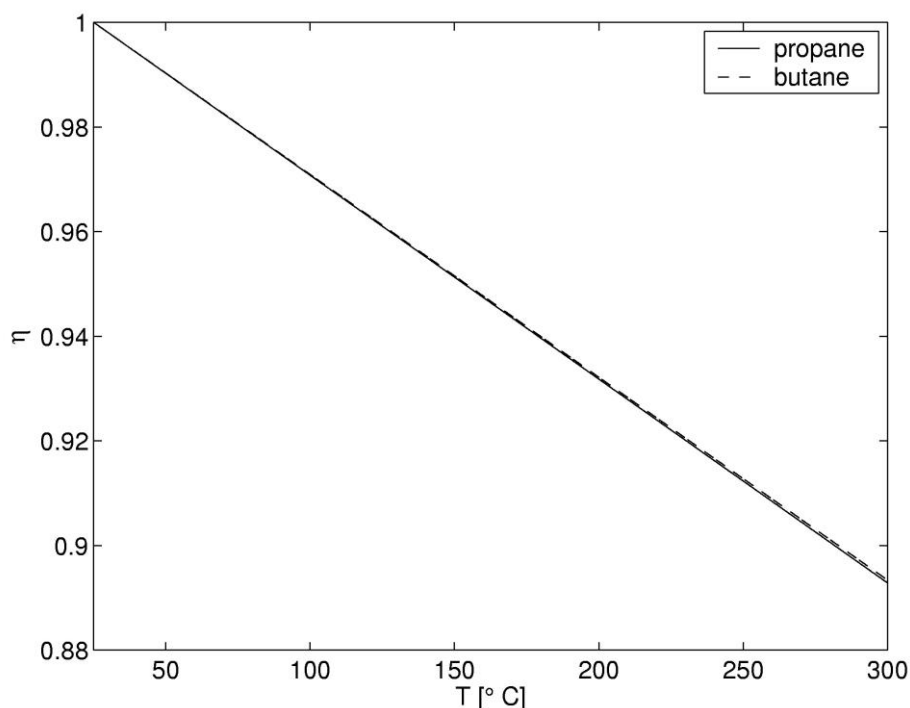
$$E(\text{butane}, T) = -2657 \text{ kJ} + (T - T_0) \times 1026.4 \text{ J K}^{-1}$$

The efficiencies are given by:

$$\text{Propane: } \eta_{\text{propane}}(T) = 1 - 3.879 \times 10^{-4} \times (T - T_0)$$

$$\text{Butane: } \eta_{\text{butane}}(T) = 1 - 3.863 \times 10^{-4} \times (T - T_0)$$

The plot shows that there is really no difference between the efficiencies of burning propane and butane.



**1.7** 
$$n_j = \rho_j \frac{V_j}{M_j}$$

$$n_{\text{propane}} = 0.493 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 \times (44.1 \text{ g mol}^{-1})^{-1} = 11.18 \text{ mol}$$

$$n_{\text{butane}} = 0.573 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 \times (58.1 \text{ g mol}^{-1})^{-1} = 9.86 \text{ mol}$$

$$E_i = n_i \cdot E(\text{propane/butane}, 373.15\text{K})$$

$$E(\text{propane}) = 11.18 \text{ mol} \times (-1984.5 \text{ kJ mol}^{-1}) = -22.19 \text{ MJ}$$

$$E(\text{butane}) = 9.86 \text{ mol} \times (-2580.0 \text{ kJ mol}^{-1}) = -25.44 \text{ MJ}$$

Despite the fact that there is less butane per volume, the energy stored in 1 dm<sup>3</sup> of butane is higher than the energy stored in 1 dm<sup>3</sup> of propane.

## THEORETICAL PROBLEM 2

### *Haber–Bosch Process*

Ammonia is one of the most important intermediates. It is used, for example, for the production of fertilizers. Usually, ammonia is produced from hydrogen and nitrogen in the Haber–Bosch process.

- 2.1 Write down the chemical equation for this reaction.
- 2.2 Calculate the thermodynamic properties (reaction enthalpy, entropy, and Gibbs energy) for this reaction under standard conditions. Use the values in Table 1. Is the reaction exothermic or endothermic? Is it exergonic or endergonic?
- 2.3 What will happen if you mix nitrogen and hydrogen gas at room temperature? Explain your reasoning.
- 2.4 Calculate the thermodynamic properties (reaction enthalpy, entropy, and Gibbs energy) for this chemical reaction at 800 K and 1300 K at standard pressure. Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

The temperature dependence of the heat capacity and the entropy are described by  $C_p(T) = a + bT + cT^2$  and  $S(T) = d + eT + fT^2$ . The values of the constants  $a - f$  can be found in Table 2.

- 2.5 Calculate the mole fraction of  $\text{NH}_3$  that would form theoretically at 298.15 K, 800 K and 1300 K and standard pressure.

Assume that all the gases behave like ideal gases and that the reactants are added in the stoichiometric ratio.

In an industrial process, the reaction has to be fast and result in high yields. Task 2.3 shows that the activation energy of the reaction is high and task 2.5 shows that the yield decreases with increasing temperatures. There are two ways of solving this contradiction.

- 2.6 The reaction can proceed at lower temperatures by using a catalyst (for example iron oxide). How does the catalyst influence the thermodynamic and kinetic properties of the reaction?
- 2.7 It is also possible to increase pressure. How does the pressure change influence the thermodynamic and kinetic properties of the reaction?
- 2.8 What are the best conditions for this reaction?

Table 1:

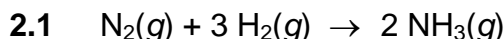
Chemical Substance	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	$C_p^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>
N <sub>2</sub> (g)	0.0	191.6	29.1
NH <sub>3</sub> (g)	- 45.9	192.8	35.1
H <sub>2</sub> (g)	0.0	130.7	28.8

Table 2:

Chemical Substance	<b>a</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	<b>b</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	<b>c</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	<b>d</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	<b>e</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	<b>f</b> (Jmol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>
N <sub>2</sub> (g)	27.3	5.2·10 <sup>-3</sup>	-1.7·10 <sup>-9</sup>	170.5	8.1·10 <sup>-2</sup>	-2.3·10 <sup>-5</sup>
NH <sub>3</sub> (g)	24.2	4.0·10 <sup>-2</sup>	-8.2·10 <sup>-6</sup>	163.8	1.1·10 <sup>-1</sup>	-2.4·10 <sup>-5</sup>
H <sub>2</sub> (g)	28.9	-5.8·10 <sup>-4</sup>	1.9·10 <sup>-6</sup>	109.8	8.1·10 <sup>-2</sup>	-2.4·10 <sup>-5</sup>

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## SOLUTION OF PREPARATORY PROBLEM 2



2.2  $\Delta H^\circ = -91.8 \text{ kJ mol}^{-1}$

$$\Delta S^\circ = -198.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -32.7 \text{ kJ mol}^{-1}$$

The reaction is exothermic and exergonic under standard conditions.

2.3 Ammonia will form instantaneously, but the activation energy for the reaction will be so high that the two gases won't react. The reaction rate will be very low.

2.4 The enthalpy of formation is described by  $\Delta_f H(T) = \Delta_f H^\circ + \int_{T_0}^T c_p(T) dT$

For  $\text{N}_2$ :  $\Delta_f H(800 \text{ K}) = 15.1 \text{ kJ mol}^{-1}$ ,  $\Delta_f H(1300 \text{ K}) = 31.5 \text{ kJ mol}^{-1}$ .

For  $\text{H}_2$ :  $\Delta_f H(800 \text{ K}) = 14.7 \text{ kJ mol}^{-1}$ ,  $\Delta_f H(1300 \text{ K}) = 29.9 \text{ kJ mol}^{-1}$ .

For  $\text{NH}_3$ :  $\Delta_f H(800 \text{ K}) = -24.1 \text{ kJ mol}^{-1}$ ,  $\Delta_f H(1300 \text{ K}) = 4.4 \text{ kJ mol}^{-1}$ .

This leads to a reaction enthalpy of:

$$\Delta H(800 \text{ K}) = -107.4 \text{ kJ mol}^{-1}, \quad \Delta H(1300 \text{ K}) = -112.4 \text{ kJ mol}^{-1}.$$

Entropy can be calculated directly with this equation..

For  $\text{N}_2$ :  $S(800 \text{ K}) = 220.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S(1300 \text{ K}) = 236.9 \text{ J mol}^{-1} \text{ K}^{-1}$ .

For  $\text{H}_2$ :  $S(800 \text{ K}) = 159.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S(1300 \text{ K}) = 174.5 \text{ J mol}^{-1} \text{ K}^{-1}$ .

For  $\text{NH}_3$ :  $S(800 \text{ K}) = 236.4 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S(1300 \text{ K}) = 266.2 \text{ J mol}^{-1} \text{ K}^{-1}$ .

This leads to a reaction entropy of:

$$S(800 \text{ K}) = -225.4 \text{ J mol}^{-1} \text{ K}^{-1}, \quad S(1300 \text{ K}) = -228.0 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Gibbs energy is:

$$\Delta G(800 \text{ K}) = 72.9 \text{ kJ mol}^{-1}, \quad \Delta G(1300 \text{ K}) = 184.0 \text{ kJ mol}^{-1}.$$

The reaction is still exothermic but now endergonic.

2.5 The equilibrium constant can be calculated from Gibbs energy according to

$$K_x(T) = \exp(-\Delta G(RT)^{-1}).$$

This leads to the following equilibrium constants:

$$K_x(298.15 \text{ K}) = 5.36 \times 10^5,$$

$$K_x(800 \text{ K}) = 1.74 \times 10^{-5},$$

$$K_x(1300 \text{ K}) = 4.04 \times 10^{-8}.$$

Using  $K_x = \frac{x_{\text{NH}_3}^2}{x_{\text{H}_2}^3 x_{\text{N}_2}}$ ,  $x_{\text{H}_2} = 3 x_{\text{N}_2}$ , and  $1 = x_{\text{NH}_3} + x_{\text{N}_2} + x_{\text{H}_2}$

we obtain  $K_x = \frac{(1 - 4 x_{\text{N}_2})^2}{27 x_{\text{N}_2}^4}$ .

This equation can be converted into  $x_{\text{N}_2}^2 + \frac{4}{\sqrt{27K_x}} x_{\text{N}_2} - \frac{1}{\sqrt{27K_x}} = 0$

which has only one solution, since  $K_x$  and  $x_{\text{N}_2}$  are always positive:

$$x_{\text{N}_2} = -\frac{2}{\sqrt{27K_x}} + \sqrt{\frac{4}{27K_x} + \frac{1}{27K_x}}.$$

We obtain the following table:

$T \text{ K}^{-1}$	$x_{\text{N}_2}$	$x_{\text{H}_2}$	$x_{\text{NH}_3}$
298.15	0.01570	0.04710	0.03720
800	0.24966	0.74898	0.00136
1300	0.24998	0.74994	0.00008

- 2.6** The catalyst reduces the activation energy of the process and increases the reaction rate. The thermodynamic equilibrium is unchanged.
- 2.7** Higher pressures will result in a higher mol fraction of  $\text{NH}_3$ , since  $K_x = K_p p^2$  increases. An increase in pressure shifts the equilibrium toward the products but does not change the reaction rate.
- 2.8** The best conditions are: high pressure, temperature as low as possible and the presence of a catalyst. The temperature has to be optimized such that the turnover is fast and the yield still acceptable.



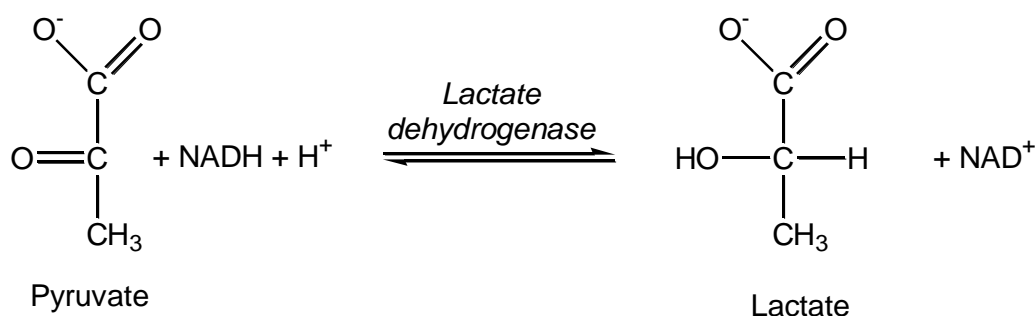
## THEORETICAL PROBLEM 3

### *Thermodynamics in Biochemistry*

Muscle cells need an input of free energy to be able to contract. One biochemical pathway for energy transfer is the breakdown of glucose to pyruvate in a process called glycolysis. In the presence of sufficient oxygen in the cell, pyruvate is oxidized to CO<sub>2</sub> and H<sub>2</sub>O to make further energy available. Under extreme conditions, such as an Olympic 100m sprint, the blood can not provide enough oxygen, so that the muscle cell produces lactate according to the following reaction:



Maurice Greene, AFP



$$\Delta G^\circ = -25.1 \text{ kJ mol}^{-1}$$

In living cells the pH value usually is about pH = 7. The proton concentration is therefore constant and can be included into  $\Delta G^\circ$  which is then called  $\Delta G^{\circ'}$ , a quantity commonly used in biochemistry.

- 3.1 Calculate  $\Delta G^\circ$  for the reaction given above.
- 3.2 Calculate the reaction constant  $K'$  (the proton concentration is included again in the constant,  $K' = K \cdot c(\text{H}^+)$ ) for the reaction above at 25°C and pH = 7.

$\Delta G^{\circ'}$  indicates the free enthalpy of the reaction under standard conditions if the concentration of all reactants (except for H<sup>+</sup>) is 1 mol dm<sup>-3</sup>. Assume the following cellular concentrations at pH = 7: pyruvate 380 μmol dm<sup>-3</sup>, NADH 50 μmol dm<sup>-3</sup>, lactate 3700 μmol dm<sup>-3</sup>, NAD<sup>+</sup> 540 μmol dm<sup>-3</sup>.

- 3.3 Calculate  $\Delta G'$  at the concentrations of the muscle cell at 25 °C.

### SOLUTION OF PREPARATORY PROBLEM 3

3.1  $\Delta G^0 = -RT \ln K$

$$= -RT \ln \frac{c(\text{lactate}) \times c(\text{NAD}^+)}{c(\text{pyruvate}) \times c(\text{NADH}) \times c(\text{H}^+)}$$

$$= -RT \ln \frac{c(\text{lactate}) \times c(\text{NAD}^+)}{c(\text{pyruvate}) \times c(\text{NADH})} - RT \ln \frac{1}{c(\text{H}^+)}$$

$$\Delta G^{0'} = -RT \ln \frac{c(\text{lactate}) \times c(\text{NAD}^+)}{c(\text{pyruvate}) \times c(\text{NADH})}$$

$$\begin{aligned}\Delta G^0 &= \Delta G^{0'} - RT \ln (c(\text{H}^+)^{-1}) \\ &= -25100 \text{ J mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298.15 \text{ K} \times \ln 10^7 \\ &= -25.1 \text{ kJ mol}^{-1} - 40.0 \text{ kJ mol}^{-1} \\ &= -65.1 \text{ kJ mol}^{-1}\end{aligned}$$

3.2  $\Delta G^{0'} = -RT \ln K'$   $K' = e^{-\Delta G^{0'}/(RT)}$

$$K' = e^{25100 / (8.314 \times 298.15)} \quad K' = 2.5 \times 10^4$$

3.3  $\Delta G' = \Delta G^{0'} + RT \ln \frac{c(\text{prod.})}{c(\text{react.})}$

$$= \Delta G^{0'} + RT \ln \frac{c(\text{lactate}) \times c(\text{NAD}^+)}{c(\text{pyruvate}) \times c(\text{NADH})}$$

$$= -25100 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298.15 \text{ K} \times \ln \frac{3700 \times 540}{380 \times 50}$$

$$\begin{aligned}&= -25.1 \text{ kJ mol}^{-1} + 11.5 \text{ kJ mol}^{-1} \\ &= -13.6 \text{ kJ mol}^{-1}\end{aligned}$$

## THEORETICAL PROBLEM 4

### Heat Conductivity

When considering the design of houses, the heat conductivity through walls, roofs, and the floor plays an important role. The heat conductivities ( $\lambda$ ) of some building materials are described in Table 1.

- 4.1 Calculate the heat flow through a wall of 150 m<sup>2</sup> (typical of a single-family house in Central Europe) that consists of a brick layer with a thickness of  $d = 24$  cm and through the same wall that consists, however, of a brick layer with a thickness of  $d = 36$  cm. There is a temperature of 25 °C inside and 10 °C outside.
- 4.2 The heat loss can be minimized by using a layer of polystyrene foam. Calculate the heat loss through a 10 cm polystyrene insulation foam. The wall area again is 150 m<sup>2</sup>.

It is advantageous to use the heat resistance  $\Lambda^{-1}$  for the calculation of the heat conductivity through a wall consisting of different layers:

$$\frac{1}{\Lambda} = \frac{d_1}{\lambda_1} + \frac{d_2}{\lambda_2} + \frac{d_3}{\lambda_3} + K$$

For the different parts of the house (window, wall) the diathermal coefficient can be calculated as:

$$k = \frac{\Lambda_1 A_1}{A_{\text{tot}}} + \frac{\Lambda_2 A_2}{A_{\text{tot}}} + \frac{\Lambda_3 A_3}{A_{\text{tot}}} + K$$

Energy-saving actions are of vital importance to decrease the energy requirements of the world. Good insulation is not only positive for the environment (reduction of CO<sub>2</sub> emissions) but also good for the economy. Presently, an energy-saving house has a maximum diathermal coefficient of 0.50 W m<sup>-2</sup>·K<sup>-1</sup>

- 4.3 Calculate the thickness of a wall that only consists of brick to achieve this requirement.
- 4.4 The wall thickness can be minimized by insulation layers. A typical wall consists of a brick layer that has a thickness of  $d_1 = 15$  cm at the outside, a concrete layer with a thickness of  $d_2 = 10$  cm, an insulation layer (polystyrene foam) of thickness  $d_3$  and a gypsum layer with a thickness of  $d_4 = 5$  cm on the inside of the wall. Calculate the thickness of the insulation layer and the total thickness of the wall to fulfil the requirements of an energy-saving house.

- 4.5** Windows increase the mean value of the energy loss. Assume a wall of 15 m<sup>2</sup> constructed as in 4.4 including a window of 4 m<sup>2</sup> with a mean diathermal coefficient of 0.70 W m<sup>-2</sup> K<sup>-1</sup>.

By what percentage has the thickness of the foam layer of 4.4 to be increased in order to achieve the same average k-value?

Table 1: Heat conductivity of different materials

Material	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )
Concrete	1.10
Building brick	0.81
Polystyrene insulation foam	0.040
Linoleum (floor covering)	0.17
Gypsum	0.35

Formula:

Heat flow through a wall: 
$$P_w = \frac{A}{d} \lambda (T_2 - T_1)$$

Area  $A$ , heat conductivity  $\lambda$ , temperature  $T$ , thickness  $d$

---

## SOLUTION OF PREPARATORY PROBLEM 4

4.1 The heat flows are:

$$P_W = 150 \text{ m}^2 \times (0.24 \text{ m})^{-1} \times 0.81 \text{ W m}^{-1} \text{ K}^{-1} \times (25^\circ\text{C} - 10^\circ\text{C}) = 7.59 \text{ kW and}$$

$$P_W = 150 \text{ m}^2 \times (0.36 \text{ m})^{-1} \times 0.81 \text{ W m}^{-1} \text{ K}^{-1} \times (25^\circ\text{C} - 10^\circ\text{C}) = 5.06 \text{ kW}$$

4.2  $P_W = 150 \text{ m}^2 \times (0.1 \text{ m})^{-1} \times 0.040 \text{ W m}^{-1} \text{ K}^{-1} \times (25^\circ\text{C} - 10^\circ\text{C}) = 0.90 \text{ kW}$

Although the wall is much thinner, the energy loss is much lower due to the much lower heat conductivity.

4.3  $k = \lambda \cdot d^{-1} \Leftrightarrow d = \lambda k^{-1} = 0.81 \text{ W m}^{-1} \text{ K}^{-1} \times (0.5 \text{ W m}^{-2} \text{ K}^{-1})^{-1} \quad d = 1.62 \text{ m}$

4.4  $\Lambda^{-1} = k^{-1} = (0.50 \text{ W m}^{-2} \text{ K}^{-1})^{-1} = d_1 \times (\lambda_1)^{-1} + d_2 \times (\lambda_2)^{-1} + d_3 \times (\lambda_3)^{-1} + d_4 \times (\lambda_4)^{-1} =$   
 $0.15 \text{ m} \times (0.81 \text{ W m}^{-1} \text{ K}^{-1})^{-1} + 0.10 \text{ m} \times (1.1 \text{ W m}^{-1} \text{ K}^{-1})^{-1} + d_3 \times (0.040 \text{ W m}^{-1} \text{ K}^{-1})^{-1}$   
 $+ 0.05 \text{ m} \times (0.35 \text{ W m}^{-1} \text{ K}^{-1})^{-1}$

The thickness of the insulation foam layer is  $d_3 = 6.3 \text{ cm}$

The total thickness is:  $15 \text{ cm} + 10 \text{ cm} + 6.3 \text{ cm} + 5 \text{ cm} = 36.3 \text{ cm}$

4.5  $k = \Lambda_1 \times A_1 \times (A_{\text{tot}})^{-1} + \Lambda_2 \times A_2 \times (A_{\text{tot}})^{-1}$

4.6  $0.50 \text{ W m}^{-2} \text{ K}^{-1} = 0.70 \text{ W m}^{-2} \text{ K}^{-1} \times 4 \text{ m}^2 \times (15 \text{ m}^2)^{-1} + \Lambda_2 \times 11 \text{ m}^2 \cdot (15 \text{ m}^2)^{-1}$   
 $\Lambda_2 = 0.427 \text{ W m}^{-2} \text{ K}^{-1}.$

The calculation is similar to that of 4.4:

The thickness of the insulation foam layer is  $d_3 = 7.7 \text{ cm}$

The total thickness is:  $5 \text{ cm} + 10 \text{ cm} + 7.7 \text{ cm} + 5 \text{ cm} = 37.7 \text{ cm}$

due to the much higher heat conductivity of the window.

The thickness of the foam layer has to be increased by 22 %.

## THEORETICAL PROBLEM 5

### *“Green” Chemistry – The Use of Supercritical CO<sub>2</sub>*

Recently, reactions in supercritical carbon dioxide (critical temperature  $T_c = 304.3$  K; critical pressure  $p_c = 72.8 \times 10^5$  Pa) have received significant attention. The density of a liquid can be easily tuned near the critical point. Moreover, it can be regarded as a “green” solvent that can replace organic solvents. This solvent has actually been used for caffeine extraction for quite a long time. The fact, however, that carbon dioxide has to be compressed is one of the few disadvantages.

- 5.1** Calculate the energy needed to compress carbon dioxide from 1 bar to 50 bar (final volume is  $50 \text{ cm}^3$ , 298 K, ideal gas).

Real gases can be described by the van-der-Waals equation (although it is still an approximation):

$$a = 3.59 \left[ p + a \left( \frac{n}{V} \right)^2 \right] (V - nb) = nRT$$

$$b = 0.0427 \text{ dm}^3 \text{ mol}^{-1}$$

- 5.2** Calculate the pressures needed to achieve a density of  $220 \text{ g dm}^{-3}$ ,  $330 \text{ g dm}^{-3}$ , and  $440 \text{ g dm}^{-3}$  at temperatures of 305 K and 350 K.

Properties, such as the solvent power of carbon dioxide and the diffusivity of reactants, are strongly dependent on the density of the fluid. The calculation in the previous task shows that the density can be tuned by pressure variations.

- 5.3** In which region can these properties of the fluid be tuned more easily – near the critical point or at higher pressure / temperature (consider the critical constants and the results of 5.2)?

The oxidation of alcohols by molecular oxygen in supercritical carbon dioxide, e.g. the oxidation of benzyl alcohol to benzaldehyde, is a supercritical process. The reaction takes place in the presence of a  $\text{Pd}/\text{Al}_2\text{O}_3$  catalyst with a selectivity of 95 %.

- 5.4** a) Write down the balanced reaction equation of the main reaction path.  
b) Which reactions can occur during further oxidation (except total oxidation)?

The use of carbon dioxide both as a solvent and as a reactant instead of phosgene or carbon monoxide is another example of supercritical processes. Both the catalytic formation of organic carbonates and formamides have already been described.

- 5.5** a) Write a balanced equation of the formation of dimethyl carbonate by the reaction of methanol with carbon dioxide. How can dimethyl carbonate form if phosgene is the reactant?
- b) Formyl-morpholine can be synthesized from carbon dioxide and morpholine using an appropriate catalyst. Which additional reactant is needed? Write down the reaction scheme.

How would the scheme change if carbon monoxide was used instead?

- 5.6** From the point of view of “green chemistry” – why should reactions be carried out in CO<sub>2</sub> instead of using carbon monoxide or phosgene (2 reasons)? Apart from the compression of carbon dioxide, what is the main obstacle in using CO<sub>2</sub> as a reactant in comparison to CO or COCl<sub>2</sub> (1 reason) ?
-

## SOLUTION OF PREPARATORY PROBLEM 5

$$5.1 \quad dW = -n R T \frac{dV}{V} \quad \text{or} \quad W = -n R T \ln \frac{p_1}{p_2}$$

$$5.2 \quad n = \frac{pV}{RT} = \frac{50 \times 10^5 \text{ Pa} \times 50 \times 10^{-6} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.10 \text{ mol}$$

$$W = -0.10 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln(1/50) = 969 \text{ J}$$

The calculation can be most easily carried out with the molar volume  $V_m = M \rho^{-1}$ .

The equation  $[p + a(n V^{-1})^2] (V - n b) = n R T$  can be simplified to

$$[p + a V_m^{-2}] (V_m - b) = R T$$

Example of the calculation

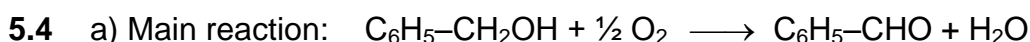
(density  $\rho = 440 \text{ g dm}^{-3}$  or  $V_m = 0.10 \text{ dm}^3 \text{ mol}^{-1}$ ;  $T = 305 \text{ K}$ )

$$[p + (3.59 \times 10^5 \text{ Pa} \times 10^{-6} \text{ m}^6 \text{ mol}^{-2}) \times (0.1^2 \times 10^{-6} \text{ m}^6 \text{ mol}^{-2})^{-1}] \cdot \\ (0.1 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} - 0.0427 \times 10^{-1} \text{ m}^3 \text{ mol}^{-1}) = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 305 \text{ K}$$

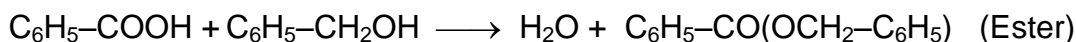
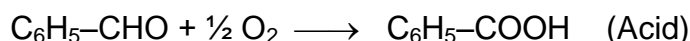
$$p = 83.5 \times 10^5 \text{ Pa}$$

$\rho \text{ (g dm}^{-3}\text{)}^{-1}$	$V_m \text{ (dm}^3 \text{ mol}^{-1}\text{)}^{-1}$	$T \text{ K}^{-1}$	$p \cdot \text{Pa}^{-1}$
220	0.200	305	$71.5 \times 10^5$
330	0.133	305	$77.9 \times 10^5$
440	0.100	305	$83.5 \times 10^5$
220	0.200	350	$95.2 \times 10^5$
330	0.133	350	$119.3 \times 10^5$
440	0.100	350	$148.8 \times 10^5$

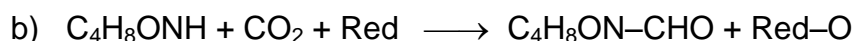
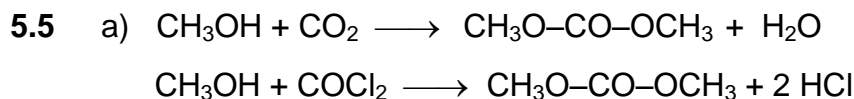
5.3 The results in the table above show that a 10 bar change in pressure near the critical temperature results in nearly double the density. Far above the critical temperature, however, such a change requires higher pressures. Hence, it is useful to work near the critical temperature/pressure.



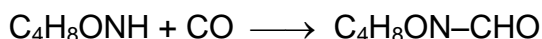
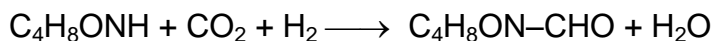
b) Side reactions:







The reaction requires a reducing agent, e.g. hydrogen, hence:



5.6 The advantage of using carbon dioxide is that it is not poisonous in contrast to carbon monoxide and phosgene.  $\text{CO}_2$  makes the process safer. Moreover, using  $\text{CO}_2$  both as a reactant and as a solvent is advantageous, since no additional solvent is necessary.

Another reason may be the reduction of the  $\text{CO}_2$ -emission, but this will not be significant.

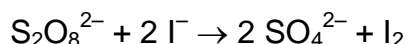
One of the disadvantages is that  $\text{CO}_2$  is much less reactive than  $\text{CO}$  or  $\text{COCl}_2$  – therefore a search for suitable catalysts is inevitable (catalysts have been found only for a few reactions, such as the formylation of amines).

## THEORETICAL PROBLEM 6

### *Chemical Kinetics of the Peroxodisulfate Ion*

The peroxodisulfate ion is one of the strongest oxidants that are known, although the oxidation reaction is relatively slow. Peroxodisulfate ions are able to oxidize all halides, except fluoride, to halogens.

The initial rate ( $r_0$ ) of the iodine-formation according to



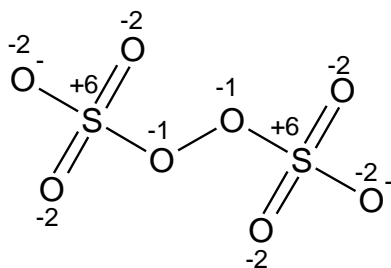
was determined as a function of the initial concentrations ( $c_0$ ) of the reactants at 25°C:

$c_0(\text{S}_2\text{O}_8^{2-}) [\text{mol dm}^{-3}]$	$c_0(\text{I}^-) [\text{mol dm}^{-3}]$	$r_0 [10^{-8} \text{ mol dm}^{-3} \cdot \text{s}^{-1}]$
0.0001	0.010	1.1
0.0002	0.010	2.2
0.0002	0.005	1.1

- 6.1 Draw the line-bond structure of the peroxodisulfate ion and determine the oxidation states of all atoms.
- 6.2 Write down the rate equation for the reaction shown above.
- 6.3 Write down the total order and the partial orders of the reaction shown above.
- 6.4 Prove that the rate constant of the reaction is  $0.011 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .  
The activation energy of the reaction mentioned above is  $42 \text{ kJ mol}^{-1}$ .
- 6.5 What temperature (in °C) has to be chosen to decuple the rate constant?  
Iodine reacts with thiosulfate ions ( $\text{S}_2\text{O}_3^{2-}$ ) forming iodide ions rapidly.
- 6.6 Write down the reaction scheme of this reaction.
- 6.7 Write down the rate equation for the reaction  
$$\text{S}_2\text{O}_8^{2-} + 2 \text{I}^- \rightarrow 2 \text{SO}_4^{2-} + \text{I}_2$$
  
assuming that there is an excess of thiosulfate ions relative to the peroxodisulfate ions and the iodide ions in the solution.

## SOLUTION OF PREPARATORY PROBLEM 6

6.1



6.2  $r = k c(\text{S}_2\text{O}_8^{2-}) c(\text{I}^-)$

6.3 reaction order: 2

partial reaction order of  $\text{S}_2\text{O}_8^{2-}$ : 1

partial reaction order of  $\text{I}^-$ : 1

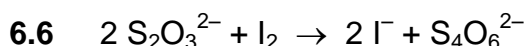
6.4 
$$k = \frac{r}{c(\text{S}_2\text{O}_8^{2-}) \times c(\text{I}^-)} = \frac{1.1 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}}{0.1 \times 10^{-3} \times 1 \times 10^{-2} \text{ mol}^2 \text{ dm}^{-6}} = 0.011 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

6.5 Using the Arrhenius equation we may write

$$k_1 = A \times e^{-\frac{E_a}{RT_1}}, \quad k_2 = A \times e^{-\frac{E_a}{RT_2}} \Rightarrow \frac{k_1}{k_2} = e^{\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

because  $k_1/k_2 = 1/10$ , it follows that

$$\ln \frac{1}{10} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \Leftrightarrow \frac{1}{T_2} = \frac{R}{E_a} \times \ln \frac{1}{10} + \frac{1}{T_1} \Rightarrow T_2 = 345 \text{ K} \approx 72^\circ \text{C}$$



6.7 It has to be noticed that the concentration of the iodide ions does not vary any longer, because iodine formed reacts quickly with thiosulfate ions (which are available in excess according to the precondition) forming iodide ions again.

Therefore the reaction is of pseudo first-order and the rate equation is given by

$$r = k' c(\text{S}_2\text{O}_8^{2-})$$

(It is important to note that the rate constant  $k'$  is different from  $k$  of the parts 6.2 – 6.5 of this problem, because it includes the pseudo-constant concentration of the iodide ions).

## THEORETICAL PROBLEM 7

### Catalytic Hydrogenation of Ethylene

At the beginning of the last century, ethylene, that is a colourless gas, was considered to be a chemical curiosity without any practical importance. Today, large amounts of ethylene are produced: in Germany, 60 kg per capita were produced in 2001.

Ethylene can be converted into ethane by various catalysts. By using a zinc oxide catalyst, the reaction is so slow that the reaction mechanism can be analyzed.

The pictures below show the reaction steps of the hydrogenation of ethylene (charges and stoichiometric coefficients are neglected in all the following tasks).

**7.1** Write down the correct order of the steps by numbering them consecutively.

No.		No.	
	$\begin{array}{c} \text{H} - \text{H} \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$		$\begin{array}{c} \text{H} \quad \text{H}_2\text{C}=\text{CH}_2 \quad \text{H} \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \\ \downarrow \end{array}$
	$\begin{array}{c} \text{H} \quad \text{H} \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$		$\begin{array}{c} \text{H}_3\text{C} - \text{CH}_3 \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$
	$\begin{array}{c} \text{H}_2\text{C}=\text{CH}_2 \\ \text{H} \quad \text{H} \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$		$\begin{array}{c} \text{H} \quad \text{H} \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$
	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\ \vdots - \text{O} - \vdots - \text{Zn} - \vdots - \text{O} - \vdots \end{array}$		

$\theta(\text{H})$  describes the fraction of surface sites that are occupied by hydrogen atoms,  $\theta(\text{C}_2\text{H}_4)$  describes the fraction of surface sites that are occupied by ethylene molecules and  $\theta(\text{C}_2\text{H}_5)$  describes the fraction of surface sites that are occupied by the adsorbed intermediate.

**7.2** Which of the following rate equations is correct, if the hydrogenation of the adsorbed intermediate is the slowest step of the reaction?

(1)  $r = k \times \theta(\text{H})$  ☐

(2)  $r = k \times \theta(\text{C}_2\text{H}_4)$  ☐

(3)  $r = k \times \theta(\text{H}) \times \theta(\text{C}_2\text{H}_4)$  ☐

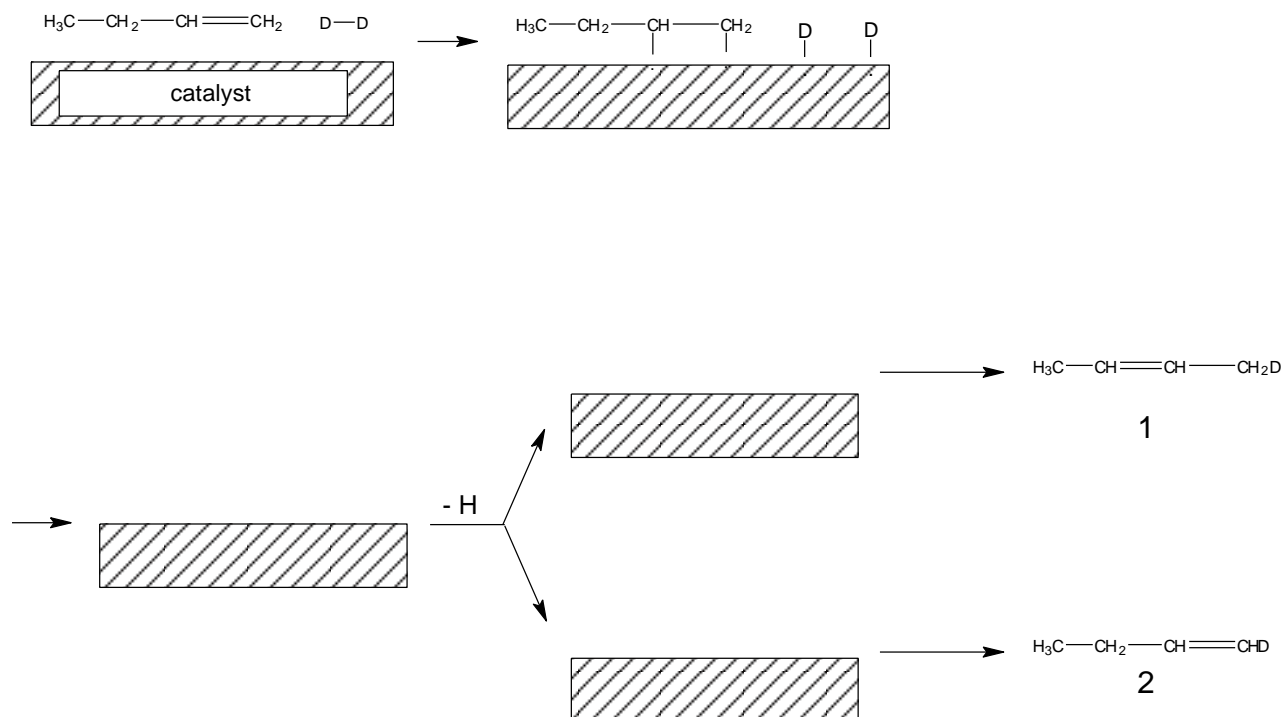
(4)  $r = k \times \theta(\text{H}) \times \theta(\text{C}_2\text{H}_5)$  ☐

When zinc oxide is used as a catalyst, the hydrogenation of ethylene is blocked by water.

**7.3** Explain this blocking by drawing the interaction between water and the catalyst analogous to that of task 1 of this problem.

If a metal catalyzes the hydrogenation of alkenes, isomer alkenes are formed in a side reaction. When  $\text{D}_2$  reacts with 1-butene the side products 1 and 2 will form.

**7.4** Complete the reaction scheme on the next page and write down the structures of the intermediates.



The fraction of surface sites that are occupied by adsorbed gas molecules ( $\theta$ ) may be described in a simple way by using the Langmuir isotherm:

$$\theta = \frac{K p}{1 + K p} \quad p: \text{gas pressure, } K: \text{adsorption-desorption equilibrium constant}$$

- 7.5** Write down a corresponding formula for the fraction  $\theta(i)$  of surface sites that are occupied by the gas  $i$ , if two or more gases are adsorbed on the catalyst.

## SOLUTION OF PREPARATORY PROBLEM 7

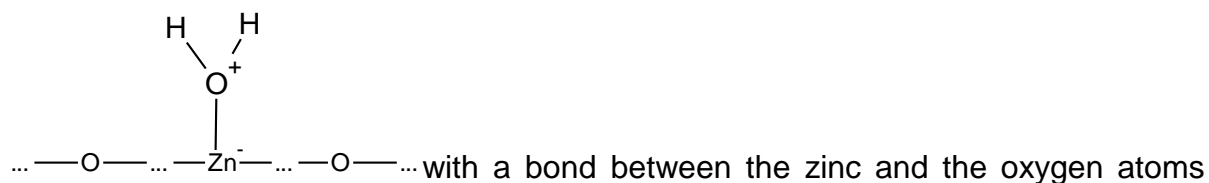
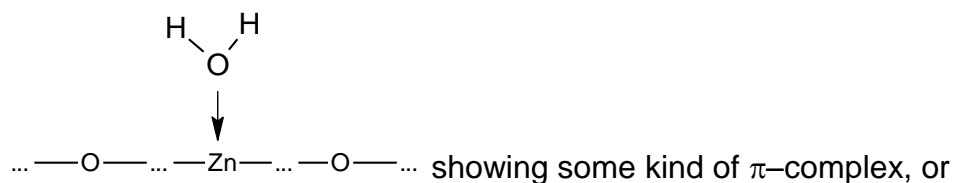
### 7.1

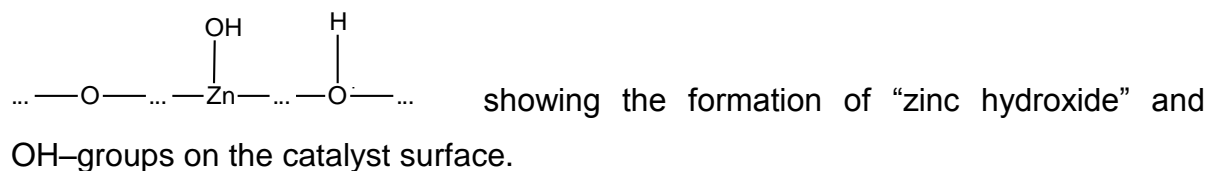
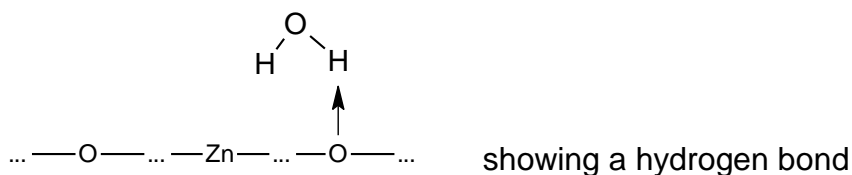
No.		No.	
1	$\begin{array}{c} \text{H} - \text{H} \\   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$	5	$\begin{array}{c} \text{H} \quad \text{H}_2\text{C}=\text{CH}_2 \quad \text{H} \\   \quad \quad \quad   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$
3	$\begin{array}{c} \text{H} \quad \quad \text{H} \\   \quad \quad   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$	7	$\begin{array}{c} \text{H}_3\text{C} - \text{CH}_3 \\   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$
4	$\begin{array}{c} \text{H}_2\text{C}=\text{CH}_2 \\   \quad \quad   \\ \text{H} \quad \quad \text{H} \\   \quad \quad   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$	2	$\begin{array}{c} \text{H} \quad \quad \text{H} \\   \quad \quad   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$
6	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{H} \\   \\ \dots - \text{O} - \dots - \text{Zn} - \dots - \text{O} - \dots \end{array}$		

**7.2** The hydrogenation of the adsorbed intermediate is the slowest step of the reaction. This is the reason why the concentration, or in this case the fraction of surface sites that are occupied, has to be part of the rate equation.

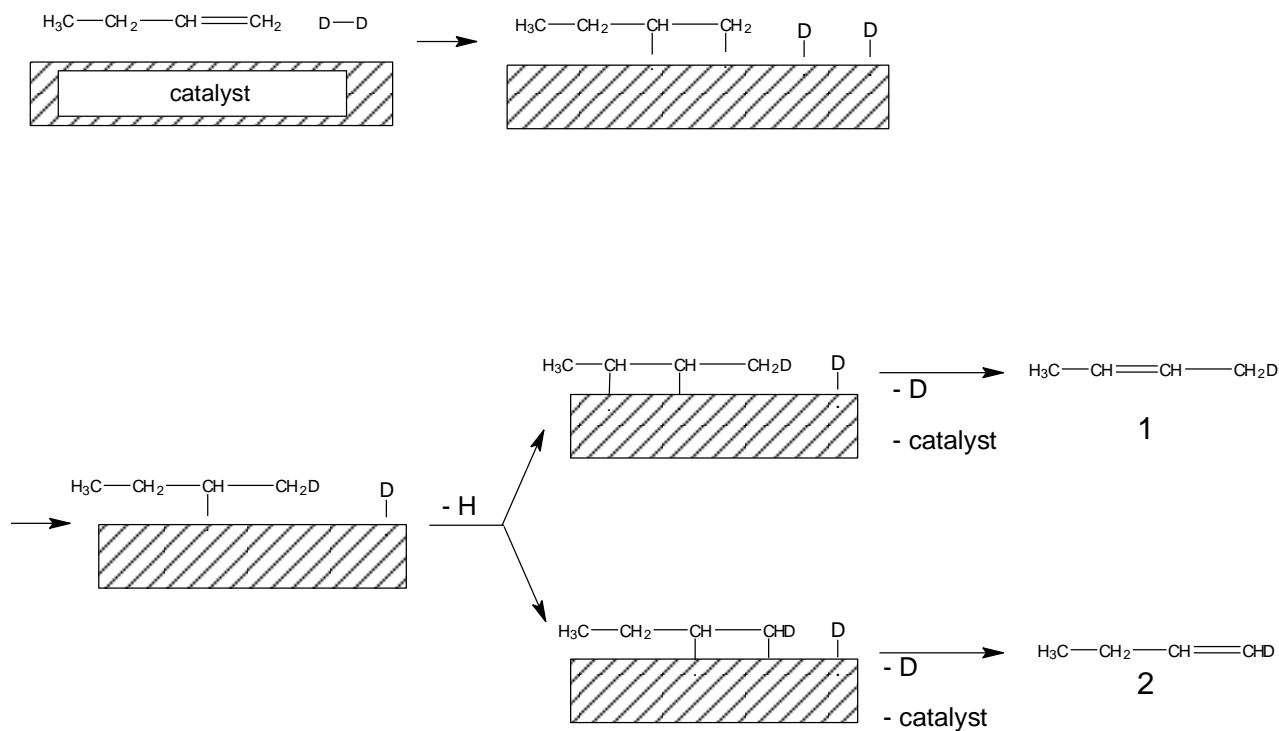
Answer (4) is correct.

**7.3** Four answers can be accepted:





## 7.4



**7.5** Knowing the derivation of the Langmuir isotherm from the law of mass action you can obtain:

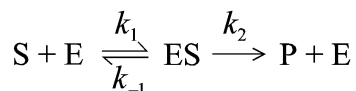
$$\theta(i) = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j}$$



## THEORETICAL PROBLEM 8

### Kinetics of an Enzymatic Reaction

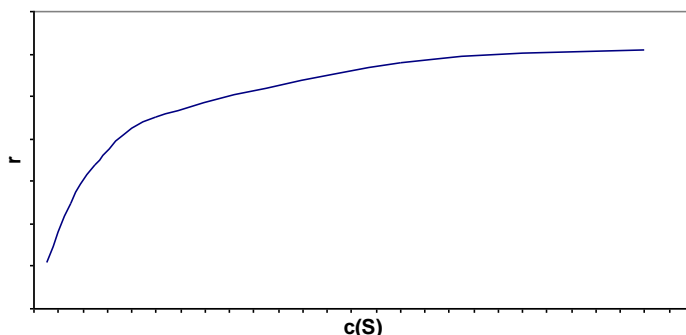
The mechanism of an enzymatic reaction may be described as:



S is the substrate, E is the enzyme, ES is the complex formed by S and E, and P is the product.  $k_1$ ,  $k_{-1}$  and  $k_2$  are the rate constants of the elementary reactions.

The rate of the enzymatic reaction,  $r$ , can be expressed as a function of the substrate concentration,  $c(S)$ :

$$r = \frac{dc(P)}{dt} = k_2 c_T(E) \frac{c(S)}{K_M + c(S)}$$



$t$  is the time,

$c(P)$  is the product concentration,

$c_T(E)$  is the total enzyme concentration

and  $K_M = (k_{-1} + k_2)/k_1$ .

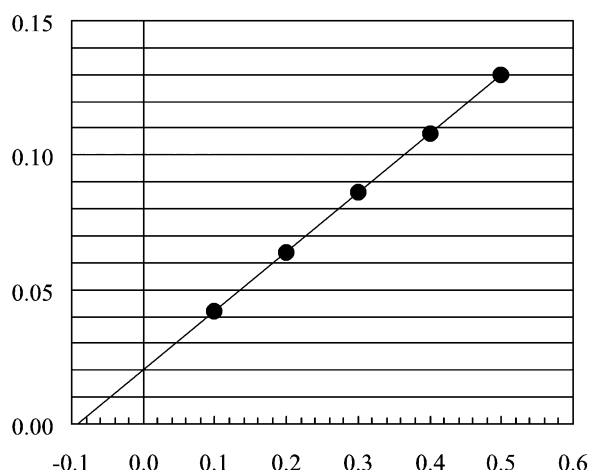
**8.1** Determine the variables  $x$ ,  $y$  and  $z$  in the following rate equations:

$$\frac{dc(S)}{dt} = -k_x c(S)c(E) + k_y c(ES) \quad \frac{dc(ES)}{dt} = +k_x c(S)c(E) - (k_{-1} + k_2)c^z(ES)$$

**8.2** Complete the following rate equation:

$$\frac{dc(E)}{dt} =$$

Penicillin (substrate) is hydrolyzed by  $\beta$ -lactamase (enzyme). The following data have been recorded when the total enzyme concentration was  $10^{-9} \text{ mol dm}^{-3}$ .

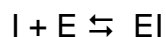


x-axis:  $c^{-1}(S) / (10^6 \text{ dm}^3 \text{ mol}^{-1})$   
y-axis:  $r^{-1} / (10^6 \text{ dm}^3 \text{ min mol}^{-1})$

**8.3** Determine the constants  $k_2$  and  $K_M$ .

If  $c(S) = 0.01 K_M$ , what is the concentration of the complex ES?

A competitive inhibitor I competes with the substrate and may block the active site of the enzyme:



**8.4** If the dissociation constant of EI is  $9.5 \times 10^{-4} \text{ mol dm}^{-3}$  and the total enzyme concentration is  $8 \times 10^{-4} \text{ mol dm}^{-3}$ , what total concentration of inhibitor will be needed to block 50 % of the enzyme molecules in the absence of substrate?

**8.5** Decide whether the following statements are true or false.

	true	false
i) The rate of the enzymatic reaction, $r$ , is reduced by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
ii) The maximum value of the rate $r$ is reduced by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
iii) The concentration of the substrate S is unaffected by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
iv) The activation energy of the enzymatic reaction is increased by the inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>

A more detailed description of an enzymatic reaction includes the reverse reaction of the product back to the substrate. At the end of the enzymatic reaction, a chemical equilibrium is reached between the substrate and the product.

**8.6** Decide whether the following statements are true or false.

	true	false
i) The concentration of the product in the equilibrium is increasing with increasing concentration of the substrate.	<input type="checkbox"/>	<input type="checkbox"/>
ii) The concentration of the product in the equilibrium is increasing with increasing concentration of the enzyme.	<input type="checkbox"/>	<input type="checkbox"/>
iii) The concentration of the product in the equilibrium is higher, when the rate constant $k_2$ is larger.	<input type="checkbox"/>	<input type="checkbox"/>

---

## SOLUTION OF PREPARATORY PROBLEM 8

8.1  $x = 1, y = -1, z = 1$

8.2 
$$\frac{dc(E)}{dt} = -k_1 c(S) c(E) + k_{-1} c(ES) + k_2 c(ES)$$

8.3 The reciprocal rate is plotted as a function of the reciprocal substrate concentration:

$$\frac{1}{r} = \frac{K_M}{k_2 c_T(E)} \times \frac{1}{c(S)} + \frac{1}{k_2 c_T(E)}$$

Intercept at  $1/c(S) = 0$  yields  $\frac{1}{r} = \frac{1}{k_2 c_T(E)} = 0.02 \times 10^6 \text{ dm}^3 \text{ min mol}^{-1}$

With  $c_T(E) = 1 \times 10^{-9} \text{ mol dm}^{-3}$  we obtain  $k_2 = 50000 \text{ min}^{-1}$

Intercept at  $1/r = 0$  yields  $\frac{1}{c(S)} = -\frac{1}{K_M} = -0.09 \times 10^6$

$$K_M = 1.1 \times 10^{-5}$$

Alternatively, the slope is  $\frac{K_M}{k_2 c_T(E)} = 0.22 \text{ min}$

$$K_M = 1.1 \times 10^{-5}$$

The rate of the enzymatic reaction is given as

$$\frac{dc(P)}{dt} = k_2 c(ES) = k_2 c_T(E) \frac{c(S)}{K_M + c(S)}$$

$$c(ES) = c_T(E) \frac{c(S)}{K_M + c(S)} \quad c(ES) = c_T(E) \frac{0.01 K_M}{K_M + 0.01 K_M}$$

$$c(ES) = 9.9 \times 10^{-3} c_T(E) \quad c(ES) = 9.9 \times 10^{-12} \text{ mol dm}^{-3}$$

8.4  $K = \frac{c(I) c(E)}{c(EI)} = \frac{c(I) \times 0.5 c_T(E)}{0.5 c_T(E)} = c(I) = 9.5 \times 10^{-4}$

The total inhibitor concentration is

$$c_T(I) = c(I) + c(EI) = K + 0.5 c_T(E) = 1.35 \times 10^{-3} \text{ mol dm}^{-3}$$

- 8.5 i) **true** (the inhibitor reduces the free enzyme concentration and thus the rate of ES formation. A lower ES concentration results and leads to a smaller reaction rate)

- ii) **false** (the maximum rate is reached for  $c(S) = \infty$  where the inhibitor concentration can be ignored)
- iii) **false** (the inhibitor reduces the free enzyme concentration and thus promotes the dissociation of the complex ES into E and S (Le Chatelier's principle))
- iv) **false** (the activation energy depends on the rate constants that are independent of concentrations)

**8.6** The enzyme is only a catalyst. The net reaction is  $S \rightleftharpoons P$

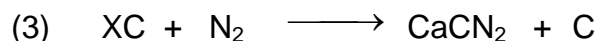
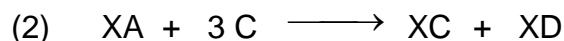
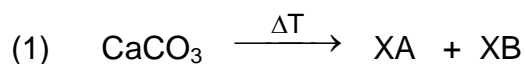
- i) **true** (because  $K = c^{\text{eq}}(P) / c^{\text{eq}}(S)$ )
  - ii) **false** (because  $K$  does not depend on the enzyme concentration)
  - iii) **true** (because  $K$  is the ratio of the rate constants for the forward and the reverse reaction)
- 
-

## THEORETICAL PROBLEM 9

### *CaCN<sub>2</sub> – An Old but still Important Fertilizer*

Calcium cyanamide (CaCN<sub>2</sub>) is a very versatile and powerful fertilizer. It can be produced easily from cheap and common chemicals such as CaCO<sub>3</sub>. The thermal decomposition of CaCO<sub>3</sub> leads to a white solid XA and a colourless gas XB which does not sustain combustion. A greyish solid XC and a gas XD form by the reduction of XA with carbon. XC and XD can be further oxidized. The reaction of XC with nitrogen finally leads to CaCN<sub>2</sub>.

**9.1** How can calcium cyanamide be synthesized? Complete the reaction scheme below.

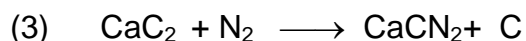
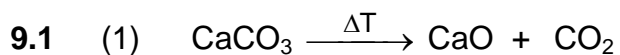


**9.2** What gas forms by the hydrolysis of CaCN<sub>2</sub>? Write down the equation of the reaction of CaCN<sub>2</sub> with water.

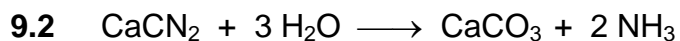
**9.3** In solid state chemistry the CN<sub>2</sub><sup>2-</sup> ion shows constitutional isomerism. The free acids of both anions (at least in the gas phase) are known. Draw the structural formulas of both isomeric free acids. Indicate on which side the equilibrium is located.

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## SOLUTION OF PREPARATORY PROBLEM 9



This process that is technically important is called the Frank-Caro process.



The first compound is the acid of the carbodiimide ion, the second is that of cyanamide. The equilibrium favours the more symmetric structure.

(Inorg.Chem. 2002, 41, 4259 – 4265)

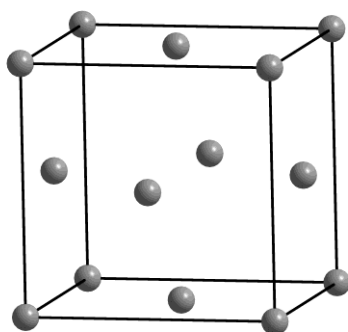
## THEORETICAL PROBLEM 10

### *Closed-Packed Structures*

About two-thirds of the metallic elements have closed-packed structures. Each atom is surrounded by as many neighbouring atoms as possible. All the atoms in the structure are identical.

- 10.1** Draw a two-dimensional model of a closed-packed assembly of spheres.
- 10.2** Change this model into a three-dimensional one. How many different possibilities are there of stacking a) three or b) an infinite number of layers? What is the coordination number of each atom?

Atoms packed together are closed-packed when they occupy the minimum volume possible (assuming they are incompressible spheres). They have the maximum possible packing efficiency, defined as the ratio of volume of atoms to volume of space used. The following arrangement is called 'cubic-F':



- 10.3** Insert the closed-packed layers into this illustration.
- 10.4** Calculate the packing efficiency and compare it with that of a cubic-primitive packing of spheres.
- 10.5** Insert the tetrahedral and octahedral cavities into a cubic closed-packed structure.

The arrangements of ions in a crystal depend to a great extent on the relative sizes of the ions as shown in the table below.

The radius of the particles X that form the holes is  $r$ .

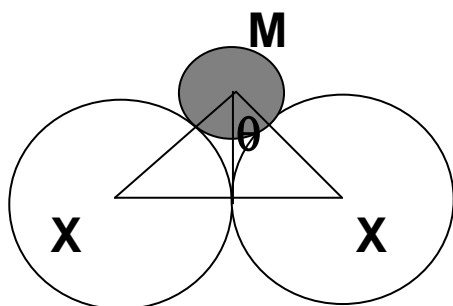
The radii of the largest particles M that fit into the holes without distorting them are  $0.225 \times r$  for a tetrahedral hole and  $0.414 \times r$  for an octahedral hole.



Radius ratios for the arrangements of rigid spheres.

Coordination number of M	Arrangement of X	Radius ratio $r(M^{m+})/r(X^{x-})$	Crystal structure corresponding to coordin. number
2	linear	$<0.150$	
3	triangular	$0.150 - 0.225$	
4	tetrahedral	$0.225 - 0.414$	ZnS
6	octahedral	$0.414 - 0.732$	NaCl
8	cubic	$0.732 - 1.00$	CsCl
12	cuboctahedron	1.0	closed packed

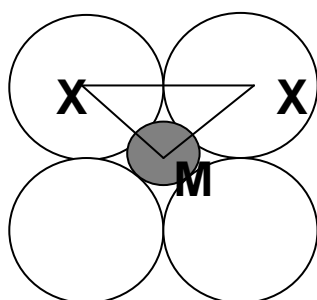
- 10.6** Show that the ideal  $r_M/r_X$  value for the cation–anion and anion–anion contacts of a tetrahedral arrangement of anions around a cation is 0.225.



One edge of a tetrahedron with two anions touching and the cation in the center of the tetrahedron.

$$2\theta = 109.5^\circ.$$

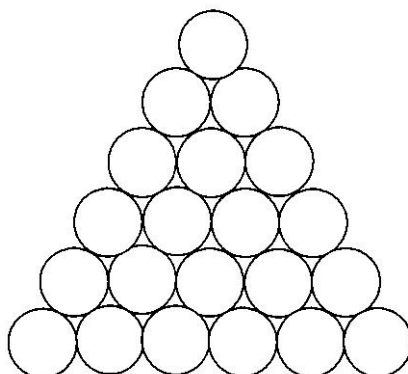
- 10.7** Calculate the ideal  $r_M/r_X$  ratio for cation–anion and anion–anion contacts of an octahedral arrangement of anions around a cation as illustrated in one plane in the figure below.



Cation–anion and anion–anion contacts in one plane of an octahedron.

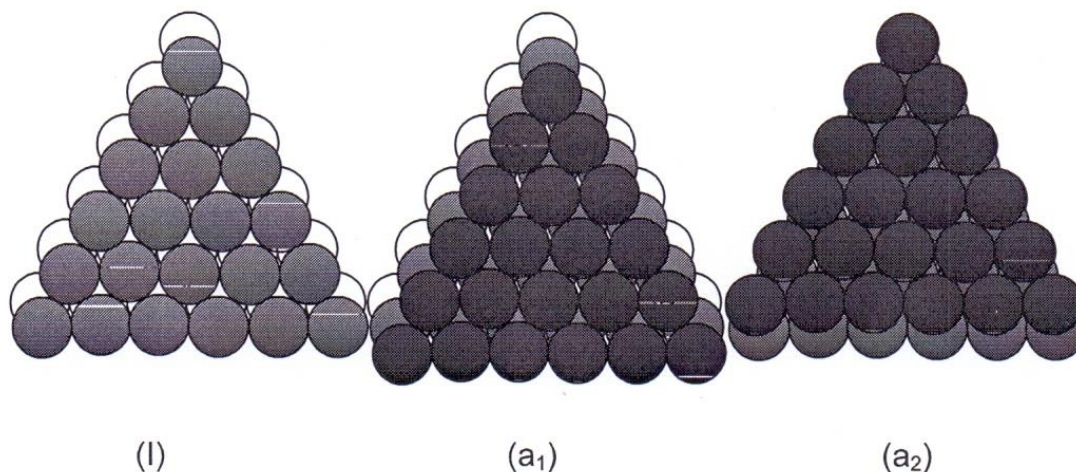
## SOLUTION OF PREPARATORY PROBLEM 10

### 10.1



In the two-dimensional model each indistinguishable atom is surrounded by six other atoms.

### 10.2

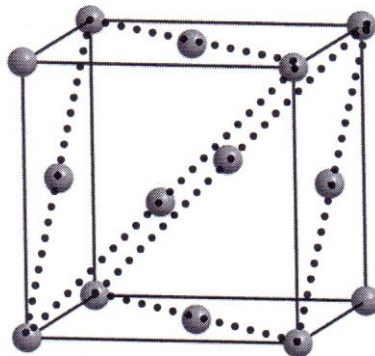


A transformation into a three-dimensional model can be achieved by stacking the 2D closed-packed layers (I). Each atom has six neighbours in the plane surrounding it, and three further atoms located in the holes above the atom and three atoms located in the holes below the atom.

- a) Looking at the second layer, there are two possibilities of putting a third layer on top. Either the atoms are put into the holes such that there is no atom directly beneath them in the first layer ( $a_1$ ), or into the same positions they occupy in the first layer ( $a_2$ ). These possibilities create the two different closed-packed structures, ABCABC (cubic closed-packed) and ABAB (hexagonal closed packed).

- b) In principle, an infinite number of stacking patterns can be generated by the combination of these two basic stacking possibilities.

### 10.3



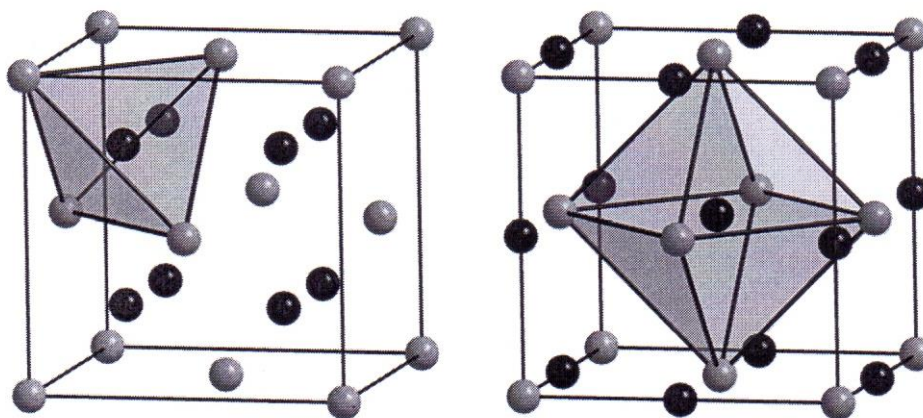
- 10.4** In this illustration, the atoms touch on the face diagonals. The length of the edges of the cube is  $2r \cdot \sqrt{2}$ . There are 4 complete atoms in the cube (8 corners with one eighth of an atom in each and 6 sides with one half of an atom in the middle of each). So the packing efficiency is:

$$\frac{4 \times \frac{4}{3} \pi r^3}{(2r\sqrt{2})^3} = \frac{\frac{16}{3} \pi r^3}{16r^3\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

A cubic primitive packing has a packing efficiency of:

$$\frac{1 \times \frac{4}{3} \pi r^3}{(2r)^3} = \frac{\frac{4}{3} \pi}{8} = 0.52 \text{ or } 52\%$$

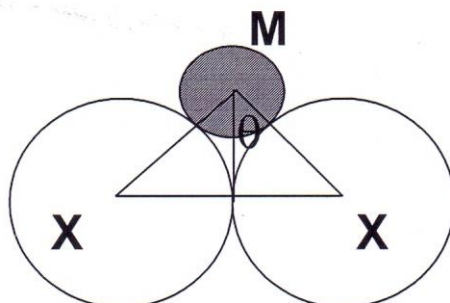
### 10.5



The elemental cube of a face centered cubic structure contains 4 packing atoms (one at the corner and three on the faces of the cube), eight tetrahedral holes (one

in each octant of the cube) and 4 octahedral holes (one in the centre of the cube, 12 additional holes in the middle of the edges of the cube, each shared of 4 cubes).

### 10.6

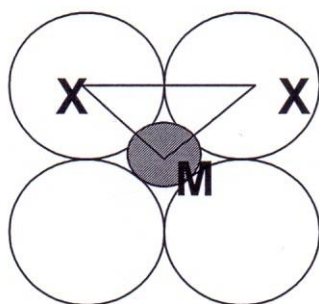


A line perpendicular to the edge divides the tetrahedral angle into two halves. The length of the edge is  $2 r_X$ . The distance from a tetrahedral vertex to the center is  $r_M + r_X$ . The angle is  $109,5^\circ / 2$ .

$$\sin \theta = r_X / (r_M + r_X) \quad \sin (109,5^\circ / 2) \cdot (r_M + r_X) = r_X$$

$$0.816 r_M = 0.184 r_X \quad r_M / r_X = 0.225$$

### 10.7



$$(2r_X)^2 = (r_M + r_X)^2 + (r_M + r_X)^2$$

$$4r_X^2 = 2 (r_M + r_X)^2$$

$$\sqrt{2} r_X = r_M + r_X$$

$$r_M / r_X = (\sqrt{2} - 1) = 0.414$$

$$r_M / r_X = 0.414$$

## THEORETICAL PROBLEM 11

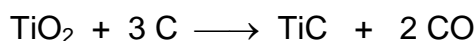
### *Titanium Carbide – A High-Tech Solid*

Transition metal carbides, such as TiC, are widely used for the production of cutting and grinding tools, because they are very hard, very corrosion-resistant and have high melting points. Apart from these properties, titanium carbide has a high electric conductivity that is almost independent of temperature, so that it is important in the electronics industry.

**11.1** What kind of structure is TiC likely to adopt, if the radii are  $r(\text{Ti}^{4+}) = 74.5$  and  $r(\text{C}^{4-}) = 141.5$  pm?

TiC is technically obtained from TiO<sub>2</sub> by the reduction with carbon. The enthalpy change of this reaction can directly be measured only with difficulty. However, the heats of combustion of the elements and of TiC can be measured directly. As energy is always conserved and the enthalpy change for a given process does not depend on the reaction pathway (this special application of the First Law of Thermodynamics is often referred to as Hess's Law), the missing thermodynamic data can be calculated.

**11.2** Calculate the enthalpy of reaction of the technical production process of TiC:



$$\Delta_f H(\text{TiO}_2) = -944.7 \text{ kJ mol}^{-1}$$

$$\Delta_f H(\text{CO}) = -110.5 \text{ kJ mol}^{-1}$$

$$\Delta_r H(\text{TiC} + 3/2 \text{O}_2 \longrightarrow \text{TiO}_2 + \text{CO}) = -870.7 \text{ kJ mol}^{-1}$$

In 1919, Born and Haber independently applied the First Law of Thermodynamics to the formation of solids from their elements. In this way, getting exact information about lattice energies for solids was possible for the first time.

Potassium chloride is isotypic to TiC and crystallizes in the NaCl structure.

**11.3** Use the given data to construct a thermodynamical Born-Haber-cycle of the formation of potassium chloride from its elements and calculate the lattice energy of potassium chloride.

$$\text{sublimation enthalpy for potassium: } \text{K(s)} \rightarrow \text{K(g)} \quad \Delta_{\text{sub}} H = 89 \text{ kJ mol}^{-1}$$

$$\text{dissociation energy of chlorine: } \text{Cl}_2(\text{g}) \rightarrow 2 \text{Cl} \quad \Delta_{\text{diss}} H = 244 \text{ kJ mol}^{-1}$$

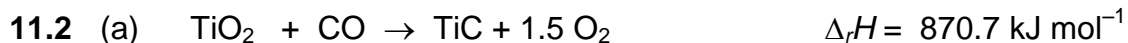
electron affinity of chlorine:	$\text{Cl}(g) + e^- \rightarrow \text{Cl}(g)$	$\Delta_{\text{EA}}H = -355 \text{ kJ mol}^{-1}$
ionization energy of potassium:	$\text{K}(g) \rightarrow \text{K}^+(g) + e^-$	$\Delta_{\text{IE}}H = 425 \text{ kJ mol}^{-1}$
enthalpy of formation for KCl:	$\text{K}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{KCl}(s)$	$\Delta_{\text{f}}H = -438 \text{ kJ mol}^{-1}$

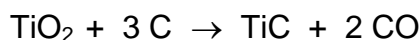
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## SOLUTION OF PREPARATORY PROBLEM 11

11.1  $r(\text{Ti}^{4+})/r(\text{C}^{4-}) = 0.527 \Leftarrow \text{NaCl-type}$

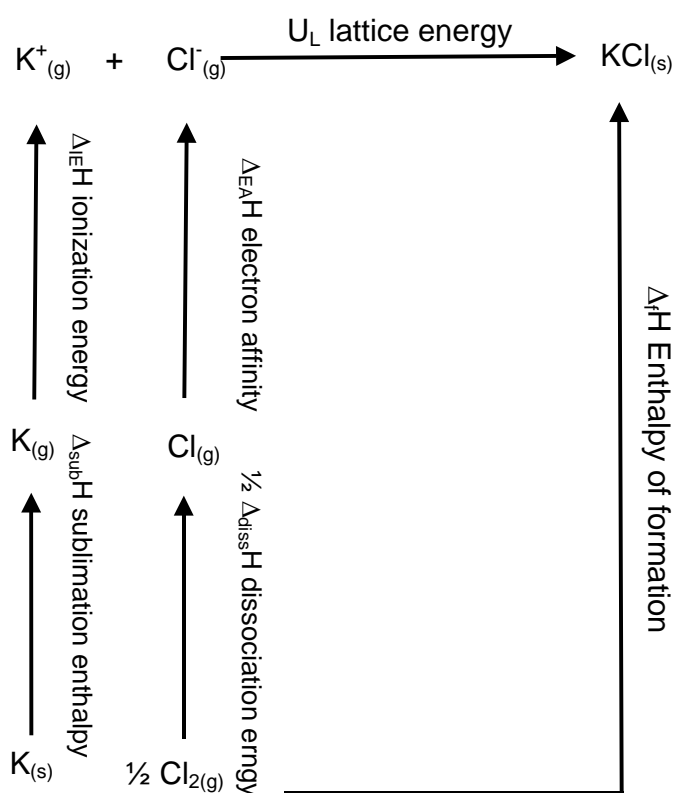


(a) + 3 (b) :



$\Delta_r H = 870.7 + 3(-110.5) \text{ kJ mol}^{-1}$   $\Delta_r H = 539.2 \text{ kJ mol}^{-1}$

11.3



$$-U_L = \Delta_{\text{sub}}H + \Delta_{\text{IE}}H + 0.5 \Delta_{\text{diss}}H + \Delta_{\text{EA}}H - \Delta_{\text{f}}H$$

$$U_L = - (89 + 425 + 122 - 355 + 438 \text{ kJ mol}^{-1})$$

$$U_L = -719 \text{ kJ mol}^{-1}$$

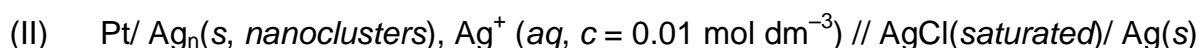
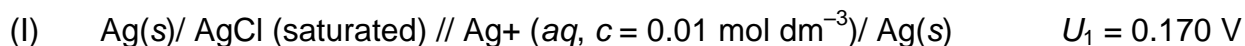
(If the lattice energy is defined in the opposite way the result will be + 719 kJ mol<sup>-1</sup>)

## THEORETICAL PROBLEM 12

### *Metal Nanoclusters*

Nanometer-sized metal clusters have different properties than the bulk materials. To investigate the electrochemical behaviour of silver nanoclusters, the following electrochemical cells are considered:

(on the right-hand side: half-cell with the higher potential)



a)  $U_2 = 0.430 \text{ V}$  for  $\text{Ag}_{10}$  nanoclusters

b)  $U_3 = 1.030 \text{ V}$  for  $\text{Ag}_5$  nanoclusters

**12.1** Calculate the solubility product of AgCl.

$\text{Ag}_5$ - and  $\text{Ag}_{10}$ -nanoclusters consist of metallic silver but nevertheless have standard potentials different from the potential of metallic bulk silver.

**12.2** Calculate the standard potentials of the  $\text{Ag}_5$  and  $\text{Ag}_{10}$  nanoclusters.

**12.3** Explain the change in standard potential of silver nanoclusters with particle sizes ranging from very small clusters to bulk silver.

**12.4** What happens:

- if you put the  $\text{Ag}_{10}$  clusters and – in a second experiment – the  $\text{Ag}_5$  clusters into an aqueous solution of  $\text{pH} = 13$ ?
- the  $\text{Ag}_{10}$  clusters and – in a second experiment – the  $\text{Ag}_5$  into an aqueous solution of  $\text{pH} = 5$
- both clusters together into an aqueous solution having a  $\text{pH}$  of 7 with  $c(\text{Cu}^{2+}) = 0.001 \text{ mol dm}^{-3}$  and  $c(\text{Ag}^+) = 1 \cdot 10^{-10} \text{ mol dm}^{-3}$ ? Calculate.

What happens if the reaction proceeds (qualitatively)?

$$E^\circ(\text{Ag} / \text{Ag}^+) = 0.800 \text{ V}$$

$$E^\circ(\text{Cu} / \text{Cu}^{2+}) = 0.345 \text{ V}$$

$$T = 298.15 \text{ K}$$



## SOLUTION OF PREPARATORY PROBLEM 12

12.1 The potential of a half-cell is described by the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \times \ln \frac{c(\text{ox})}{c(\text{red})}$$

The total voltage is:  $U = E(\text{cathode}) - E(\text{anode})$

$$E = E^0 + \frac{RT}{F} - \ln c(\text{Ag}^+)$$

$$U_1 = E_2 - E_1 \text{ and } U_1 = \frac{RT}{F} \times \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

and with  $U_1 = 0.170 \text{ V}$   $c_2(\text{Ag}^+) = 0.01 \text{ mol dm}^{-3}$   $c_1(\text{Ag}^+) = x \text{ mol dm}^{-3}$

$$0.170 \text{ V} = \frac{8.314 \times 298.15}{96485} \text{ V} \times \ln \frac{c_2(\text{Ag}^+)}{c_1(\text{Ag}^+)}$$

$$c_1(\text{Ag}^+) = 1.337 \times 10^{-5} \text{ mol dm}^{-3}$$

In the saturated solution  $c(\text{Ag}^+) = c(\text{Cl}^-) = 1.337 \times 10^{-5} \text{ mol dm}^{-3}$  and thus,

$$K_{\text{sp}} = (1.337 \times 10^{-5})^2 \quad K_{\text{sp}} = 1.788 \times 10^{-10}$$

12.2 For the right cell of (II):

$$E(\text{AgCl}) = 0.8 \text{ V} + \frac{RT}{F} \times \ln 1.337 \times 10^{-5}$$

$$E(\text{AgCl}) = 0.512 \text{ V}$$

Thus:  $U = E(\text{AgCl}) - E(\text{Ag}_n, \text{Ag}^+)$

$$\text{and } E(\text{Ag}_n / \text{Ag}^+) = E^0(\text{Ag}_n / \text{Ag}^+) + \frac{RT}{F} \times \ln 0.01$$

$$\text{Ag}_{10}: E(\text{Ag}_{10} / \text{Ag}^+) = 0.512 \text{ V} - 0.430 \text{ V} = 0.082 \text{ V}$$

$$E^0(\text{Ag}_{10} / \text{Ag}^+) = 0.082 \text{ V} - \frac{RT}{F} \times \ln 0.01$$

$$E^0(\text{Ag}_{10} / \text{Ag}^+) = 0.200 \text{ V}$$

$$\text{Ag}_5: E(\text{Ag}_5 / \text{Ag}^+) = 0.512 \text{ V} - 1.030 \text{ V} = -0.518 \text{ V}$$

$$E^0(\text{Ag}_5 / \text{Ag}^+) = -0.518 \text{ V} - \frac{RT}{F} \times \ln 0.01$$

$$E^0(\text{Ag}_5 / \text{Ag}^+) = -0.400 \text{ V}$$

**12.3** The standard potential increases with increasing particle size until it reaches the bulk value at a certain particle size.

The potential is lower for smaller particles, because they have a larger surface and the process of crystallization is energetically less favourable for the surface atoms. Thus, the free energy of formation of metallic silver is larger (less negative) for smaller particles, i.e. the standard potential is lower. The effect decreases with increasing particle size due to the decreasing relative amount of surface atoms.

Additional remark: However, the potential does not continuously increase with increasing size. The electrochemical potentials of some small clusters of a certain size are much higher. This is due to complete shells of these clusters (clusters consist of a “magic number” of atoms) which make them more stable.

(Instead of the crystallization energy you can also argue with the sublimation energies of silver atoms.)

**12.4 i)** For a solution with a pH of 13:

$$E(\text{H}_2/2 \text{H}^+) = \frac{RT}{F} \times \ln(1 \times 10^{-7}) \quad E(\text{H}_2/2 \text{H}^+) = -0.769 \text{ V}$$

As an estimate, this potential can be compared with the standard potentials of the silver clusters calculated in 12.2. Both are higher than the standard potential of hydrogen. Thus, the silver clusters behave as noble metals and are not oxidized in this solution. No reaction takes place.

Quantitatively, a small amount of silver is oxidized into  $\text{Ag}^+$  ions until equilibrium is reached and  $E(\text{Ag}_n/\text{Ag}^+) = E(\text{H}_2/2 \text{H}^+)$ .

$$E^0(\text{Ag}_n/\text{Ag}^+) + \frac{RT}{F} \times \ln c(\text{Ag}^+) = -0.769 \text{ V}$$

$$\text{for Ag}_{10}: c(\text{Ag}^+) = 4.17 \times 10^{-17} \text{ mol dm}^{-3}$$

$$\text{for Ag}_5: c(\text{Ag}^+) = 5.78 \times 10^{-7} \text{ mol dm}^{-3}$$

**ii)** For a solution with a pH of 5:

$$E(\text{H}_2/2 \text{H}^+) = \frac{RT}{F} \times \ln 1 \times 10^{-2} \quad E(\text{H}_2/2 \text{H}^+) = -0.269 \text{ V}$$

As an estimate, the standard potential of the  $\text{Ag}_{10}$  clusters is higher than the standard potential of the hydrogen. No reaction takes place. The standard potential of the  $\text{Ag}_5$  clusters is lower than the standard potential of hydrogen. Thus, hydronium ions will be reduced to hydrogen while  $\text{Ag}_5$  clusters (metallic silver) are oxidized into silver ions: The  $\text{Ag}$ -clusters dissolve.

Quantitatively, equilibrium is reached for Ag<sub>10</sub> at:  $c(\text{Ag}^+) = 4.16 \times 10^{-9} \text{ mol dm}^{-3}$  and for Ag<sub>5</sub> at :  $c(\text{Ag}^+) = 57.29 \text{ mol dm}^{-3}$  (which will probably not be reached in a diluted solution and all nanoclusters dissolve)

(After some time, silver ions that are present in the solution can also be reduced to metallic bulk silver. Under this condition, this reduction will preferably take place, because the electrochemical potential is even higher than that of the hydronium–ion reduction.)

iii) Potentials of all possible reactions are considered:

$$1. \quad E(\text{Cu}/\text{Cu}^{2+}) = 0.345 \text{ V} + 0.5 \times \frac{RT}{F} \times \ln 0.001 = 0.256 \text{ V}$$

$$2. \quad E(\text{Ag}/\text{Ag}^+) = 0.800 \text{ V} + \frac{RT}{F} \times \ln 1.10^{-10} = 0.208 \text{ V}$$

$$3. \quad E(\text{Ag}_{10}/\text{Ag}^+) = 0.200 \text{ V} + \frac{RT}{F} \times \ln 1.10^{-10} = -0.392 \text{ V}$$

$$4. \quad E(\text{Ag}_5/\text{Ag}^+) = -0.400 \text{ V} + \frac{RT}{F} \times \ln 1.10^{-10} = -0.992 \text{ V}$$

$$5. \quad E(\text{H}_2/2 \text{H}^+) = \frac{RT}{F} \times \ln 1.10^{-7} = -0.414 \text{ V}$$

The reduction with the highest potential and the oxidation with the lowest potential will preferably take place: Copper(II) ions will be reduced into metallic copper while Ag<sub>5</sub> clusters dissolve and form silver(I) ions.

After some time, the silver concentration of the solution increases, Ag<sub>5</sub> clusters are used up and the concentration of copper ions decreases. Since the latter is comparably high, it is expected to have minor influence. The next possible steps of the reaction are the following:

After the Ag<sub>5</sub> clusters are used up, Ag<sub>10</sub> clusters will start to be oxidized. (Note that if a hydrogen electrode was present, H<sub>2</sub> would be oxidized. In this system, however, there are protons instead of H<sub>2</sub>).

After the increase of the silver ion concentration, the potential of the silver ion reduction (into metallic bulk silver) increases, so that it might exceed the potential of the copper reduction. Afterwards, the silver ions will be reduced to metallic silver (after further dissolution of silver nanoclusters).

## THEORETICAL PROBLEM 13

### *Absorption of Light by Molecules*

Absorption of light by molecules is the first step of all photochemical reactions. The Beer – Lambert law relates the absorbance  $A$  of a solution containing an absorbing species of molar concentration  $c$  with the optical path length  $d$ :

$$A = \log \frac{P_0}{P} = \varepsilon c d$$

$\varepsilon$  is the molar absorptivity (also called extinction coefficient).

Light can be considered as a stream of photons, each carrying an energy of

$$E = h \frac{c}{\lambda}$$

$h$  is Planck's constant,  $\lambda$  is the wavelength and  $c$  the speed of light.

A solution with a dye concentration of  $c = 4 \times 10^{-6} \text{ mol dm}^{-3}$  has a molar absorptivity of  $\varepsilon = 1.5 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . It is illuminated with green laser light at a wavelength of 514.5 nm and with a power of  $P_0 = 10 \text{ nW}$ .

**13.1** What is the percentage of light that is absorbed by the sample after a path length of 1  $\mu\text{m}$ ?

**13.2** Calculate the number of photons per second absorbed by the sample.

The absorption cross section of a molecule is the effective area that captures all incoming photons under low illumination conditions (like an idealized solar cell that would capture all light photons hitting its surface). At room temperature, this corresponds roughly to the molecular area exposed to the light beam. If you calculate it from the molar absorptivity, imagine that all molecules interacting with the light are arranged periodically in a plane perpendicular to the incoming light beam.

**13.3** What area is occupied by each molecule?

**13.4** Calculate the molecular absorption cross section in units of  $\text{\AA}^2$ .

A crucial photochemical reaction for life on our planet is photosynthesis, which converts the absorbed light energy into chemical energy. One photon of 680 nm is necessary to produce one molecule of ATP. Under physiological conditions, the reaction requires an energy of 59 kJ per mol of ATP.

**13.5** What is the energy efficiency of photosynthesis?

## SOLUTION OF PREPARATORY PROBLEM 13

**13.1**  $A = \varepsilon c d = 1.5 \times 10^5 \text{ mol}^{-1} \text{ dm}^{-3} \text{ cm}^{-1} \times 4 \times 10^{-6} \text{ mol dm}^{-3} \times 1 \times 10^{-4} \text{ cm} = 6 \times 10^{-5}$

Since  $A = \log(P_0/P)$ , the ratio  $P/P_0$  is 0.999862. This is the percentage of photons exiting the sample, so that the percentage of photons absorbed by the solution is:

$$\frac{P_0 - P}{P_0} = 1 - \frac{P}{P_0} = 1.38 \times 10^{-4} \text{ or } 0.0138 \text{ \%}.$$

**13.2** According to our previous result, 0.0138 % of the 10 nW laser light entering the sample solution are absorbed:

$$P_{\text{abs}} = 1.38 \times 10^{-4} \times 10 \text{ nW} = 1.38 \times 10^{-3} \text{ nW} = 1.38 \times 10^{-12} \text{ J s}^{-1}$$

The energy of one photon is:

$$E = hc / \lambda = 6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1} / 514.5 \times 10^{-9} \text{ m} = 3.86 \times 10^{-19} \text{ J}$$

The number of photons absorbed by the solution per second is:

$$N_{\text{abs}} = 1.38 \times 10^{-12} \text{ J s}^{-1} / 3.86 \times 10^{-19} \text{ J} = 3.58 \times 10^6 \text{ s}^{-1}.$$

**13.3** Let's imagine that the laser illuminates an area of  $1 \text{ cm}^2$  of the dye solution. The light beam passes through a volume of  $V = 1 \text{ cm}^2 \times 1 \text{ }\mu\text{m} = 1 \times 10^{-7} \text{ dm}^3$ . The number of illuminated molecules is:

$$N = c V N_A = 4 \times 10^{-6} \text{ mol dm}^{-3} \times 1 \times 10^{-7} \text{ dm}^3 \times 6.022 \times 10^{23} \text{ mol}^{-1} = 2.409 \times 10^{11}$$

Each molecule would therefore occupy an area of

$$S_{\text{mol}} = 1 \text{ cm}^2 / 2.409 \times 10^{11} = 4.15 \times 10^{-12} \text{ cm}^2 \text{ or } 415 \text{ nm}^2, \text{ if it was projected onto a plane.}$$

**13.4** The molecular absorption cross section  $\sigma$  is the area of one molecule that captures all incoming photons. Under the experimental conditions, only 0.0138 % of the light interacting with one molecule is absorbed, so that  $\sigma$  is:

$$\sigma = 1.38 \times 10^{-4} \times 415 \text{ nm}^2 = 0.057 \text{ nm}^2 = 5.7 \text{ }\text{\AA}^2$$

**13.5** The energy of one 680 nm photon is:

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}}{680 \times 10^{-9} \text{ m}} = 2.92 \times 10^{-19} \text{ J}$$

Photosynthesis requires 59 kJ per mol of ATP, which corresponds to

$$E_{\text{ATP}} = 59 \times 10^3 \text{ J mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 9.80 \times 10^{-20} \text{ J per ATP molecule.}$$

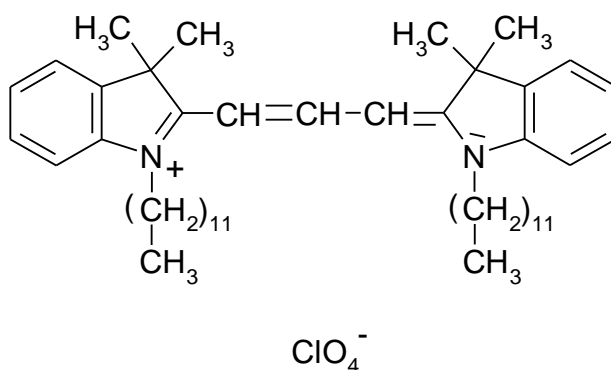
The energy efficiency of photosynthesis is:

$$\eta = 9.80 \times 10^{-20} \text{ J} / 2.92 \times 10^{-19} \text{ J} = 0.34 \text{ or } 34 \text{ \%}.$$

## THEORETICAL PROBLEM 14

### Observing Single Molecules

Since pioneering work in the early 1990s, the areas of single molecule detection and microscopy have exploded and expanded from chemistry and physics into life sciences. Great progress came about with the demonstration of room-temperature imaging (with a near-field scanning optical microscope) of the carbocyanine dye 1,1'-didodecyl-3,3,3',3'-tetramethylindo-carbocyanine perchlorate (diIC<sub>12</sub>). In this experiment, dye molecules are spread on a sample surface and localized according to their fluorescence signals. The structure of diIC<sub>12</sub> is shown below.



**14.1** Indicate which part of the diIC<sub>12</sub> molecule is responsible for its fluorescence. Mark the correct answer.

- (1) The benzene rings
- (2) The dodecyl side chains
- (3) The four methyl groups at the heterocyclic rings
- (4) The C–N chain connecting the two benzene rings
- (5) The perchlorate ion

The surface densities of the molecules have to be sufficiently low, if you want to observe them as individual fluorescent spots under a microscope. No more than 10 molecules per  $\mu\text{m}^2$  on the sample surface is a good value.

10  $\mu\text{dm}^3$  of a solution of diIC<sub>12</sub> in methanol are deposited on a very clean glass cover slide. The drop covers a circular area having a diameter of 4 mm.

**14.2** Calculate the molar concentration of the solution necessary to obtain the value of 10 molecules per  $\mu\text{m}^2$ . (For this calculation we assume that the transfer of the dye molecules from solution to the sample surface by evaporation of the solvent is homogeneous on the whole wetted area.)

The sample is illuminated with the 543.5 nm–line of a green He–Ne laser. The excitation power is adjusted so that the illuminated area (100 nm in diameter) is hit by  $3 \times 10^{10}$  photons per second.

**14.3** What is the excitation power that has been used?

The absorption cross section is an important parameter for the calculation of the expected fluorescence signal from a single molecule. It may be regarded as the effective area of the molecule that captures all incoming photons. At room temperature, this value corresponds approximately to the size of the dye molecule.

**14.4** An illuminated  $\text{dilC}_{12}$  molecule absorbs  $2.3 \times 10^5$  photons per second under the described conditions. Calculate the absorption cross section of the  $\text{dilC}_{12}$  molecule in  $\text{\AA}^2$  (It can be assumed that the 100 nm diameter area is uniformly illuminated).

The fluorescence quantum yield, i.e. the average number of fluorescence photons created for each absorbed photon, is 0.7 for  $\text{dilC}_{12}$  (7 fluorescence photons are created for every 10 absorbed photons). The collection efficiency of the generated fluorescence photons by the experimental setup (including filters to suppress remaining excitation light) is 20 %, and the photon detection efficiency of the highly sensitive photodetector is 55 % over the range of the molecular fluorescence.

**14.5** How many fluorescence photons will actually be detected on average by the photodetector during a 10 ms acquisition window if one  $\text{dilC}_{12}$  molecule is located in the illuminated area?

The fluorescence image is constructed by raster scanning the illuminated area across the sample surface.

**14.6** What diameter do you expect for the fluorescence spot corresponding to one single dye molecule? Mark the correct answer.

- (1) One pixel
- (2) 543.5 nm
- (3) 100 nm
- (4) 200 nm
- (5) Approximately 1  $\mu\text{m}$

## SOLUTION OF PREPARATORY PROBLEM 14

**14.1** Molecular fluorescence in the visible region is due to delocalized electrons in extended  $\pi$ -systems, so the correct answer is:

(4) i. e. : The C–N chain connecting the two benzene rings.

**14.2** A circle with a diameter of 4 mm covers a surface area of

$$S = \pi r^2 \text{ with } r = 2 \times 10^{-3} \text{ m, so } S = 1.26 \times 10^{-5} \text{ m}^2$$

The number of molecules in this area is:

$$10 / (10^{-6} \text{ m})^2 \times 1.26 \times 10^{-5} \text{ m}^2 = 126 \times 10^6 \text{ molecules}$$

They are transferred onto the surface by the evaporation of  $10 \text{ } \mu\text{dm}^3$  of solution, so the concentration has to be

$$126 \times 10^6 / (10 \times 10^{-6} \text{ dm}^3) = 1.26 \times 10^{13} \text{ molecules per dm}^3$$

which corresponds to a molar concentration of

$$c = 1.26 \times 10^{13} \text{ dm}^{-3} / (6.022 \times 10^{23} \text{ mol}^{-1}) = 2.1 \times 10^{-11} \text{ mol dm}^{-3}$$

**14.3** When  $E = hc / \lambda$ , the energy per photon is:

$$E = hc / \lambda = 6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1} / 543.5 \times 10^{-9} \text{ m} = 3.66 \times 10^{-19} \text{ J}$$

$3 \times 10^{10}$  photons per second amount to an excitation power of

$$P = 3.65 \times 10^{-19} \text{ J} \times 3 \times 10^{10} \text{ s}^{-1} = 1.1 \times 10^{-8} \text{ J s}^{-1} = 11 \text{ nW}$$

**14.4** On average, there are 10 molecules per  $\mu\text{m}^2$ , so that one molecule occupies statistically an area of  $S_{\text{mol}} = (1 \times 10^{-6} \text{ m})^2 / 10 = 1 \times 10^{-13} \text{ m}^2$ .

The total illuminated area of  $\pi \times (50 \times 10^{-9} \text{ m})^2 = 7.85 \times 10^{-15} \text{ m}^2$  receives  $3 \times 10^{10}$  photons per second, and the area occupied by a single molecule receives  $3 \times 10^{10} \text{ s}^{-1} \times 1 \times 10^{-13} \text{ m}^2 / (7.85 \times 10^{-15} \text{ m}^2) = 3.82 \times 10^{11}$  photons per second. Only  $2.3 \times 10^5$  photons are absorbed every second, so the area which is capturing photons is:

$$\sigma = 1 \times 10^{-13} \text{ m}^2 \times 2.3 \times 10^5 \text{ s}^{-1} / (3.82 \times 10^{11} \text{ s}^{-1}) = 6 \times 10^{-20} \text{ m}^2 \text{ or } 6 \text{ } \text{\AA}^2$$

$$(\text{or } \sigma = (7.85 \times 10^{-15} \text{ m}^2 / 3 \times 10^{10} \text{ s}^{-1}) \times 2.3 \times 10^5 \text{ s}^{-1} = 6 \times 10^{-20} \text{ m}^2)$$

**14.5** A  $\text{dilC}_{12}$  molecule that absorbs  $2.3 \times 10^5$  photons per second emits

$N_{\text{fluor}} = 0.7 \times 2.3 \times 10^5 \text{ s}^{-1} = 161 \times 10^3$  fluorescence photons per second. Due to the detection efficiency, this results in  $N_{\text{det}} = 161 \times 10^3 \text{ s}^{-1} \times 0.2 \times 0.55 = 17\,710$  detected photons per second. In a time interval of 10 ms, the number of detected photons is:  $17\,710 \text{ s}^{-1} \times 10 \times 10^{-3} \text{ s} = 177$  photons.

**14.6** Each point in the illuminated sample area is hit by the same number of photons per second (uniform illumination). A molecule that is located in the spot's center is



emitting as many fluorescence photons as if it was sitting anywhere else in the illuminated spot. As the illuminated area is raster-scanned across the sample surface, the molecule will be visible as long as it is inside the illuminated area. This is the reason why the fluorescence spot of one molecule will have a size equal to the illuminated area, i.e. 100 nm in diameter (14.3).

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## THEORETICAL PROBLEM 15

### *Infrared Spectroscopy of Tetrahedral Molecules*

Fig. 1: IR spectrum of  $\text{CF}_4$ , intensity vs. wavenumber  $\tilde{\nu}$  in  $\text{cm}^{-1}$

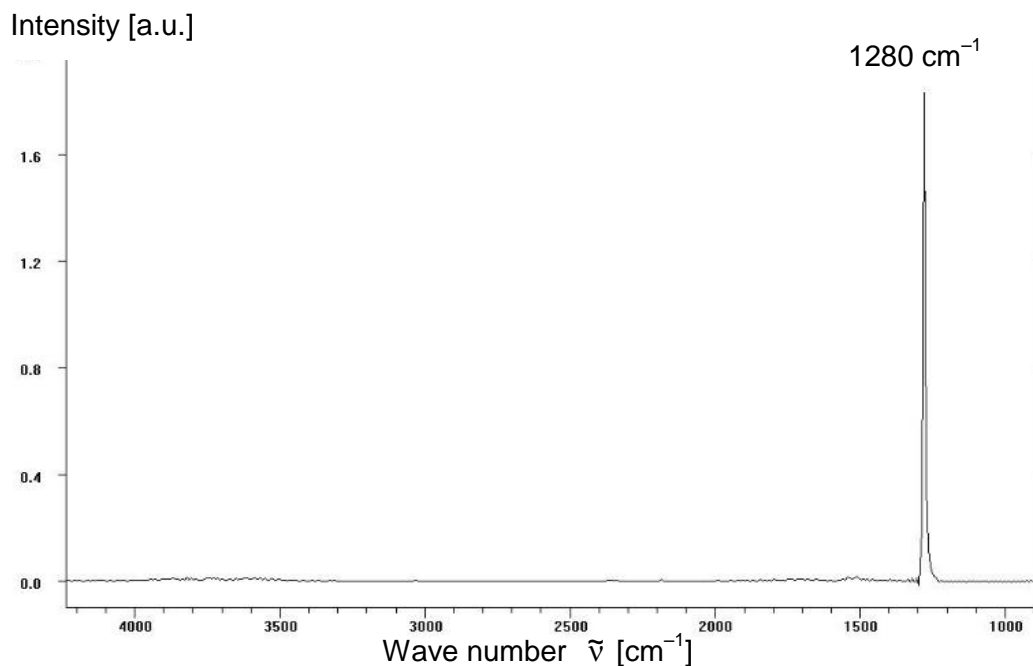
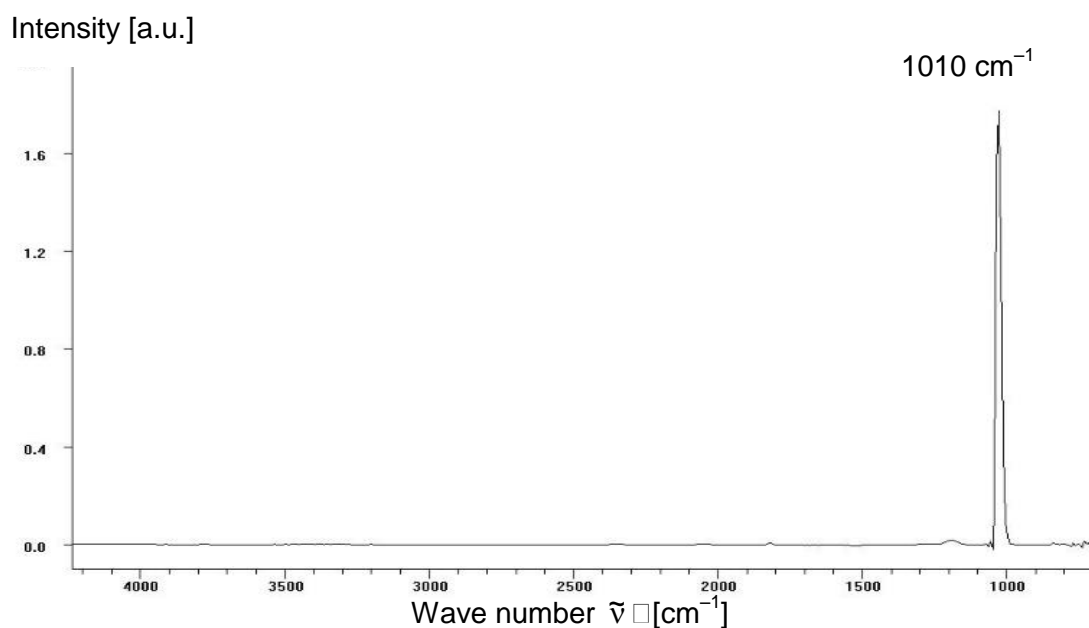


Fig. 2: IR spectrum of  $\text{SiF}_4$ , intensity vs. wavenumber  $\tilde{\nu}$  in  $\text{cm}^{-1}$



The IR spectrum indicates vibrations that depend on the force constant  $k$  of the bonds that keep the atoms together and the so-called reduced mass  $\mu$ .

The reduced mass for the highest frequency vibration in a  $XY_4$  molecule is given by

$$\mu = \frac{3 m_x \times m_y}{3 m_x + 4 m_y} \quad \text{and the vibrational frequency } \nu \text{ is given by } 2\pi\nu = \sqrt{\frac{k}{\mu}}.$$

- 15.1** Calculate the force constant of  $CF_4$  and  $SiF_4$  and compare their relative strengths with each other.

The heats of formation of  $CF_4$  and  $SiF_4$  are  $-1222 \text{ kJ mol}^{-1}$  and  $-1615 \text{ kJmol}^{-1}$ .

- 15.2** What kind of relation is there between them and the force constants of vibration that you have calculated?

The enthalpies of vaporization of carbon and silicon are  $717 \text{ kJmol}^{-1}$  and  $439 \text{ kJmol}^{-1}$ .

- 15.3** Take these values into account and comment on the relation between the heat of formation of the gases and the vibrational frequencies again.

## SOLUTION OF PREPARATORY PROBLEM 15

$$15.1 \quad 2\pi\nu = \sqrt{\frac{k}{\mu}} \Leftrightarrow \quad k = 4\pi^2\nu^2\mu, \quad \nu = c \tilde{\nu}$$

$$\begin{array}{lll} \text{from the diagram: } \tilde{\nu}(\text{CF}_4) = 1280 \text{ cm}^{-1} & & \tilde{\nu}(\text{SiF}_4) = 1010 \text{ cm}^{-1} \\ \text{hence } \nu(\text{CF}_4) = 38.4 \times 10^{12} \text{ s}^{-1} & & \nu(\text{SiF}_4) = 30.3 \times 10^{12} \text{ s}^{-1} \\ \mu = \frac{3 m_{\text{X}} \times m_{\text{Y}}}{3 m_{\text{X}} + 4 m_{\text{Y}}} & \mu(\text{CF}_4) = 6.11 \text{ g mol}^{-1} N_{\text{A}}^{-1} & \mu(\text{SiF}_4) = 9.99 \text{ g mol}^{-1} N_{\text{A}}^{-1} \\ & \mu(\text{CF}_4) = 1.01 \times 10^{-23} \text{ g} & \mu(\text{SiF}_4) = 1.66 \times 10^{-23} \text{ g} \end{array}$$

$$\begin{array}{ll} \text{hence } k(\text{CF}_4) = 4\pi^2 (38.4 \times 10^{12} \text{ s}^{-1})^2 \times 1.01 \times 10^{-23} \text{ g} & k(\text{CF}_4) = 588 \text{ N m}^{-1} \\ \text{and } k(\text{SiF}_4) = 4\pi^2 (30.3 \times 10^{12} \text{ s}^{-1})^2 \times 1.66 \times 10^{-23} \text{ g} & k(\text{SiF}_4) = 602 \text{ N m}^{-1} \end{array}$$

The force constants of the two compounds are almost identical.

- 15.2** The heats of formation and the force constants do not match. They are not expected to match, since the initial states of the compounds need to be taken into account. In addition, the vibrational force constant describes the potential just in the vicinity of the zero point but not far away from it.
- 15.3** Taking into account the heat of vaporization, we obtain the heats of formation of  $\text{CF}_4$  and  $\text{SiF}_4$  from C and Si vapours of  $-1939 \text{ kJ mol}^{-1}$  and  $-2054 \text{ kJ mol}^{-1}$ . This is the reason why we can assume a similar shape of the energy curve of breaking the bonds between C and F and between Si and F, since the extrapolation from the curvature close to the bonding distance to the rest of the curve is quite good.

<http://www.ansyco.de/IR-Spektren>

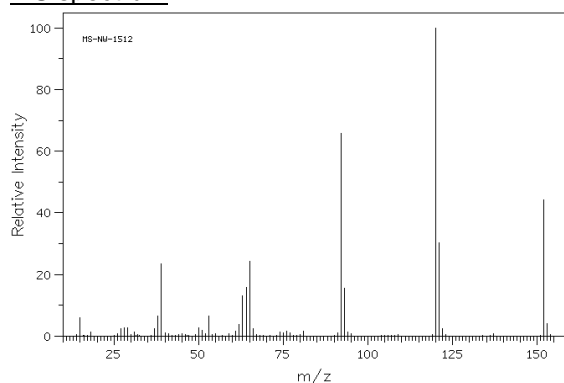
## THEORETICAL PROBLEM 16

### *Spectroscopy in Bioorganic Chemistry*

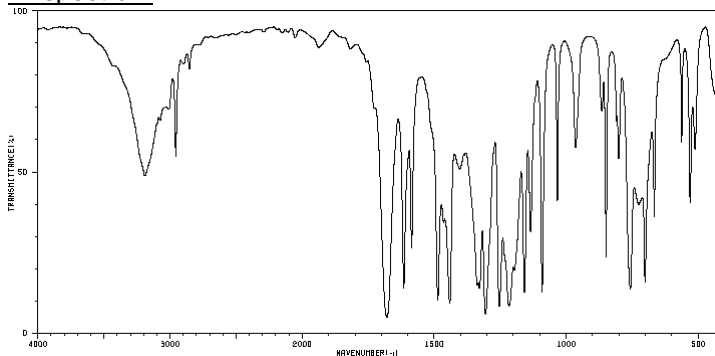
It is well known that strawberries help to reduce minor headaches. The substance **A** that is responsible for this effect is also used as an aroma substance in bubble gums. However, it does not taste like strawberries!

5.00 g of substance **A** yield 2.37 g of water and 6.24 L of carbon dioxide (at 303.7 K and 106.3 kPa). In addition, the infrared (IR), the mass (MS), the  $^1\text{H}$ -NMR, and the  $^{13}\text{C}$ -NMR spectra of the substance have been recorded:

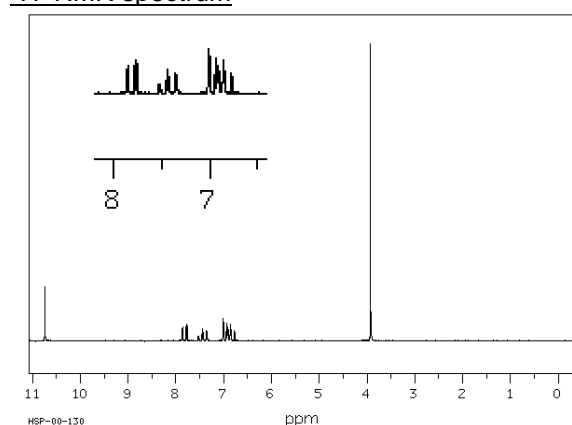
MS spectrum



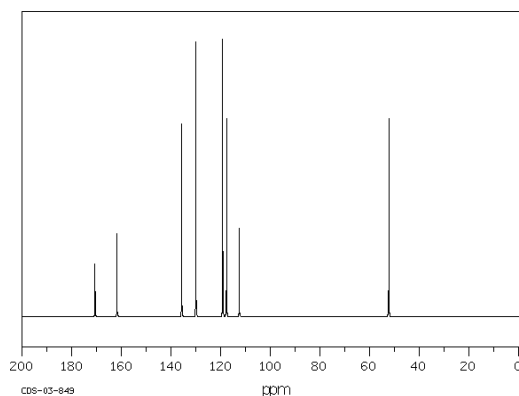
IR spectrum



$^1\text{H}$ -NMR spectrum



$^{13}\text{C}$ -NMR spectrum



- 16.1** Determine the molecular weight of the substance from the MS spectrum.
- 16.2** Determine the molecular formula of the substance from the elementary analysis.
- 16.3** Suggest one fragment B (molecular formula and structure(s)) for the signals at  $m/z = 39$  in the MS spectrum. Suggest a probable fragment C (molecular formula and structure(s)) for  $m/z = 65$  that contains B.
- 16.4** The two groups of signals around  $3200\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  in the IR spectrum are typical of a total of four structural features. Give information about the structures of

these four functional groups. What additional information can be given, if the substance contains an –OH group?

Table of IR absorptions:

3800	3400	3000	2600	2200	1800	group
<b>v</b>						O–H (free)
	<b>v</b>					O–H (hydrogen bond)
		<b>v</b>				O–H (intramolecular h. bond)
		<b>s</b>				C–H in C≡C–H
		<b>m</b>				C–H in C=C–H
		<b>w</b>				C–H in C÷C–H
			<b>s</b>			C–H (alkanes)
				<b>w</b>		C≡C
					<b>m</b>	C=C=C
					<b>w</b>	C=C
					<b>s</b>	C÷C÷C
					<b>s</b>	C=O

The interatomic bond that absorbs the light is bold. The intensities correspond to strong (s), medium (m), weak (w) and varying intensity (v). An aromatic bond is marked by “÷”.

- 16.5** Assign the total of six signals at 4.0 ppm, 6.5 – 8.0 ppm, and 10.8 ppm in the <sup>1</sup>H–NMR spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).

Simplified table of <sup>13</sup>C–NMR chemical shifts:

C=O	C÷C, C=C	C≡C		O–C	CH, CH <sub>2</sub> , CH <sub>3</sub>
200 190 180 170 ppm	160 150 140 130 120 110	100 90 80 70	60 50	40 30 20 10	

An aromatic bond is marked a “÷”.

- 16.6** Assign the signals at 52 ppm, 170 ppm, and 110 – 165 ppm in the <sup>13</sup>C–NMR spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).

Simplified table of <sup>1</sup>H–NMR chemical shifts:

OH, COOH, CHO	C÷CH	C=CH	OCH <sub>x</sub>	CH	CH <sub>2</sub>	CH <sub>3</sub>
12 ppm 10	9 8 7 6	5	4	3	2	1

An aromatic bond is marked by “÷”.

A very simple rule helps to understand NMR spectra: The chemical shift increases with decreasing electron density at the nuclei. This is the reason why you may estimate relative chemical shift values from I– and M– effects.

You will have to combine the chemical shift information with your knowledge about I– and M– effects to make distinctions between potential isomers. You may also consider the fine splitting of the signals at 6.8, 6.9, 7.5, and 7.8 ppm in the <sup>1</sup>H–NMR spectrum and the –O–H band in the IR spectrum.

**16.7** Suggest one molecular structure for the unknown substance. Assign the resonances at 6.8, 6.9, 7.5, and 7.8 ppm in the <sup>1</sup>H–NMR spectrum and the signals at 52 and 161 ppm in the <sup>13</sup>C–NMR spectrum to individual atoms in your solution structure. According to your solution, suggest fragments that explain the signals at m/z=92 and m/z=120 in the MS spectrum. Write down the structural feature that is responsible for the low wave number of the –O–H band.

**16.8** The substance A is related to a drug widely used against headaches. Write down the chemical structure of this drug.

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## SOLUTION OF PREPARATORY PROBLEM 16

Mass spectrometry: <http://masspec.scripps.edu/information/intro/>

IR spectroscopy: <http://www.chem.ucla.edu/~webspectra/irintro.html/>

NMR spectroscopy: <http://chipo.chem.uic.edu/web1/ocol/spec/NMR.htm>

### 16.1 152 g mol<sup>-1</sup>

The molecular weight corresponds to the peak with the highest m/z in the mass spectrum. The smaller peak at 153 g mol<sup>-1</sup> is due to molecules with one <sup>13</sup>C isotope (8 carbon atoms × 1% <sup>13</sup>C isotopes in nature ≈ 8% of the total signal at 152 g mol<sup>-1</sup>).

### 16.2 C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>

$$n(\text{H}) = 2 \, m(\text{H}_2\text{O}) / M(\text{H}_2\text{O}) = 2 \times 2.37 \, \text{g} / 18.02 \, \text{g mol}^{-1} = 0.263 \, \text{mol}.$$

$$n(\text{C}) = p \, V(\text{CO}_2) (R \, T)^{-1} = \frac{106.3 \, \text{kPa} \times 6.24 \, \text{dm}^3}{8.314 \, \text{J mol}^{-1} \text{K}^{-1} \times 303.7 \, \text{K}} = 0.263 \, \text{mol}$$

$$n(\text{O}) = (m(\text{A}) - n(\text{H}) \, M(\text{H}) - n(\text{C}) \, M(\text{C})) / M(\text{O})$$

$$= (5.00 \, \text{g} - 0.263 \, \text{mol} \times 1.01 \, \text{g mol}^{-1} - 0.263 \, \text{mol} \times 12.01 \, \text{g mol}^{-1}) (16.00 \, \text{g mol}^{-1})^{-1} \\ = 0.098 \, \text{mol}$$

$$n(\text{A}) = m(\text{A}) (M(\text{A}))^{-1} \approx 5.00 \, \text{g} (152 \, \text{g mol}^{-1})^{-1} = 0.033 \, \text{mol}$$

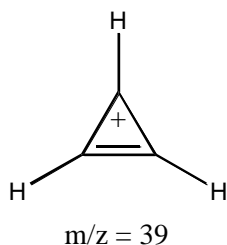
$$N(\text{O}) = n(\text{O}) / n(\text{A}) = 3$$

$$N(\text{H}) = n(\text{H}) / n(\text{A}) = 8$$

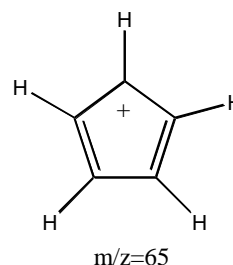
$$N(\text{C}) = n(\text{C}) / n(\text{A}) = 8$$

### 16.3

B: C<sub>3</sub>H<sub>3</sub><sup>+</sup>



C: C<sub>5</sub>H<sub>5</sub><sup>+</sup>



Note that for m/z = 39 only one fragment that has the molecular formula C<sub>3</sub>H<sub>3</sub><sup>+</sup> will be chemically meaningful, if the molecule only contains C, H, and O. The same is true for m/z = 65 and C<sub>5</sub>H<sub>5</sub><sup>+</sup> and if it has to contain C<sub>3</sub>H<sub>3</sub><sup>+</sup>.

Both fragments are typical of benzenes. Other (non-cyclic) structures of those fragments should also be considered as correct solutions, if they are chemically meaningful.

### 16.4 O–H, C–H for the signals around 3200 cm<sup>-1</sup>,

C=O, benzene for the signals around 1700 cm<sup>-1</sup>,

the O–H group is involved in a (intra-molecular) hydrogen bond.

(Since it is impossible to distinguish between the signals within these two groups without additional information, the following is not thought to be part of the solution:



Broad peak at 3200 cm<sup>-1</sup>: C–H

Sharp peak at 2900 cm<sup>-1</sup>: O–H

Broad peak at 1700 cm<sup>-1</sup>: C=O

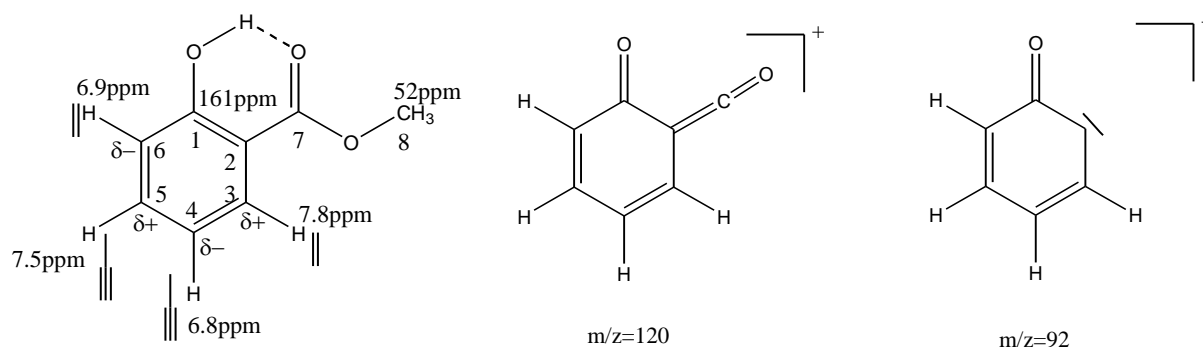
Sharp peaks around 1600 cm<sup>-1</sup>: benzene )

**16.5** 4.0 ppm: OCH<sub>3</sub>, 6.5 – 8.0 ppm: C<sub>6</sub>H<sub>4</sub>, 10.8 ppm: OH

**16.6** 52 ppm: CH<sub>3</sub>, 170 ppm: C=O, 110 – 165 ppm: C<sub>6</sub>H<sub>4</sub>

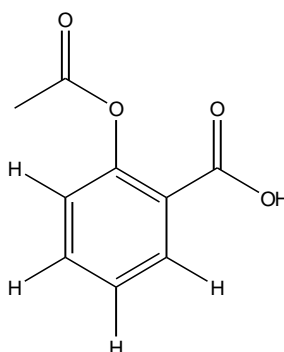
This information can directly be obtained from the chemical shift tables.

**16.7** Methylsalicylate.



The intra-molecular hydrogen bond in the figure explains the low wavelength of the O–H band. It defines the ortho-position of the substitution as well as the fine splitting of the <sup>1</sup>H signals of the aromatic system. The relative large chemical shifts of the carbon atoms C–8 and C–1 at 52 ppm and 161 ppm are explained by a –I effect of the oxygen they are bond to. The assignment of the hydrogen chemical shifts in the aromatic ring is done in the following way: ±M effects define an alternating scheme of positive and negative partial charges at the aromatic ring. H–6 and H–4 have lower chemical shifts than H–5 and H–3. H–4 and H–5 have two neighbouring hydrogen atoms. Their signals are triplets that are shown in the figure. H–3 and H–6 have only one neighbouring hydrogen atom each. Their signals are doublets. All four signals are uniquely assigned by this information. The signals at m/z = 120 and m/z = 92 are caused by loss of CH<sub>3</sub>–OH (methanol) or rather CH<sub>3</sub>–COOH (acetic acid).

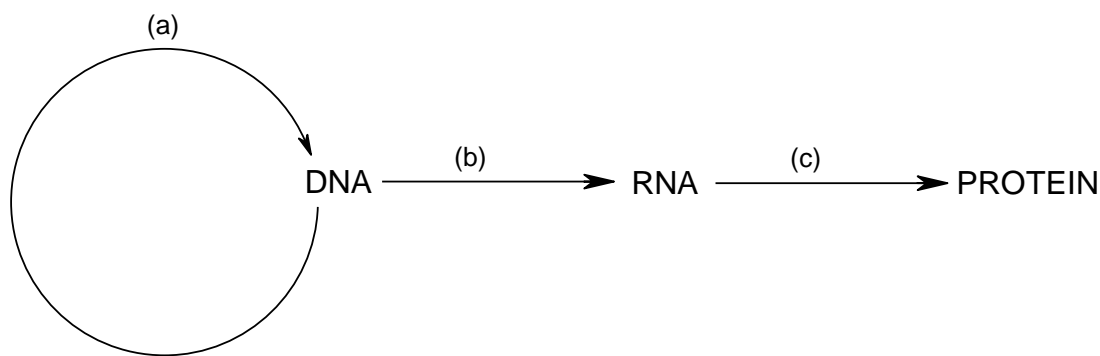
**16.8** Acetylsalicylic acid (Aspirin)



## THEORETICAL PROBLEM 17

### DNA, RNA, Proteins

The “central dogma of Molecular Biology” describes the transfer of genetic information from DNA via RNA to protein:



(a): replication

(b): transcription

(c): translation

The chemical structures of the biopolymers DNA, RNA and proteins enable them to play such important roles for all forms of life. Fifty years ago, in 1953, James Watson and Francis Crick published a structure of DNA in the journal “Nature” which involves specific interactions between nucleobases in complementary strands.

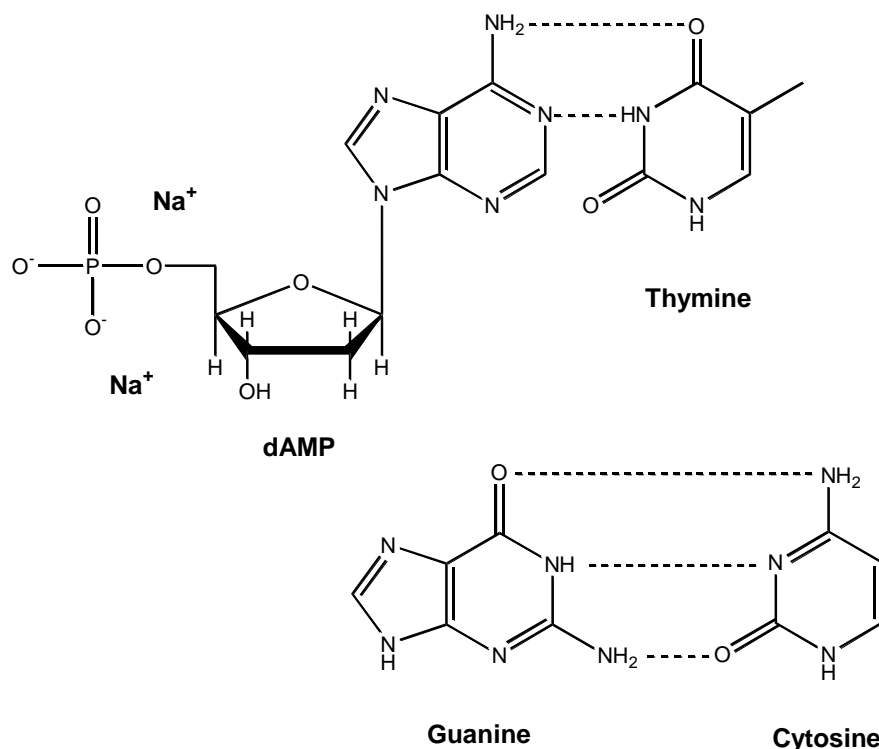
- 17.1** Draw the line–bond structure of the nucleotide 2’–deoxyadenosine 5’–mono–phosphate (dAMP, disodium salt) and of the bases cytosine, guanine, and thymine. Indicate the correct hydrogen bonds between the nucleobases as they occur in the Watson–Crick double strand.
- 17.2** How does the composition of RNA differ from that of DNA, and how does that affect the chemical stability of the molecule?

Proteins are probably the most versatile biomolecules, with immensely varying properties that are determined by their amino–acid sequence.

- 17.3** Write down three general functions of proteins.
- 17.4** Draw a reaction scheme with line–bond structures that shows how two amino acids combine to form a dipeptide. What conformation does the peptide bond usually adopt?
- Which high–molecular weight particle catalyses the formation of peptide bonds in human cells during translation?
- 17.5** Draw the stereochemical formula of the tripeptide L–Ser–L–Val–L–Gly indicating the charges at the isoelectric point.

## SOLUTION OF PREPARATORY PROBLEM 17

### 17.1



**17.2** RNA contains ribose instead of 2'-deoxyribose as the sugar moiety. Uracil (in RNA) takes the place of the nucleobase thymine (in DNA).

The 2'-OH group in ribose affects the stability of RNA against base-catalysed hydrolysis, which is initiated by deprotonation of the 2'-OH group and results in backbone cleavage. This 2'-OH group is missing in DNA which is therefore more stable than RNA.

### 17.3 Proteins

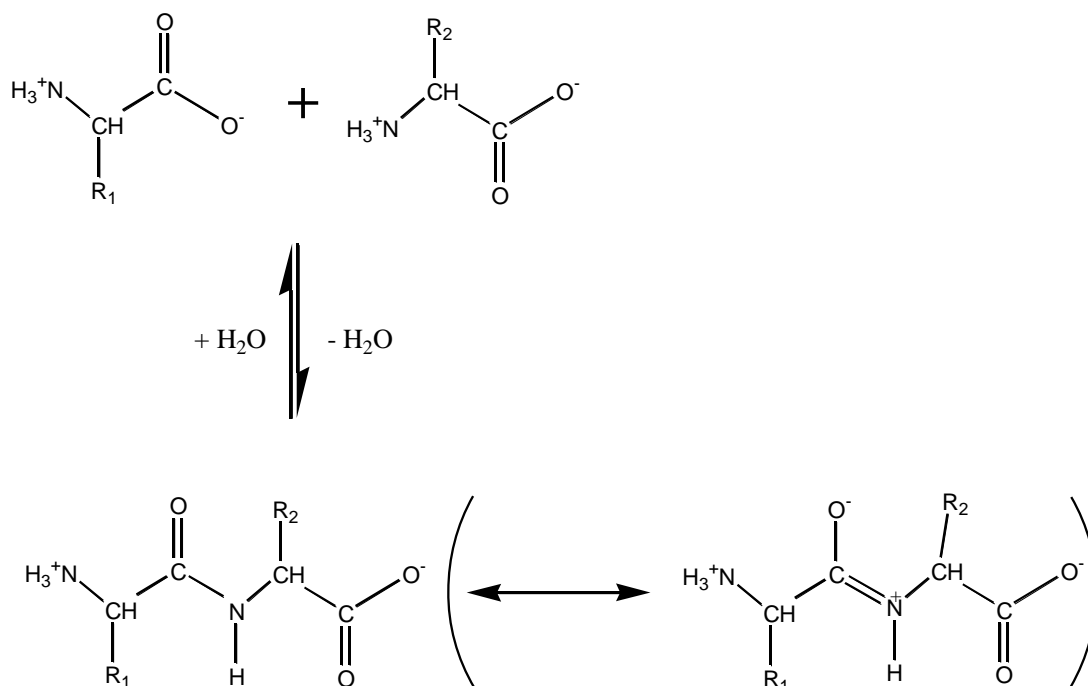
- build structures (cytoskeleton, keratin, connective tissue,...)
- generate motive forces (myosin,...)
- transport ions/small molecules (ion carriers, protein complexes,...)
- catalyse reactions (enzymes)
- fight against infections (immune response)

Other answers are also possible.

**17.4** Reaction scheme of peptide formation see next page.

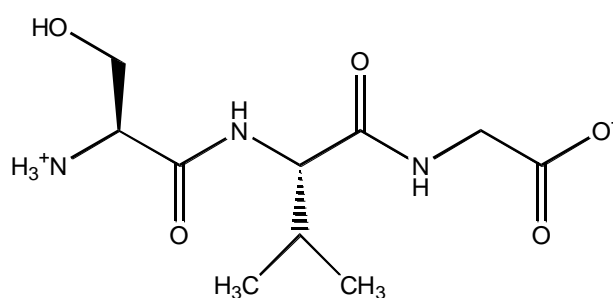
The peptide bond is almost planar (due to the partial double-bond as indicated in the figure). The two C $\alpha$  carbon atoms are arranged in trans-configuration.

The human ribosome is a particle made up by 4 ribosomal RNA molecules and several dozen protein subunits with a total molecular weight of 4,200,000 u. It binds to the messenger RNA and, depending on the base sequence, catalyses the formation of peptide bonds between the COO<sup>-</sup> group of the nascent polypeptide chain and the NH<sub>3</sub><sup>+</sup> group of the correct activated amino acid.



not part of the solution

### 17.5 Tripeptide SVG (note the zwitterionic state):



## THEORETICAL PROBLEM 18

### *Fatty Acid Degradation*

Grizzly bears love eating fish. Since the rivers are frozen in winter, they have to build up body fat in autumn which they burn during hibernation.



**18.1** Draw a typical triglyceride and name its building blocks. Mark centres of chirality.

The reaction cascade specific to fatty acid degradation is called “ $\beta$ -oxidation”. It takes place in the mitochondria of the bear’s cells. In each cycle of  $\beta$ -oxidation an acetyl group is split off the fatty acid and two different reaction partners **A**, **B** are reduced.

**18.2** Write down the complete names and the commonly used abbreviations of the molecules **A** and **B**. Draw the line bond structures of the reactive moieties of these molecules in the oxidized and reduced forms.

The acetyl group is further oxidized in a second reaction cycle, which takes place in the matrix of the mitochondrion.

**18.3** What is the name of this reaction cycle? Which oxidation product is released from the cycle? What are the reduced products?

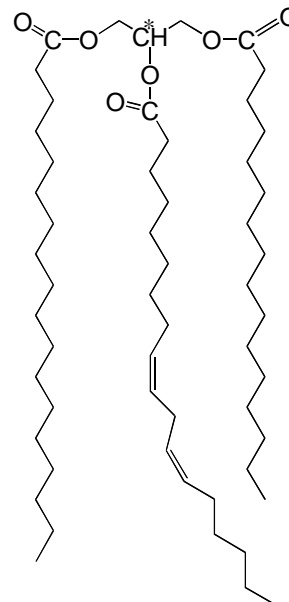
The reduced products **A** and **B** are reoxidized to build up adenosine triphosphate (ATP) in a third cascade of reactions, called the respiratory chain, at the inner mitochondrial membrane.

**18.4** What is the oxidation product of the respiratory chain? How is the free energy stored at the inner mitochondrial membrane independently of chemical bonds, and how is it used for the synthesis of ATP?

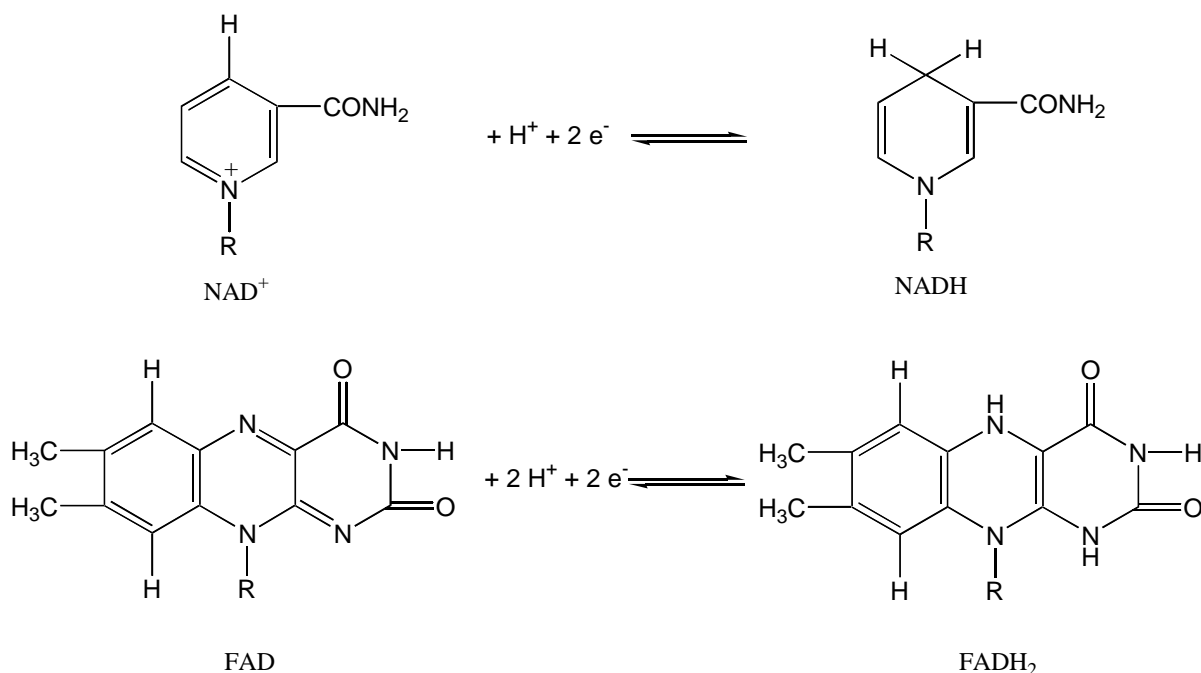
**18.5** Write down the molecular formula of the overall oxidation reaction of a fatty acid in these three reaction cascades. What roles do **A** and **B** play in these reaction cascades?

## SOLUTION OF PREPARATORY PROBLEM 18

- 18.1** Glycerol (chirality centre marked by \*),  
saturated or unsaturated fatty acids, e.g.,  
stearic acid (C18, position 1)  
linoleic acid (C18, position 2)  
palmitic acid (C16, position 3)



- 18.2** NADH nicotinamide adenine dinucleotide



FADH<sub>2</sub>      flavin adenine dinucleotide

- 18.3** Krebs–cycle; alternative names are: citric acid cycle or tricarboxylic acid cycle.  
The oxidation product is CO<sub>2</sub>  
The reduced products are NADH and FADH<sub>2</sub>
- 18.4** The oxidation product is H<sub>2</sub>O.

The free energy is stored at the inner mitochondrial membrane as a proton concentration gradient across the membrane. The re-entry of protons into the mitochondria causes ATP synthesis, catalysed by the enzyme ATP-synthase involving a unique rotary mechanism.

**18.5** For example for palmitic acid:  $\text{C}_{16}\text{H}_{32}\text{O}_2 + 23 \text{O}_2 \longrightarrow 16 \text{CO}_2 + 16 \text{H}_2\text{O}$

NADH and FADH<sub>2</sub> are electron carriers – they carry redox equivalents from the β-oxidation and the Krebs cycle to the respiratory chain.

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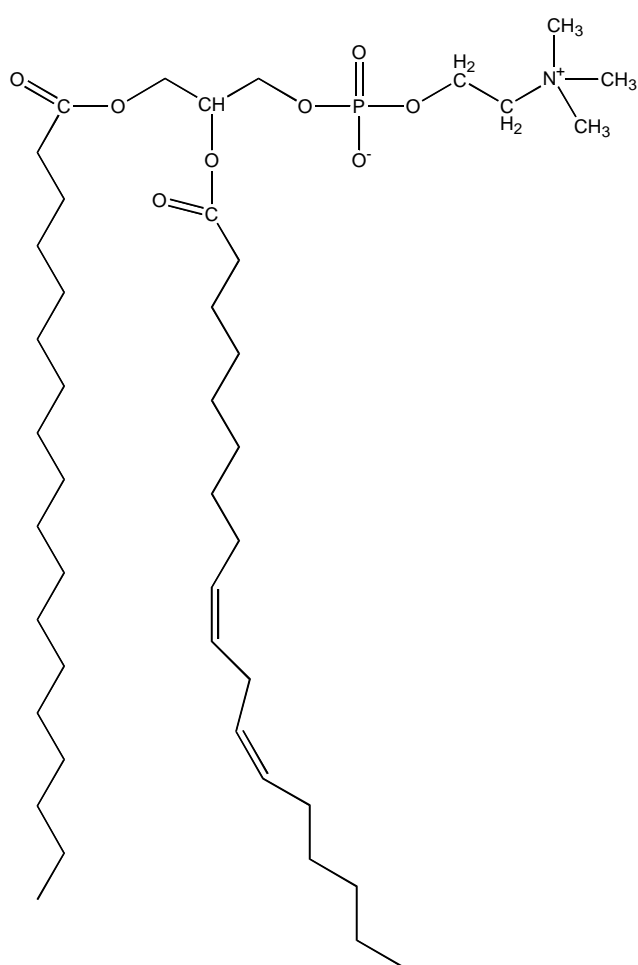
## THEORETICAL PROBLEM 19

### Lipids

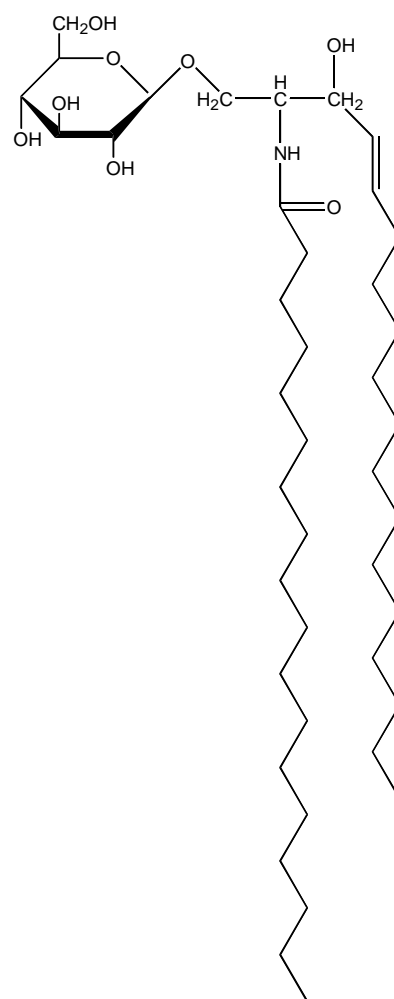
Lipids are important components of our nutrition, and they fulfill a variety of important roles in the body – although we do not always want to be reminded of their presence!

Lipids can be classified according to their hydrophobicity: apolar or neutral lipids with overall hydrophobic structures store energy in our fat cells, whereas polar lipids, which contain a polar “head group” and one or more apolar “tails”, are found in the membranes around each cell of our body.

In addition to the common phospholipids like lecithin, other polar lipids like cerebroside are present in membranes surrounding human cells.



Lecithin (phosphatidyl choline)



Cerebroside



**19.1** Name the building blocks of lecithin. Indicate the head and tail structures of both lipids in the structure above.

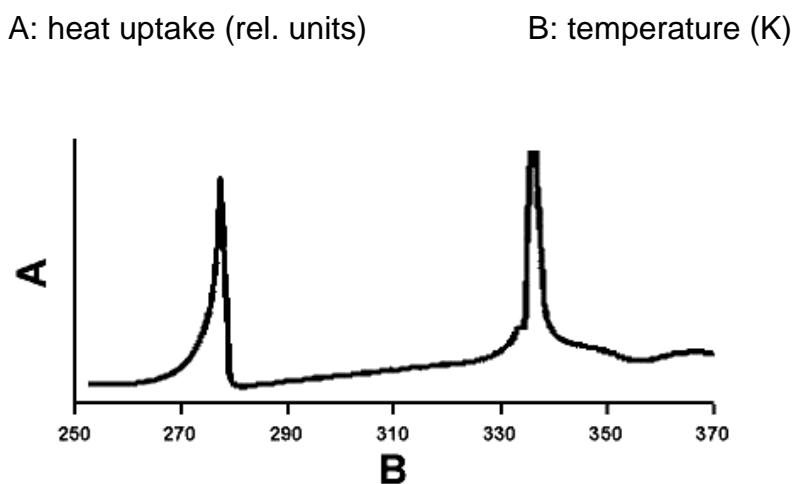
Lipids are substances that are soluble in organic solvents like chloroform, but hardly soluble in water.

**19.2** If lipids are mixed with water, what aggregates can they form? Describe two characteristic superstructures which are commonly found in biological systems, including our food. How are the lipid head groups oriented towards the water? Which factor determines the superstructure formed by a lipid?

Together with other lipids cerebroside are found on the surface of human cells. In contrast to the head group of cholesterol which points to the inside as well as to the outside, the head group of cerebroside is found exclusively pointing to the outer surface of human cells.

**19.3** Why does this arrangement not dissipate into the entropically favoured arrangement with the head groups of the cerebroside pointing to the inside and outside?

The differential scanning calorimetry plot below refers to a mixture of 60% distearyl phosphatidyl choline and 40% water.



**19.4** Explain the two peaks in the diagram. How can a living cell control the position of the second peak to adapt the properties of its membrane to the demands of life?

In blood, lipids are transported in the form of lipoproteins, which consist of polar and apolar lipids, as well as proteins with hydrophilic and hydrophobic surfaces.

In western countries lipoprotein levels are elevated in the blood of many people due to a high fat diet. Especially high amounts of cholesterol and cholesterol–esters in some lipoproteins lead to modifications of blood vessels and lipid deposition (atherosclerosis). This can finally result in a blockage of the blood flow in the arteries supplying the heart with oxygen: a heart attack occurs, one of the most common causes of death.

**19.5** How could lipids and proteins form lipoproteins, stable superstructures which can be easily transported in blood? How would

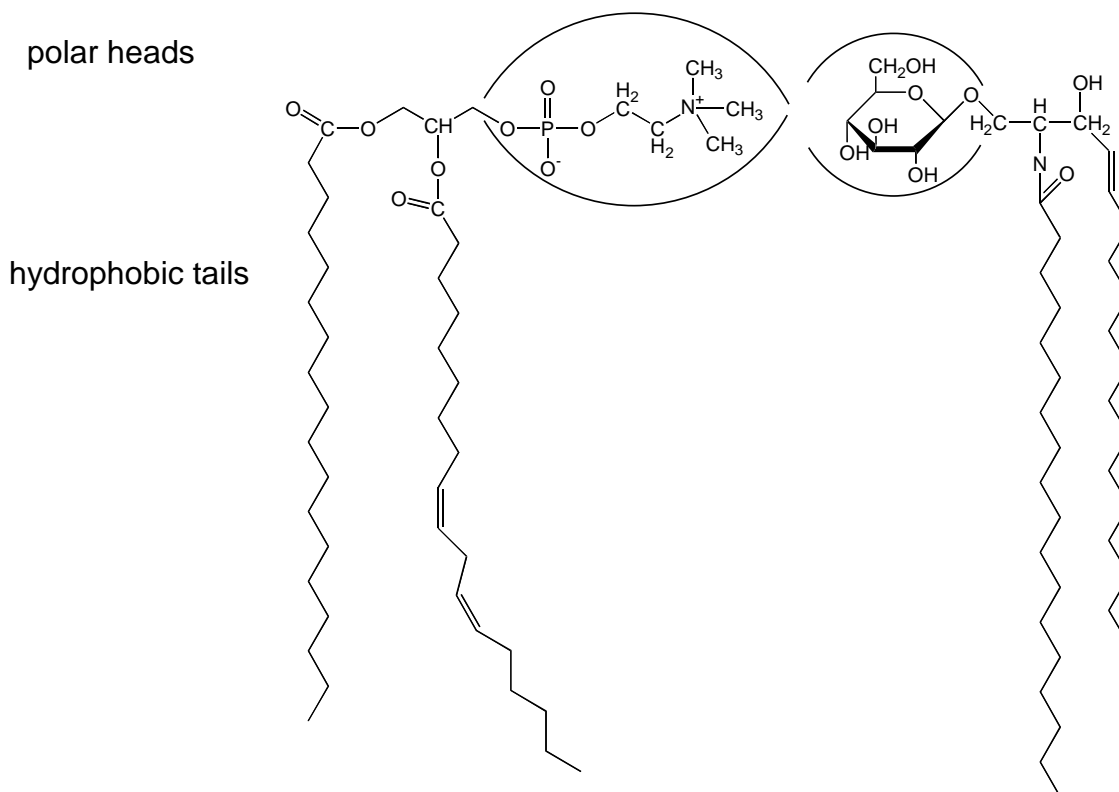
a) cholesterol

b) esters of cholesterol with fatty acids be incorporated into lipoproteins?

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## SOLUTION OF PREPARATORY PROBLEM 19

### 19.1 Glycerol, phosphate, choline, 2 fatty acids (in this case stearic and linoleic acid)



### 19.2 Micelles and vesicles (lipid monolayers, lipid bilayers).

Micelles: spheroidal with (hydrophilic) head groups facing outwards; diameter depends on tail lengths, no water inside.

Vesicles: spheroidal lipid bilayers with head groups facing inwards and outwards, filled with water.

Micelles will form if the polar head group of the lipid has a much larger cross section than the hydrophobic part. Naturally occurring phospholipids carry two bulky fatty acids which do not fit into a micelle, therefore a vesicle (a lipid bilayer) forms.

### 19.3 The polar head groups from the outer layer of the membrane would have to cross the hydrophobic part of the membrane bilayer surrounding the cell to reach the more stable symmetric arrangement. This so-called “flip flop” mechanism has a high activation energy preventing the rearrangement of the cerebroside molecules into a symmetric distribution.

### 19.4 The peak at about 273 K indicates the phase transition from ice to water. The peak at about 335 K results from a phase transition of the phosphatidyl choline in the

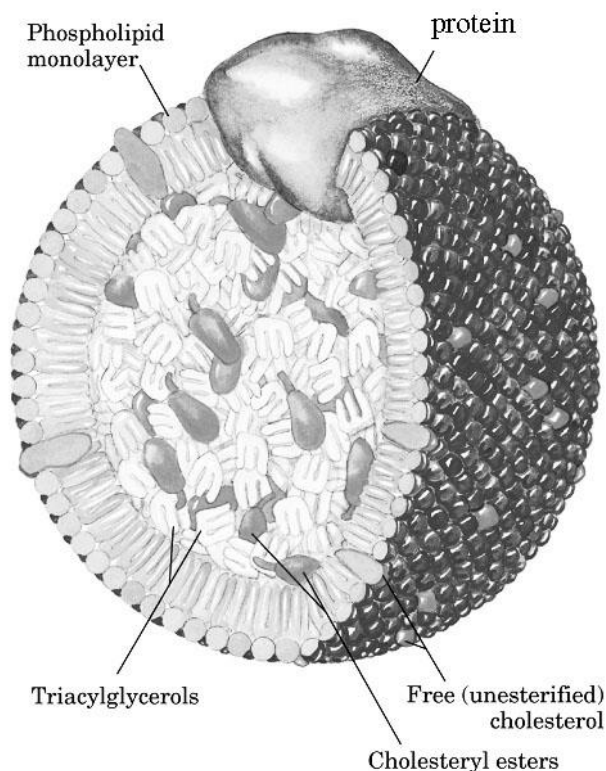
vesicles: At low temperatures, in the so-called liquid-crystalline phase, the C–C bonds of the hydrocarbon chains of the saturated fatty acids are in the single-trans conformation leading to a rigid, highly ordered array of many straight chains. Above the transition temperature, this order is disturbed by kinks in the hydrocarbon chains due to different conformations in some of the C–C bonds leading to a more disordered, fluid phase of the vesicles.

The fluidity of biological membranes is well controlled. Cells can reduce the transition temperature by introducing lipids with shorter fatty acids or with unsaturated fatty acids (the naturally occurring cis-conformation leads to a kink and disrupts the order). The incorporation of cholesterol, which prevents the packing of hydrocarbon chains of the other lipids is another way to control the phase of the membrane.

**19.5** Lipoproteins are supramolecular structures of lipids and proteins forming micelles with the polar surfaces of the proteins and the head groups of the polar lipids (phospholipids, free cholesterol) facing outwards. The apolar lipids (triacylglycerols, cholesteryl esters) together with the hydrophobic surfaces of the proteins and the hydrophobic part of the polar lipids are hidden in the interior.

- a) The OH-group of cholesterol represents the polar head group and faces outwards, the apolar steroid ring system faces inwards.
- b) Cholesteryl esters are hydrophobic lipids buried in the interior of the lipoproteins.

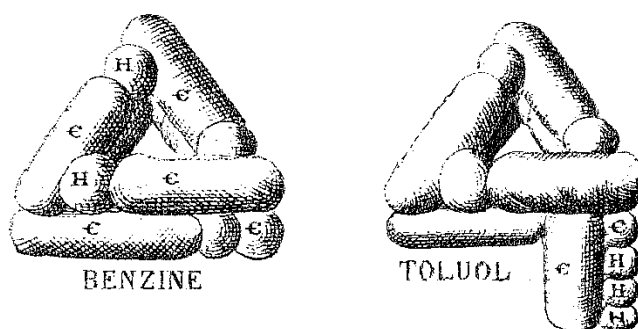
Structure of a lipoprotein  
(adapted from Lehninger,  
Biochemistry)



## THEORETICAL PROBLEM 20

### *Kekulé, Benzene and the Problem of Aromaticity*

In 1865, the German chemist August Kekulé proposed a cyclic structure for benzene, an aromatic-smelling hydrocarbon with the empirical formula  $C_6H_6$ , that was discovered in 1825 by Michael Faraday. Kekulé proposed that carbon has four valences and that it can form carbon-carbon single bonds (1/4 overlap) or double bonds (2/4 overlap). In his model, benzene has alternating single and double bonds. The remaining 6 valences are saturated with bonds to the six hydrogen atoms. These are copies of his original work:



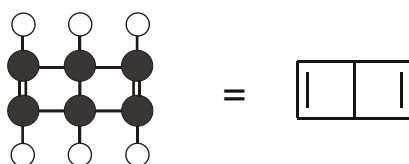
However, at that time it was already known that there is only one isomer of ortho disubstituted benzenes. If benzene had alternating single and double bonds there would be two isomers, one with a double bond between the substituents and one with a single bond. Kekulé solved this contradiction by assuming that the single and double bonds in benzene are “somehow combined in a common benzene nucleus”.

Now, we know that benzene is a planar, regular hexagon with all the C–C bonds of equal lengths and that its chemical reactivity is different from that of a normal olefin.

**20.1** Draw resonance structures that explain the electronic structure of benzene.

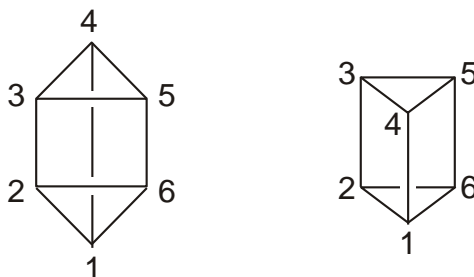
**20.2** Draw the structures of all conceivable disubstituted benzene isomers bearing two identical substituents ( $C_6H_4R_2$ ).

An alternative benzene structure was proposed by Staedeler. Nowadays it is known as the Dewar benzene structure:

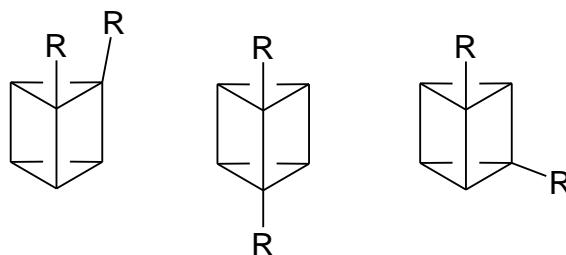


**20.3** How many isomers of Dewar benzene will be conceivable if it is substituted with two identical substituents? Draw the structures.

Shortly after, A. Ladenburg, who used to be Professor for Organic Chemistry here in Kiel, proposed the so-called Ladenburg benzene structure (now called prisman):



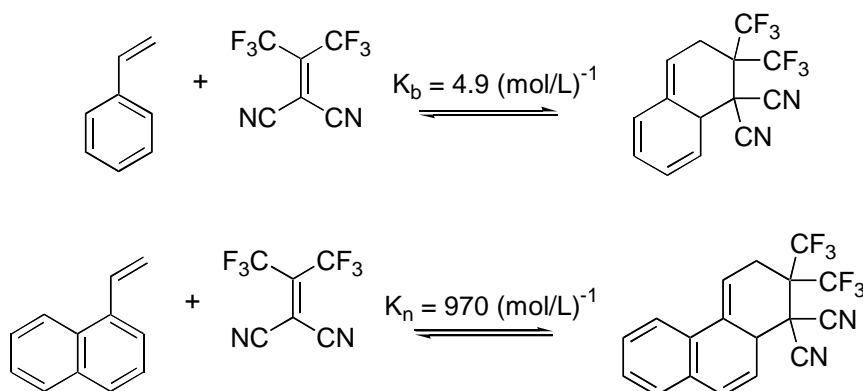
According to Prof. Ladenburg, the benzene model is in agreement with the fact that there are three disubstituted benzene isomers:



Ladenburg was wrong. The list above is not complete.

**20.4** There is a 4th isomer. What does it look like?

Aromatic compounds are more stable than their non-aromatic counterparts. There are different ways to measure the so-called aromatic stabilization energy. The following experiment was performed to compare the stabilization energy of benzene with naphthalene:



The equilibrium constants  $K_b$  and  $K_n$  were measured for both reactions at 300 K.

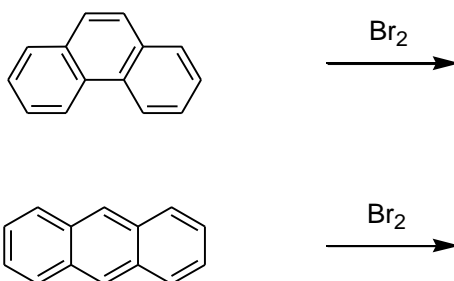
**20.5** Calculate the free enthalpies of reaction  $\Delta_r G$  for both reactions.

**20.6** Calculate the enthalpy of reaction  $\Delta_r H$  for each reaction assuming that for both reactions  $\Delta S$  is  $-125 \text{ J mol}^{-1} \text{ K}^{-1}$  and the temperature is 300 K.

**20.7** Why is the second reaction more exothermic than the first?

Write down all resonance structures of the starting materials and products and count those having favourable benzene resonances.

What do you think are the products of the following reactions (use the same arguments)?



**20.8** Fill in the structures of the reaction products.

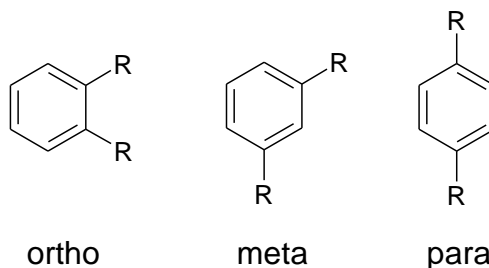
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## SOLUTION OF PREPARATORY PROBLEM 20

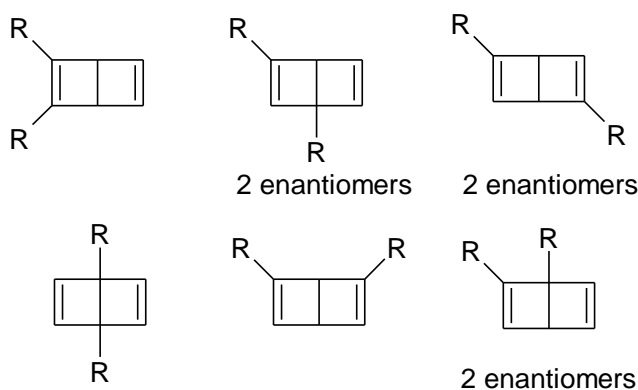
**20.1** Kekulé originally suggested two equilibrating structures with alternating single and double bonds. According to Kekulé, the single bonds would be longer than the double bonds and the structures would have irregular hexagonal shapes. Spectroscopy, however, has shown that benzene has a planar ring, with all the carbon–carbon bond distances having the same length of 1.397 Å (C–C typically 1.48 Å, C=C typically 1.34 Å). Since there are equal distances between the atoms, and the locations of the  $\pi$  electrons in the two Kekulé structures are the only difference, they are in fact resonance structures.



**20.2** Two substituents attached to a benzene ring can be positioned in three different ways:

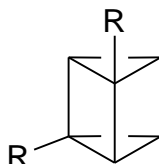


**20.3** Dewar benzene was one of the structures proposed for benzene in the early days of organic chemistry. There are six different structural isomers of a disubstituted Dewar benzene, three of them are chiral and occur in two enantiomeric forms. Because only three benzene isomers  $C_6H_4R_2$  have been found by experiment, the Dewar benzene structure cannot be correct. However, Dewar benzene can be synthesized but it is much less stable than benzene because of its considerable angle strain and its lack of aromatic stabilization.





- 20.4** The missing fourth isomer is an enantiomer of one of the structures that Ladenburg originally suggested. So he did not notice that one of his proposed structures is chiral.



- 20.5** The free enthalpies of reaction  $\Delta_r G$  can be calculated from the equilibrium constant  $K$  according to the following equation:

$$\Delta_r G = -RT \ln K$$

$$K_b = 4.9$$

$$\Delta_r G_b = -3.964 \text{ J mol}^{-1}$$

$$K_n = 970$$

$$\Delta_r G_n = -17.154 \text{ J mol}^{-1}$$

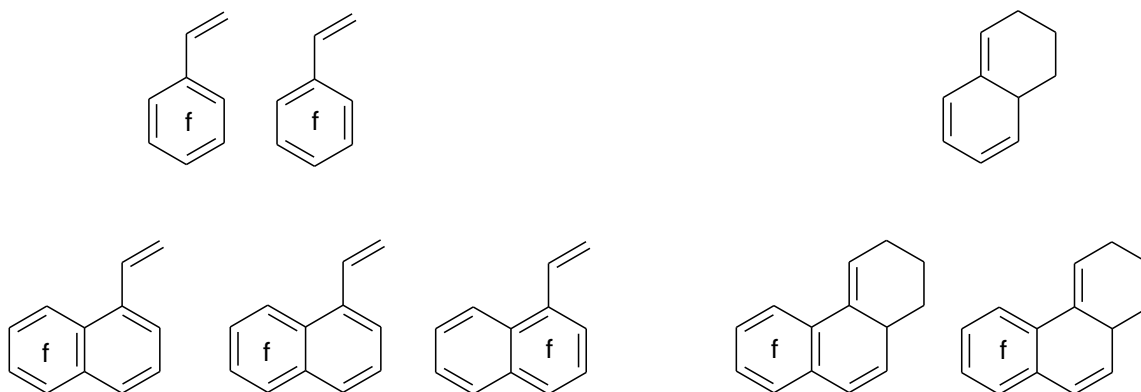
- 20.6**  $\Delta_r G = \Delta_r H - T \Delta S$

$$\Delta S_b = \Delta S_n = -125 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta_r H_b = -41.464 \text{ J mol}^{-1}$$

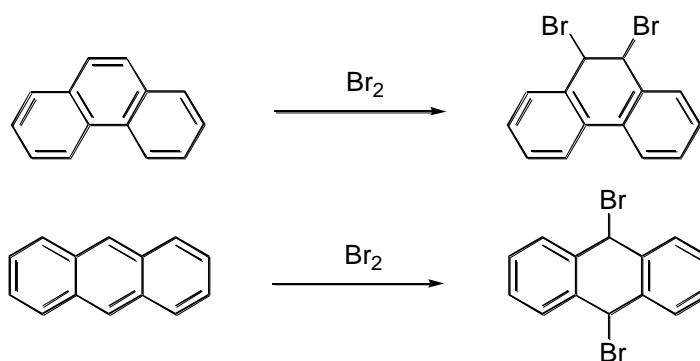
$$\Delta_r H_n = -54.654 \text{ J mol}^{-1}$$

- 20.7** In this Diels–Alder reaction, the aromatic  $\pi$ -system of styrene is completely destroyed. The product is not aromatic any more. Consequently, this loss in aromatic stabilization reduces the reaction enthalpy  $\Delta_r H$ . Vinyl naphthalene makes the resulting product still be aromatic, only a part of the aromatic system is destroyed. Hence, the energetic loss in this case is less than compared to styrene (naphthalene is not twice as stable as benzene) and the reaction is therefore more exothermic.



f: favourable mesomeric benzene substructure

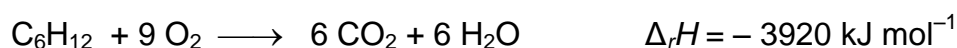
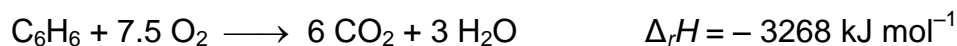
**20.8** Bromine is electrophilically added to the (formal) middle double bond in the phenanthrene molecule. In anthracene, it is added to the opposing carbon atoms. These products contain two aromatic benzene rings. The aromatic stabilization is hence larger than in the alternative products with naphthalene rings.



## THEORETICAL PROBLEM 21

### *Benzene and Cyclohexane*

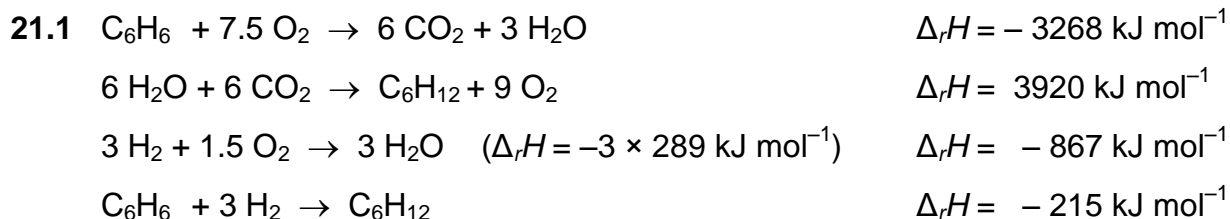
**21.1** How can the enthalpy of the hydrogenation of benzene be calculated from its enthalpy of combustion and the enthalpies of combustion of cyclohexane and hydrogen? Make use of Hess's law.



The energy difference between the formula proposed by Kekulé and the real bonding situation can be estimated by comparing the theoretically estimated and experimentally found enthalpies of hydrogenation for benzene. The enthalpy of hydrogenation of cyclohexene is  $120 \text{ kJ mol}^{-1}$ . This value is the energy of hydrogenation of a double bond.

**21.2** Calculate the expected enthalpy of hydrogenation of a six-membered ring with three double bonds and compare it with the value obtained in 21.1. What is the reason for this difference?

## SOLUTION OF PREPARATORY PROBLEM 21



21.2 Making use of the enthalpy of hydrogenation of cyclohexane, the approximate value for a six-membered ring with three double bonds is

$$3 \times (-120 \text{ kJ mol}^{-1}) = -360 \text{ kJ mol}^{-1}$$

Thus aromatic benzene is more stable compared to a compound with three double bonds by a difference in enthalpy of hydrogenation of

$$-(360 - 215) \text{ kJ mol}^{-1} = -145 \text{ kJ mol}^{-1}, \text{ resonance energy or delocalization energy.}$$

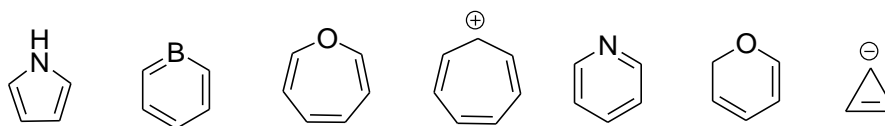
## THEORETICAL PROBLEM 22

### *Non-Benzoid Aromatic Systems*

Since the discovery of benzene, a lot of compounds have been identified that behave similarly. They all have some common features. According to Hückel's rule, an aromatic system must have the following properties:

- cyclic
- fully conjugated
- planar
- $4n + 2$   $\pi$  electrons

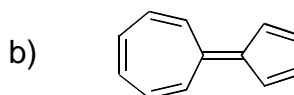
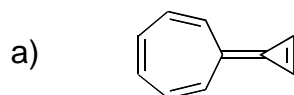
**22.1** Write down the number of  $\pi$ -electrons in each of the compounds shown below.



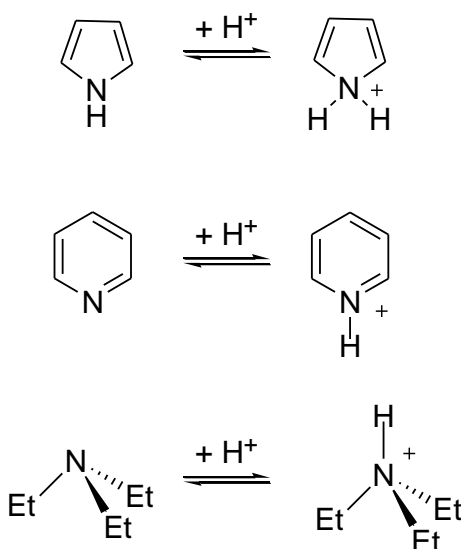
**22.2** Which compounds are aromatic?

Let us now consider some examples of how aromaticity influences the chemical properties of molecules.

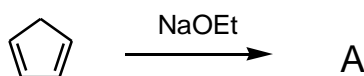
**22.3** Which of the following two compounds would you expect to have a greater dipole moment? Support your answer by writing the corresponding (plausible) resonance structures.



**22.4** Which of the following three compounds can be protonated more easily? Assign the three  $pK_b$  values (8.8, 13.5, 3.1) to these three compounds:

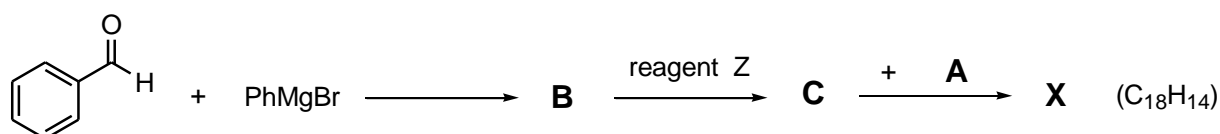


Cyclopentadiene ( $C_5H_6$ ) is not an aromatic compound because it is not completely conjugated. However, in contrast to acyclic dienes, it can quite easily react with a strong base such as sodium ethoxide to form a crystalline salt.



- 22.5** Write down a structure for compound A.  
**22.6** Is A aromatic according to Hückels–rule?  
**22.7** How many signals in the  $^1H$  NMR do you expect for A?

If A reacts in the following sequence, a stable, deep red compound X will form:



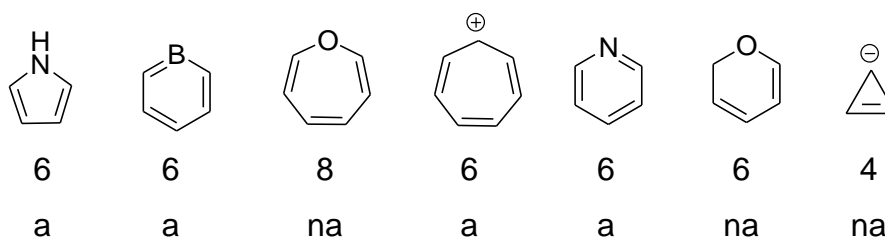
Hint: C has the following elemental composition: C 85.69 %, H 5.53 %.

- 22.8** Write down structures for the compounds B, C and X.  
**22.9** Suggest a plausible reagent Z.  
**22.10** Cyclopentadiene has to be freshly distilled before use in the above synthesis, because it dimerizes upon prolonged standing. Suggest a structure for this dimer.

## SOLUTION OF PREPARATORY PROBLEM 22

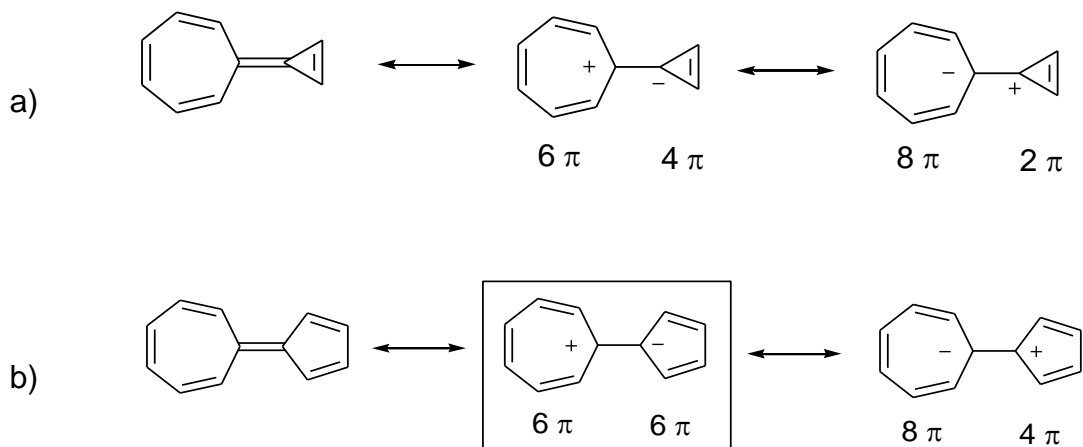
### 22.1 & 22.2

Each double bond and each heteroatom (O, N) with lone pairs donates 2  $\pi$ -electrons as well as a negative charge. Boron or a positive charge does not donate any electrons to the  $\pi$ -system but provide an empty p-orbital for delocalization.



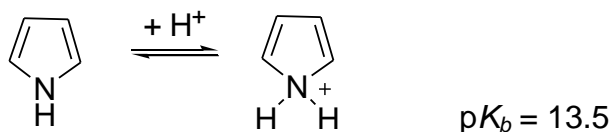
a = aromatic ; na = non-aromatic according to Hückel's rule

### 22.3

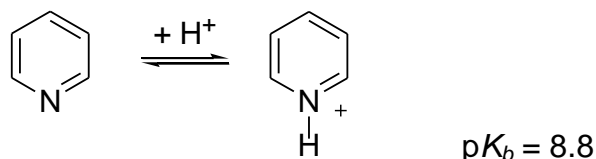


Charge separation is more favourable in compound b), because there is one mesomeric resonance structure in which both rings are formally aromatic according to Hückel's rule. In all other resonance structures at least one of the rings is formally anti-aromatic ( $4n$   $\pi$ -electrons). Hence, compound b) resembles electronically a cycloheptatrienyl cation fused to a cyclopentadiene anion and therefore possesses a large dipole moment.

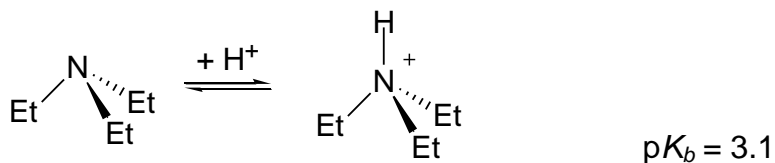
## 22.4



The lone pair of nitrogen in pyrrole is involved in the aromatic  $\pi$ -system. Protonation destroys the aromatic sextet (only 4  $\pi$ -electrons left,  $\pi$ -system not fully conjugated any more, because the protonated nitrogen is  $sp^3$ -hybridized). Pyrrole is hence only a very weak base.



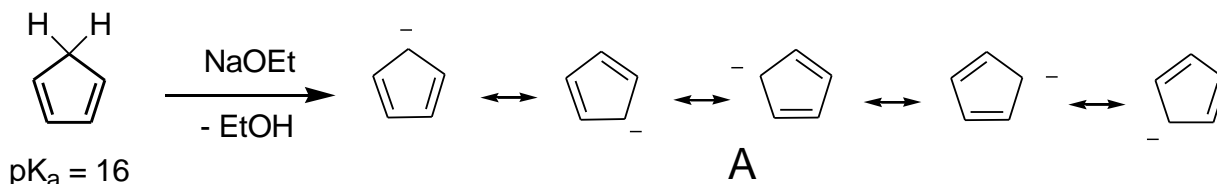
The lone pair of nitrogen in pyridine is not involved in the aromatic  $\pi$ -system; protonation is easier than in pyrrole. Nitrogen, however, is  $sp^2$ -hybridized and therefore less electronegative and more difficult to protonate than in a normal amine in which nitrogen is  $sp^3$ -hybridized.



Triethyl amine is the most basic compound in this series. The higher the p-character of the lone pair, the easier is protonation.

## 22.5 – 22.7

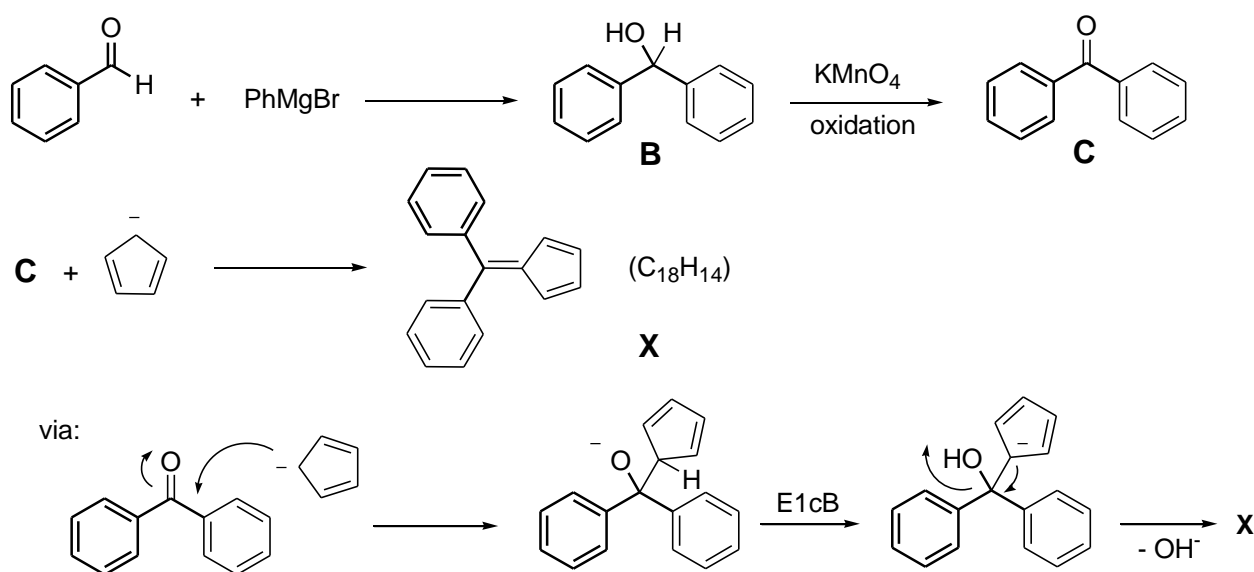
As a hydrocarbon, cyclopentadiene is unusually acidic ( $pK_a = 16$ ). The increased acidity is due to the stability of the cyclopentadienide anion containing 6  $\pi$ -electrons and in which the delocalization is extended over all 5 carbon atoms in complete cyclically conjugated system. Hence, the anion is aromatic. Just as in benzene, the anion is symmetric ( $D_{5h}$ -symmetry), all C–C and all C–H bonds are the same. Therefore, the  $^1\text{H}$  NMR spectrum only shows one signal.



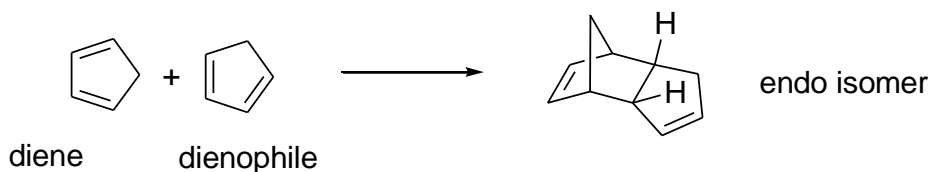


## 22.8 & 22.9

The first step in this synthesis is the nucleophilic addition of the Grignard reagent to the carbonyl group. Benzhydrol (B), an alcohol, forms. According to the elemental composition of C, C is the oxidation product of B, the ketone. This oxidation can be carried out with  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7$ , as there are no other oxidizable functional groups in the molecule. The cyclopentadienide anion is a potent nucleophile that adds to the carbonyl group. After the elimination of water (E1cB mechanism) it forms the corresponding fulvene derivative X.



**22.10** Cyclopentadiene is a 1,3-diene that easily reacts in a Diels–Alder [4+2]–cycloaddition. In this kind of reaction, it is so reactive that after a short time one molecule of 1,3-cyclopentadiene (reacting as a diene) will combine with another molecule (reacting as an olefine) to form a dimer. This bicyclic dimer is the endo adduct according to the rules of the Diels–Alder–reaction. Cyclopentadiene is not available commercially. However, the dimerization is reversible and can be reversed when the adduct is heated.

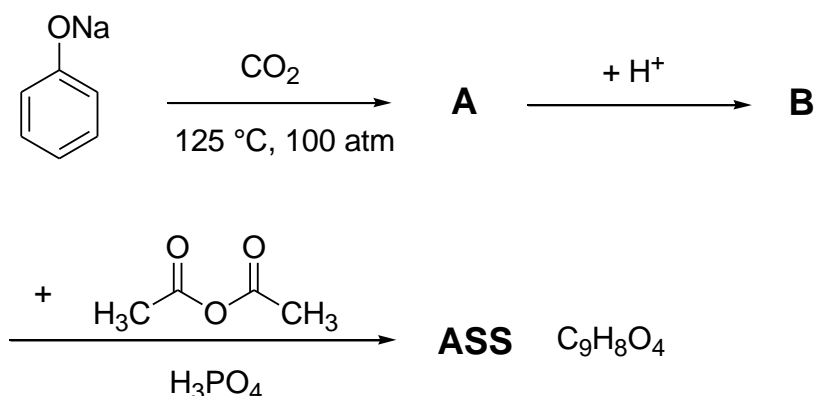


## THEORETICAL PROBLEM 23

### *Pain Relievers*

#### Aspirin:

Probably the most commonly used drug of all time is acetylsalicylic acid (ASS), which was released on the market as a pain reliever under the trade name Aspirin® by a German company in 1899. Now, billions of tablets are sold each year. Acetylsalicylic acid can be synthesized according to the following scheme:



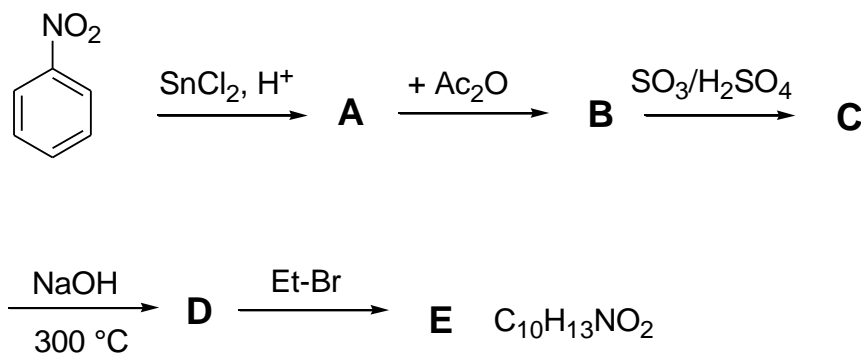
**23.1** Give structural formulas for A, B and ASS.

**23.2** Decide whether the following statements concerning acetylsalicylic acid are true, false or whether no decision is possible.

	true	false	no decision possible
ASS is more soluble in water at a pH of 2 than at a pH of 9.	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
A further electrophilic substitution will occur ortho to the COOH group.	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
The conjugate base is less water soluble than the acid.	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
The NMR spectrum shows only two CH signals in the aromatic region.	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
The <sup>1</sup> H NMR in D <sub>2</sub> O/DMSO mixtures shows 5 signals.	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

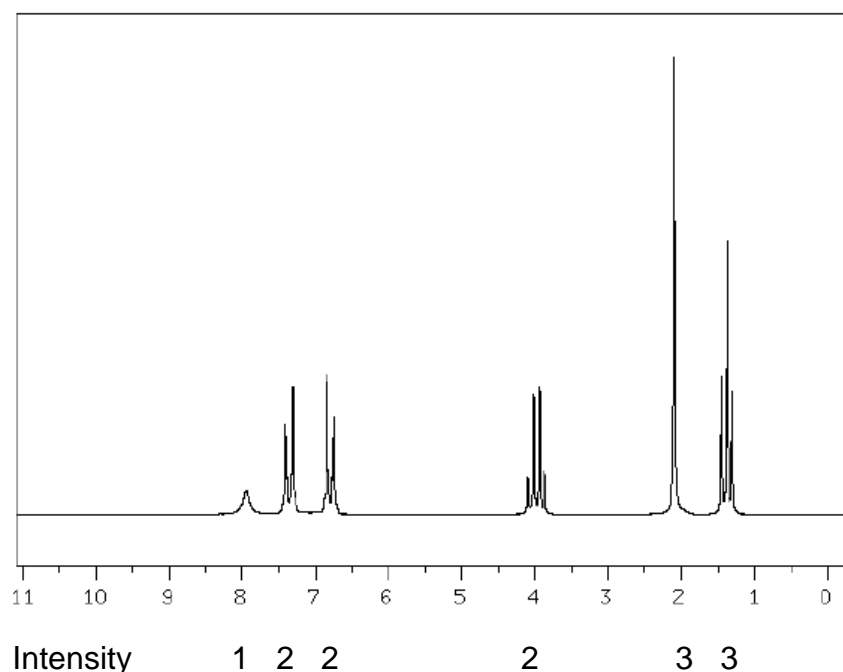
Phenacetin:

One of the first synthetic drugs, that has been commercially available since 1888, is Phenacetin, a mild analgesic. Due to side effects, it was removed from the market in 1986. Phenacetin E can be synthesized according to the following scheme:



The  $^1\text{H}$  NMR spectrum of E is shown on the next page.

**23.3** Write down structural formulas for A to E. Assign the NMR signals in the figure (see next page) to the corresponding protons in the structure of E. Explain the splitting pattern of the signals. (table of  $^1\text{H}$ -NMR chemical shifts on page 24)



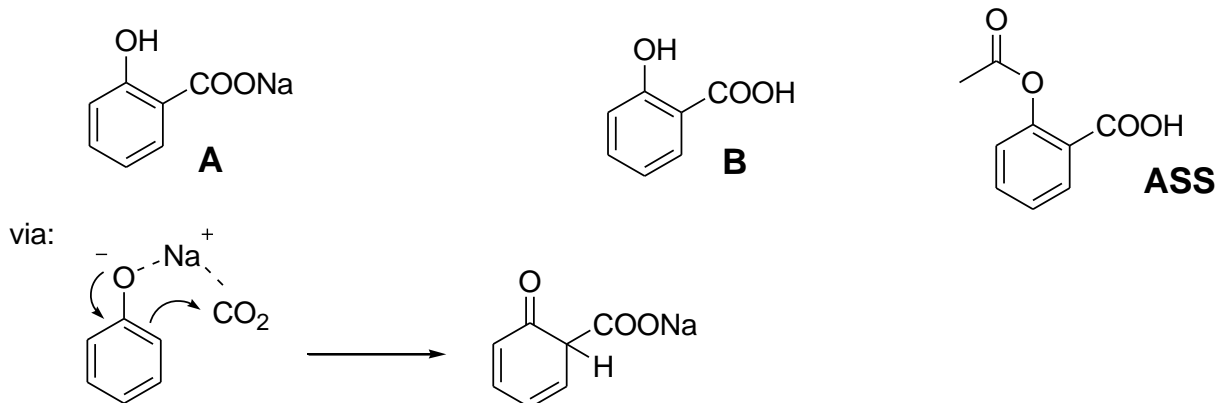
**23.4** If you compare acetylsalicylic acid (ASS) and phenacetin (E), which of the following statements are true, false or can not be evaluated?

	true	false	no decision possible
At pH = 9 phenacetin is more polar than acetyl salicylic acid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Both compounds can be deprotonated by NaHCO <sub>3</sub>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
The aromatic ring in phenacetin is more electron-rich than in acetylsalicylic acid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
None of them is chiral	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
On a silica gel TLC plate, developed with 5% acetic acid in ethyl acetate, the <i>R<sub>f</sub></i> value for phenacetin is larger than for acetylsalicylic acid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

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## SOLUTION OF PREPARATORY PROBLEM 23

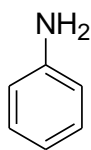
**23.1** The first step is the Kolbe–Schmitt reaction in which - after protonation - salicylic acid (B) forms. The reaction with acetic anhydride results in the formation of acetylsalicylic acid ASS.



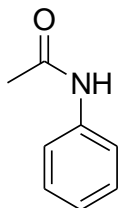
**23.2**

	true	false	no decision possible
more soluble in water at a pH of 2 than at a pH of 9 (The anion (pH = 9) is more soluble than the acid)	<input type="checkbox"/>	X	<input type="checkbox"/>
A further electrophilic substitution will occur ortho to the COOH group. (COOH directs meta and OAc para $\Rightarrow$ attack at C4)	<input type="checkbox"/>	X	<input type="checkbox"/>
The conjugate base is less water soluble than the acid (the carboxylate is negatively charged and hence more polar and soluble)	<input type="checkbox"/>	X	<input type="checkbox"/>
The NMR spectrum shows only two CH signals in the aromatic region. (ASS shows 4 CH signals)	<input type="checkbox"/>	X	<input type="checkbox"/>
The $^1\text{H}$ NMR in $\text{D}_2\text{O}$ / DMSO mixtures shows 5 signals. (The COOH proton is exchanged for D)	X	<input type="checkbox"/>	<input type="checkbox"/>

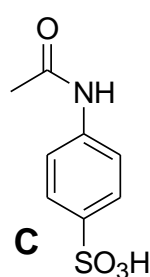
**23.3** There is the following reaction sequence: reduction of the nitro group to the amine (A), acylation (B) and sulfonation in the para position to form C (ortho substitution is not consistent with the symmetric NMR, because that would require 4 CH signals (see spectrum). The reaction with NaOH under harsh conditions results in the formation of the phenol D which is finally alkylated to ether E (Williamson ether synthesis).



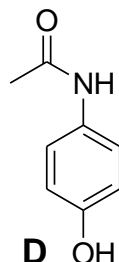
**A**



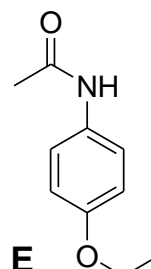
**B**



**C**

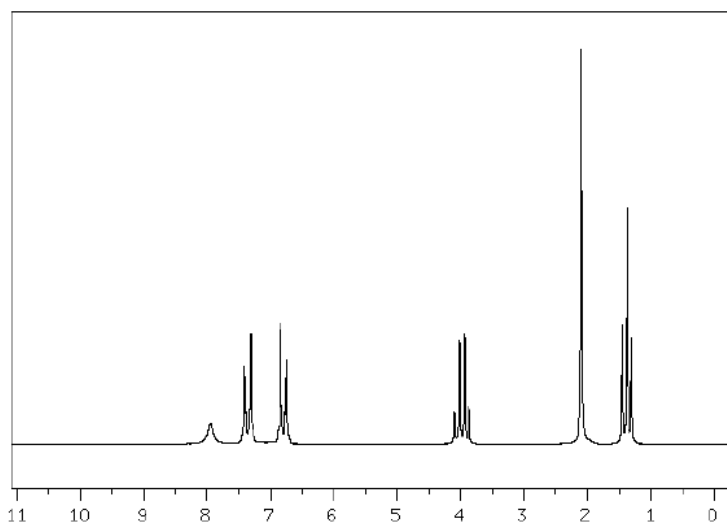
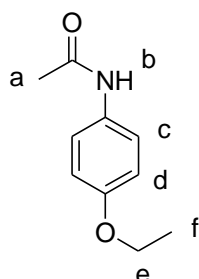


**D**



**E**

NMR spectrum:



signal

b c, d

e

a f

An unambiguous assignment of c and d is not possible from the given NMR spectrum.

#### 23.4

At pH = 9 phenacetin is more polar than acetylsalicylic acid (ASS can be deprotonated to form an anion, phenacetin not)

true

false

no  
decision  
possible

☐

X

☐

Both compounds can be deprotonated by NaHCO<sub>3</sub>

☐

X

☐

The aromatic ring in phenacetin is more electron rich than in acetylsalicylic acid (two donor substituents, ASS has two acceptor groups)

X

☐

☐

None of them is chiral.

X

☐

☐

On a silica gel TLC plate, developed with 5% acetic phenacetin is larger than for acetylsalicylic acid. (AS lower *R<sub>f</sub>*)

X

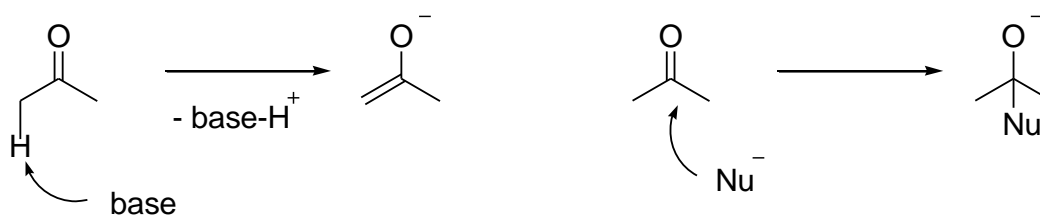
☐

☐

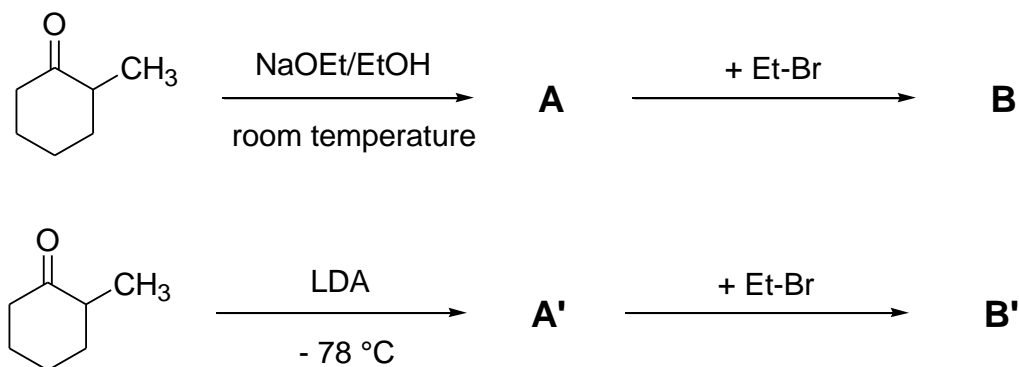
## THEORETICAL PROBLEM 24

### Carbonyl Chemistry

The carbonyl group C=O is a very versatile functional group in organic chemistry as it allows a wide range of chemical reactions among them some very useful C–C bond forming reactions. The deprotonation in the  $\alpha$  position to form an enolate and the attack of a nucleophile on the carbonyl C-atom are the two most important ways in which a C=O can react:



A lot of stereo- and regiochemical issues are associated with both these reactions, especially when the carbonyl compound is not symmetrical. Have a look, for example, at the following regioselective alkylation of 2-methyl-cyclohexanone (only mono-alkylation shall be considered):

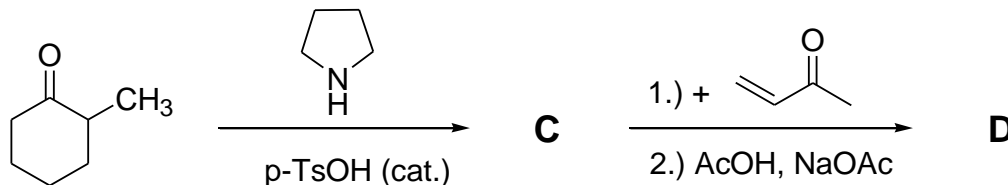


LDA: lithium diisopropyl amide, Pr<sub>2</sub>NLi, a strong non-nucleophilic base

**24.1** Write down the structures of A, A', B and B' (ignore stereochemistry here) and explain the different results of the two reactions with regard to the reaction conditions.

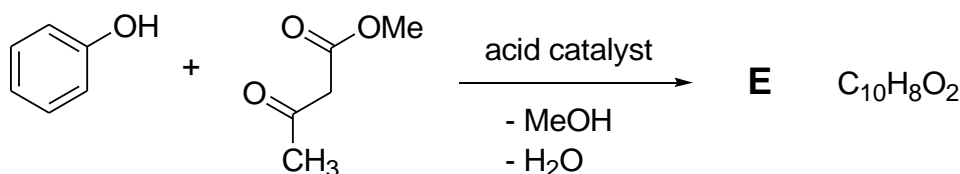
**24.2** Why can butyllithium (BuLi) not be used for deprotonation?

The direct alkylation of enolates is often not very efficient for a preparative synthesis due to problems with further di- or tri-alkylation. Hence, enamines are sometimes used as an alternative.



- 24.3** Write down the mechanism of the formation of enamine **C**. What about regiochemistry here?
- 24.4** Explain with appropriate resonance structures why enamines react with electrophiles.
- 24.5** Write down the structure of the reaction product **D** (ignore stereochemistry here).

Consider the following reaction sequence for the synthesis of a coumarin derivative (nowadays solid phase bound acids such as Nafion H or Amberlyst are used as acid catalysts).



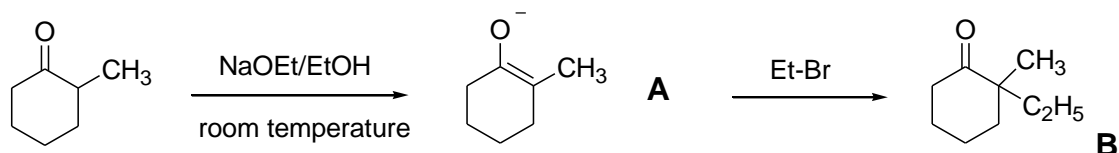
- 24.6** Write down the structure of **E** and explain its formation.

\_\_\_\_\_

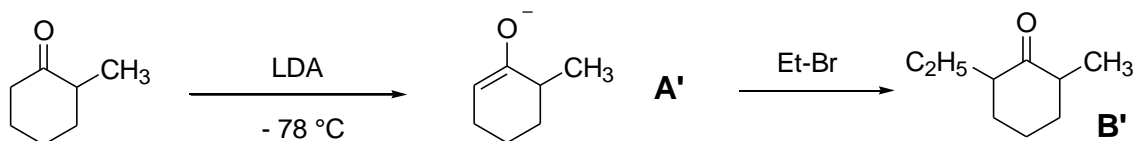


## SOLUTION OF PREPARATORY PROBLEM 24

### 24.1



reversible deprotonation, thermodynamic control, more substituted enolate forms

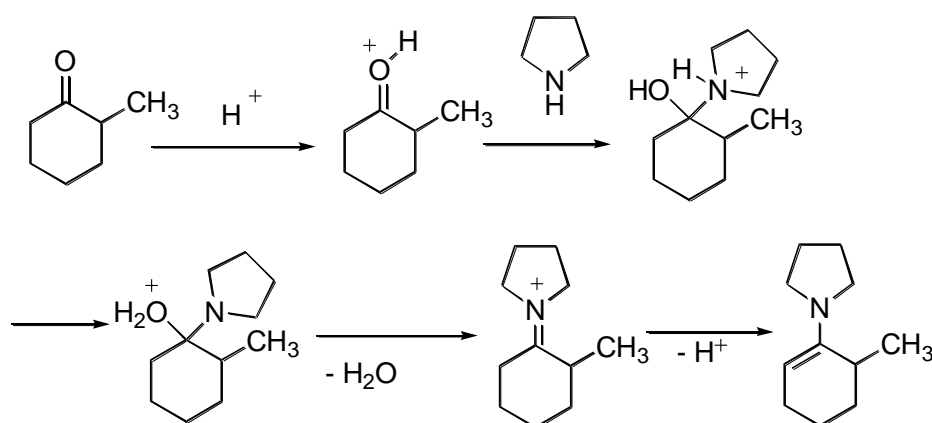


irreversible deprotonation, kinetic control, the more acidic proton is removed, less substituted enolate forms

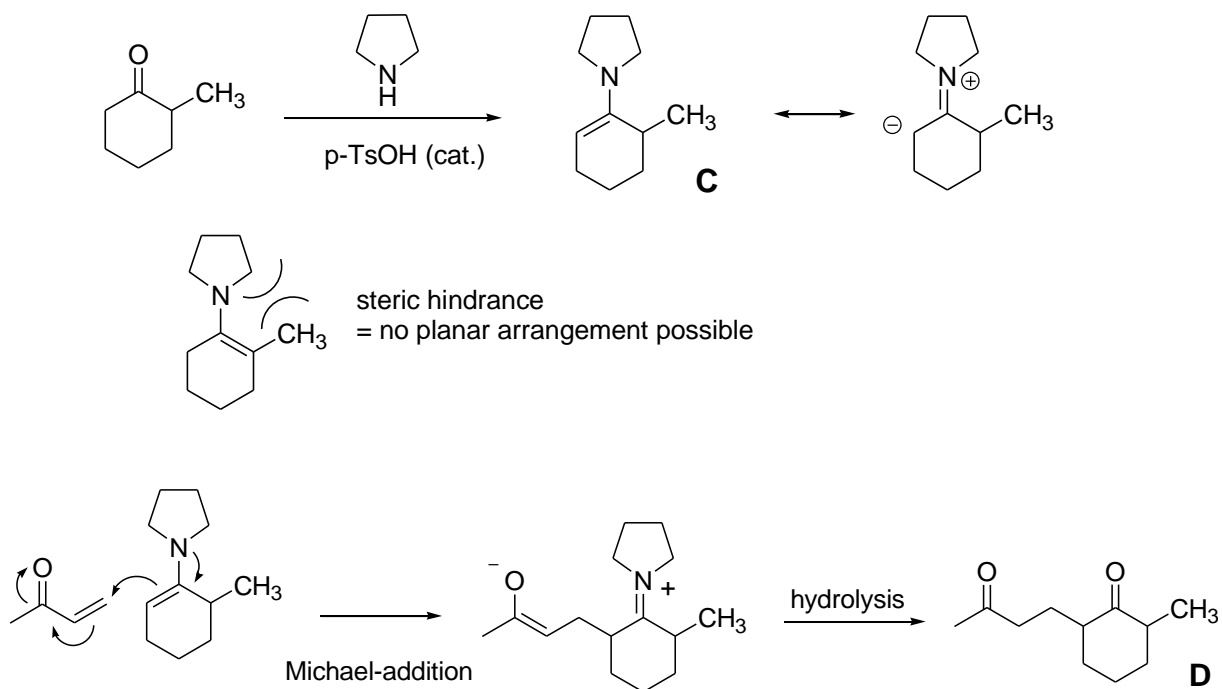
**24.2** BuLi can also act as a nucleophile and attacks the carbonyl C-atom. Therefore a non-nucleophilic base such as LDA has to be used.

### 24.3 – 24.5

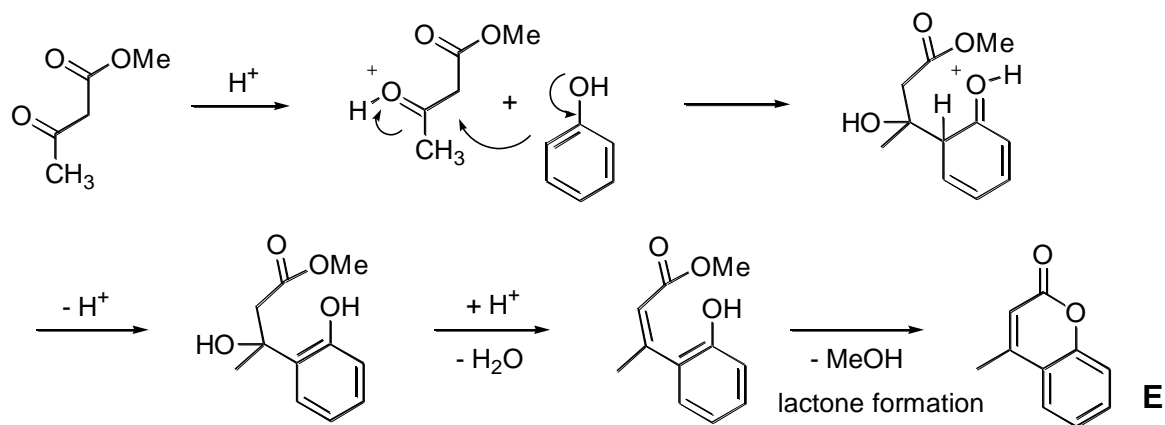
Formation of the enamine.



Enamines are nucleophilic, because the nitrogen lone pair transfers electron density to the  $\beta$ -carbon (see resonance structure on the right side).



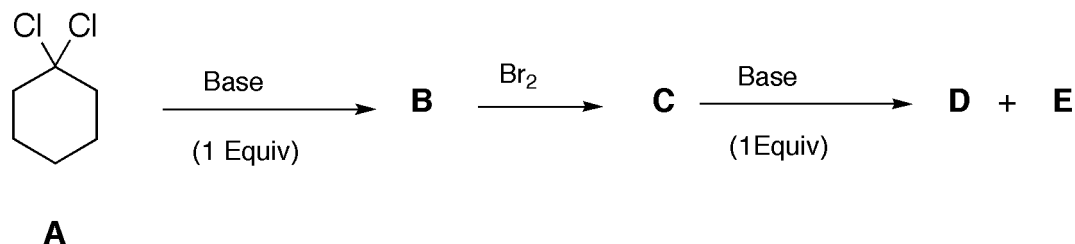
## 24.6



## THEORETICAL PROBLEM 25

### Cyclohexanes

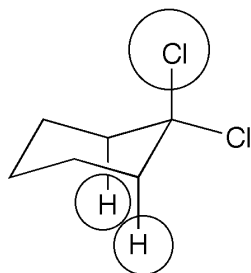
**B** forms in the reaction of **A** with a strong, non nucleophilic base. **B** reacts with bromine to form racemic **C**. The final products **D** (major) and **E** (minor) form by the reaction of **C** with a strong, non nucleophilic base.



- 25.1** Draw a 3-D structure of **A** in its most stable conformation. Circle the atoms that are possibly involved in the reaction to **B**.
- 25.2** Draw the structure of **B**.
- 25.3** Draw a 3-D structure of **C** (only one enantiomer needs to be drawn) in its most stable conformation. Circle the atoms that are possibly involved in the reaction of **C** to **D** and **E**.
- 25.4** Draw the structures of **D** and **E**.
- 
-

## SOLUTION OF PREPARATORY PROBLEM 25

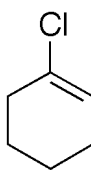
25.1



The chair is the most stable conformation of a cyclohexane ring. Large substituents prefer the equatorial position.

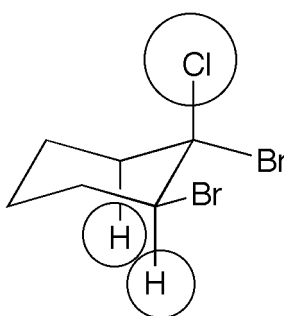
In an elimination reaction of an E<sub>2</sub> type, the groups that are eliminated must have antiperiplanar positions. This is only possible in a chair conformation if both groups are in axial positions.

25.2

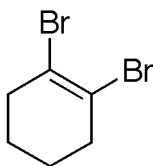


B

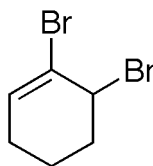
25.3



25.4



D



E

Because of the electron-attracting effect of bromine, the proton of a carbon that is bound to a bromine substituent, becomes more acidic. This proton is therefore removed more easily by a base and **D** becomes the major product.

## THEORETICAL PROBLEM 26

### *Chiral Compounds*

There are a number of compounds with the molecular formula  $C_4H_8O$  but only a few of them are chiral.

- 26.1** What are the compounds having at least one chiral centre (asymmetric carbon atom)? Draw their structural formulae (line-bond structures) with all chiral centres marked by an asterisk.
- 26.2** Some of them show (S)-configuration at all their chiral centres. Draw their configurational formulae.
- 26.3** If there is a meso-compound with this molecular formula draw its configurational formula.
- 
-

## SOLUTION OF PREPARATORY PROBLEM 26

There are five molecules with asymmetric C atoms – three of them have one chiral centre and two of them have two chiral centres. One of the latter is symmetric so that there is a meso– compound.

26.1

26.2

26.3


## THEORETICAL PROBLEM 27

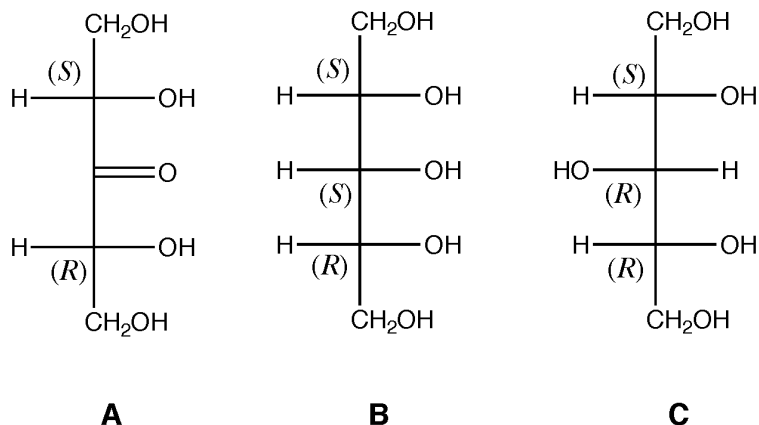
### *Monosaccharides*

A monosaccharide A has a molecular weight of 150 Da. The two stereoisomers B and C, that are both optically inactive, form when A reacts with NaBH<sub>4</sub>.

- 27.1** Draw the structures of A, B and C according to the Fischer projection.
- 27.2** Determine at all stereocenters in A up to C the absolute configuration according to the CIP (R/S) nomenclature.
- 27.3** Show all different stereoisomers of B and indicate their stereochemical relationship.
- 
-

## SOLUTION OF PREPARATORY PROBLEM 27

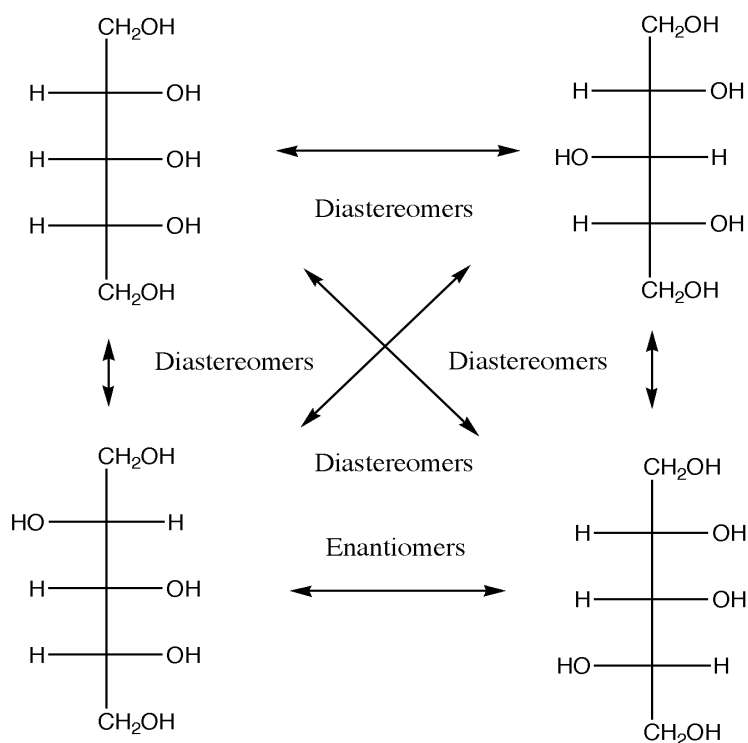
### 27.1 and 27.2



A monosaccharide has the general formula  $C_n(H_2O)_n$ . Consequently, a molecular weight of 150 Da can only be reached by the formula  $C_5(H_2O)_5$ . After reduction, **B** and **C** are the only two possible products that are optically inactive. These two products can only be formed from **A** as the common precursor.

If two groups only differ in chirality, the (*R*)-center has a higher priority than the (*S*)-center.

### 27.3

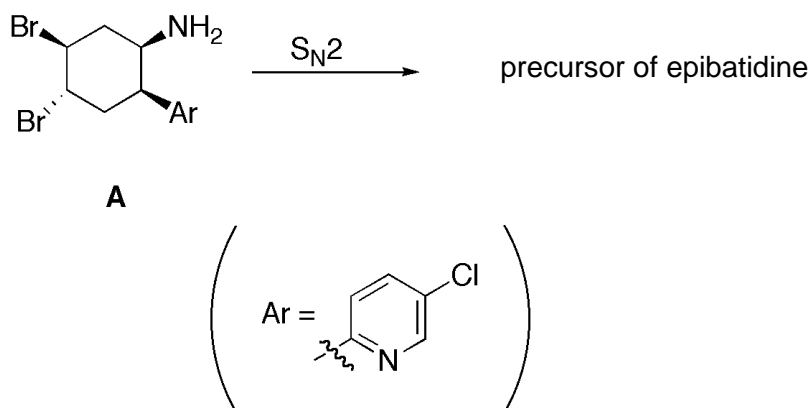




## THEORETICAL PROBLEM 28

### *Epibatidine*

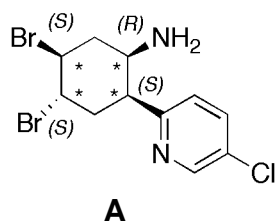
Epibatidine, isolated from tropical frogs, is about 200 times more effective as a pain reliever than morphine and is not addictive. In the synthesis towards epibatidine, A is converted to B by an intramolecular S<sub>N</sub>2 reaction.



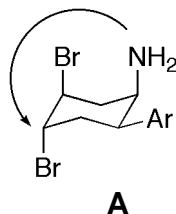
- 28.1** Mark all asymmetric stereocenters in A by an \*.
- 28.2** Determine the absolute configuration of A according to the CIP (R/S) nomenclature at all stereocenters.
- 28.3** Draw a 3-D structure of A indicating from where the reaction to B takes place. Indicate the course of the reaction by an arrow between the reaction centres.
- 28.4** Draw a 3-D structure of B.
- \_\_\_\_\_

## SOLUTION OF PREPARATORY PROBLEM 28

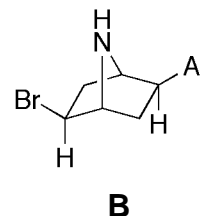
28.1 & 28.2



28.3



28.4



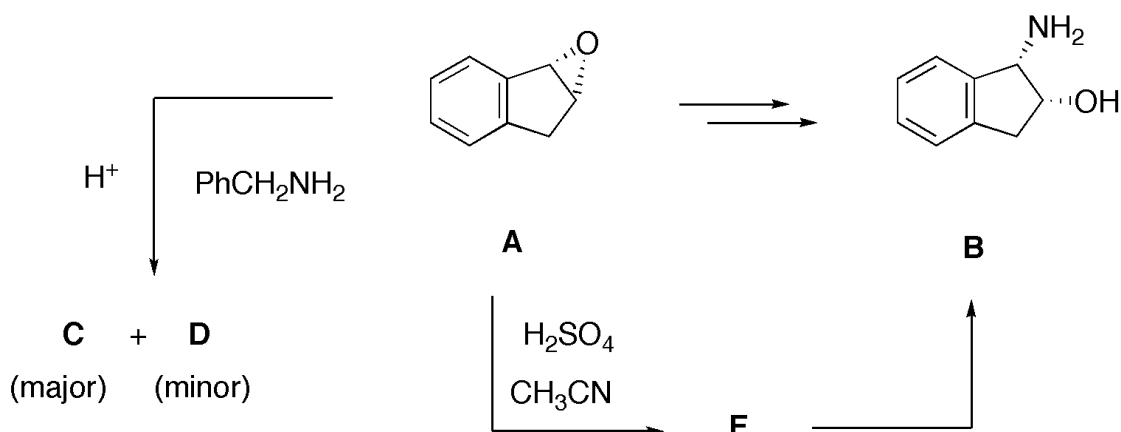
In a nucleophilic substitution ( $S_N2$ ), the nucleophile attacks the reaction centre at the back side with respect to the leaving group. In order to reach the reaction centre, the nucleophilic group (amino group) must take an axial position and subsequently replaces the bromine atom that points away from the incoming nucleophilic group.

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## THEORETICAL PROBLEM 29

### Crixivan®

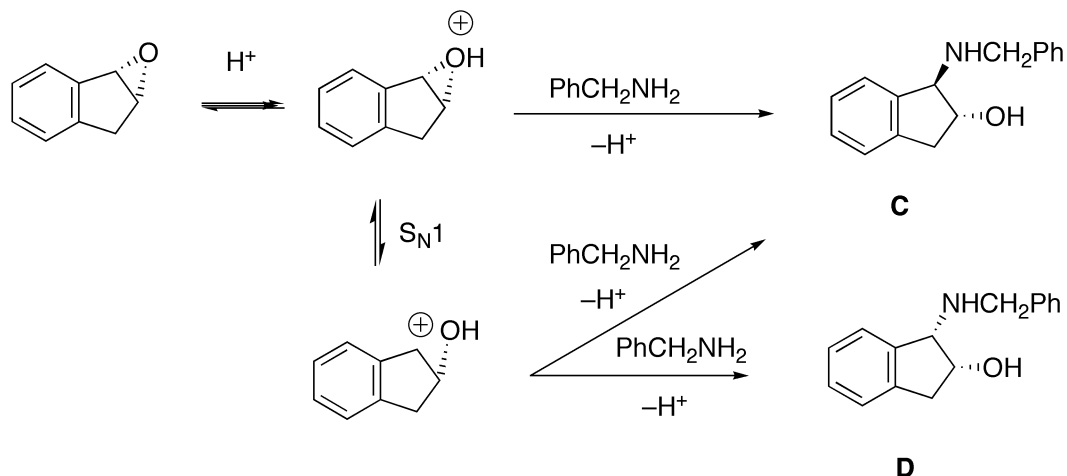
Amino alcohol B is an important intermediate in the synthesis of Crixivan® that is a potent HIV protease inhibitor. Chemists from Merck wanted to use the epoxide A as a starting material of the synthesis process.



- 29.1** Upon treatment of A with benzyl amine in the presence of a weak acidic catalyst, they obtained mainly the undesired amino alcohol C along with some of the desired product D that could serve as a precursor of B. Draw the structure of C and a mechanism leading to this compound. Take into account stereochemical and regiochemical issues.
- 29.2** After the treatment of A with concentrated H<sub>2</sub>SO<sub>4</sub> and acetonitrile under thermodynamic conditions, only E formed that was subsequently hydrolyzed to B. Draw the structure of E and a mechanism leading to this compound. Take into account stereochemical and regiochemical issues.

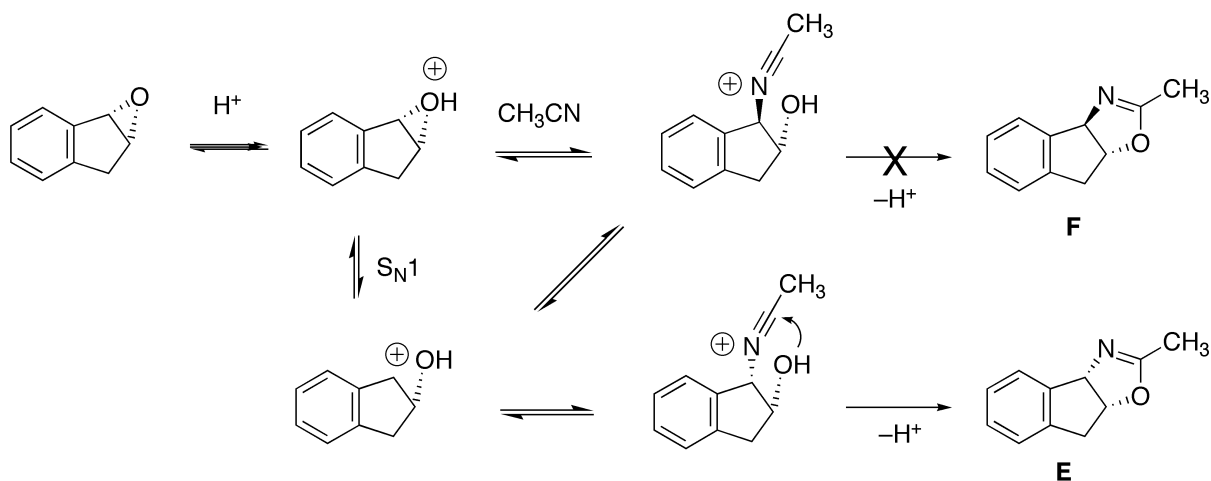
## SOLUTION OF PREPARATORY PROBLEM 29

### 29.1



Formation of **C** ( $\text{S}_{\text{N}}2$  pathway): back side attack on benzylic position; the positive charge in the transition state at the reaction centre is stabilized by the phenyl group.  
Formation of **C** and **D** ( $\text{S}_{\text{N}}1$  pathway): regioselective opening at the benzylic position due to resonance stabilization of the resulting carbocation by the phenyl group.

### 29.2



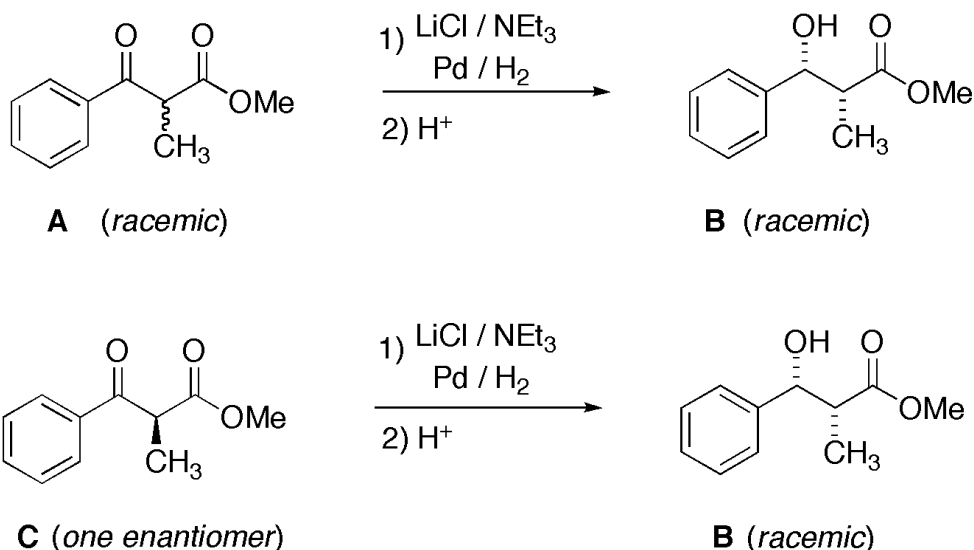
Only the cis-anellated product **E** can form. The trans-anellated compound **F** can not form from two five membered rings because of severe ring strain.

## THEORETICAL PROBLEM 30

### Stereoselective Reduction

In 2001, Prof. R. Noyori received the Nobel prize for his development of stereoselective reductions of C=C and C=O double bonds.

Let us consider a simplified model reaction to understand some of the basic control elements necessary to achieve a stereoselective hydrogenation reaction. For example, racemic  $\beta$ -ketoester A can be reduced by hydrogen to racemic B with a high diastereoselectivity in the presence of a metal catalyst that will chemoselectively hydrogenate C=C double bonds. Enantiomerically pure  $\beta$ -ketoester C is diastereoselectively reduced to racemic B. An additive (1 equivalent) such as lithium chloride proved to be highly important for the high diastereocontrol in the reaction.



- 30.1** Draw the structures of the enantiomers forming racemic B.
- 30.2** There are two diastereomers to the compounds of 30.1 that form a racemic B\*. Draw their structures.
- 30.3** Develop a model showing that in the reaction described above only B (but no B\*) forms.

## SOLUTION OF PREPARATORY PROBLEM 30

### 30.1 enantiomers of B

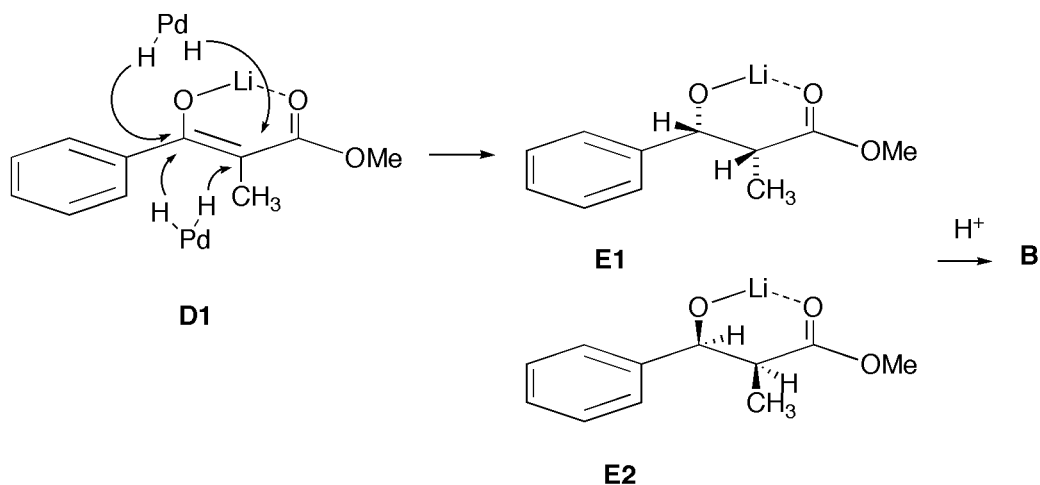
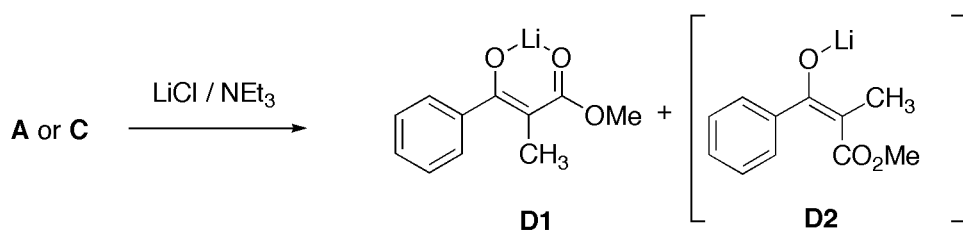


### 30.2 enantiomers of B\*



### 30.3. stereoselective

hydrogenation



Obviously, **A** and **C** must be reduced by a common, achiral intermediate, since **C** is racemized in the process. The racemization of **C** can be understood by the formation of the enolate **D1**, which forms with a higher preference than **D2**, because of the strong chelation effect of  $\text{Li}^+$  present as an additive in the reaction mixture. The donation of hydrogen by the metal in the usual way (syn-addition) from the top or the bottom of **D1** leads to racemic **E1/E2** as single diastereomers. Hydrolysis leads to racemic **B**.

## THEORETICAL PROBLEM 31

### Surfactant Micelles

Surfactants, amphiphilic molecules with a hydrophilic head group and a hydrophobic tail, have been used for washing since 2500 B.C. In aqueous solutions, they self-assemble, i.e. organize spontaneously into aggregated structures, so-called micelles. This concept of structuring is not only widely found in nature and in many every-day applications but it has recently become of interest for the controlled design of more complex structures in the nanometer size range as well.

Self-assembly takes place above a certain concentration, the so-called critical micelle concentration (cmc).

Micellar aggregates are separated from solutions of varying initial surfactant concentrations  $c_0$ , and the surfactant concentration in the remaining solution  $c_1$  is determined.

$c_0 \text{ (g dm}^{-3}\text{)}^{-1}$	0.5	0.75	1	1.5
$c_1 \text{ (g dm}^{-3}\text{)}^{-1}$	0.5	0.75	0.75	0.75

**31.1** What is the cmc of the surfactant?

**31.2** Why do amphiphilic molecules aggregate in aqueous solution?

**31.3** Sketch the osmotic pressure as a function of surfactant mass concentration and indicate the cmc.

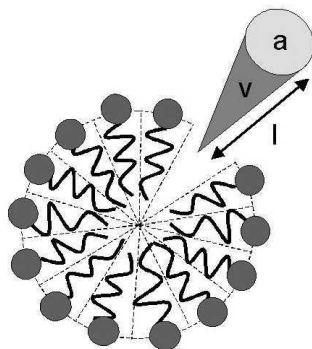
There is the general aggregation equilibrium of  $N$  molecules of A in an aggregate B with the equilibrium constant  $K$ .  $c(A)$  and  $c(B)$  are the molar concentrations of monomers and aggregates, and  $c_0$  the total concentration of monomers in the solution.

**31.4** a) Determine a relationship between  $K$ ,  $c_0$ ,  $N$  and  $c(A)$ .

$N = 50$  and  $K = 10^{90} \text{ L}^{49} \text{ mol}^{-49}$  ( $\text{L} = \text{dm}^3$ ) are values of self-assembly of a typical surfactant.

b) Calculate  $c_0$ ,  $c(A)$  and  $c(B)$  if the fractions  $f = c(A)/c_0$  of surfactant molecules present as monomers are 0.9999, 0.5, 0.01,  $10^{-3}$  and  $10^{-4}$  respectively.

Depending on the surfactant architecture, micelles can have different shapes. In this context, surfactant molecules are characterized by the area  $a$  of their head group, the length  $l$  of the molecule and the volume  $v$  of the molecule, being combined in the so-called packing parameter  $v \cdot (a \cdot l)^{-1}$ .



**31.5** Based on geometrical considerations, determine conditions for the packing parameter so that the amphiphile can form:

- a) spherical aggregates
- b) cylindrical aggregates (disregard end caps)
- c) flat aggregates (bilayers)

for sodium dodecyl sulfate (SDS):

$$V = 0.35 \text{ nm}^3, a = 0.57 \text{ nm}^2 \text{ and the (maximum "liquid") length } l = 1.67 \text{ nm}$$

- 31.6** a) Which shape do SDS micelles in aqueous solution have? Calculate.  
(Hint: Are the ideal values calculated in 31.5 lower or upper values?)
- b) What do you think will form after the addition of a base?

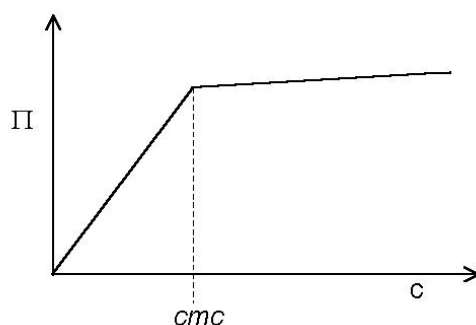


## SOLUTION OF PREPARATORY PROBLEM 31

31.1 The cmc is  $c = 0.75 \text{ g dm}^{-3}$ .

31.2 Amphiphilic molecules contain a hydrophilic part which is “water-soluble” and a hydrophobic part which is “water insoluble”, i.e. the free energy for the dissolution of the hydrophilic part in water is negative, while it is positive for the hydrophobic part. When micellar aggregates are formed, exposure of hydrophobic parts of the molecule to the aqueous phase is avoided (“hydrophobic interaction”). In addition, hydrophilic head groups can interact with water (negative hydration energy).

31.3



31.4

a)  $K = \frac{c(B)}{c(A)^N}$  and  $c(A) + N \cdot c(B) = c_0$

relationship:  $K = \frac{c_0 - c(A)}{N c(A)^N}$

b) When  $c(A) = f \cdot c_0$ ,  $c(A) = \left( \frac{1-f}{f N K} \right)^{\frac{1}{N-1}}$

$f$	0.9999	0.5	0.01	$1 \cdot 10^{-3}$	$10^{-4}$
$c(A) \text{ mol}^{-1} \text{ dm}^3$	0.011	0.013	0.015	0.015	0.016
$c_0 \text{ mol}^{-1} \text{ dm}^3$	0.011	0.027	1.477	15.481	162.265
$N c(B) \text{ mol}^{-1} \text{ dm}^3$	$1.11 \cdot 10^{-6}$	0.013	1.462	15.466	162.249
$c(B) \text{ mol}^{-1} \text{ dm}^3$	$2.23 \cdot 10^{-8}$	$2.69 \cdot 10^{-4}$	0.029	0.309	3.245

- 31.5 a) For spherical aggregates with radius  $l$  and aggregation number  $N$ , micelle volume  $V$  and micelle surface  $A$  are:

$$(I) \quad V = N v = \frac{4\pi l^3}{3} \quad (v = \text{volume of surfactant molecule})$$

$$(II) \quad A = N a = 4\pi l^2 \quad (a = \text{head group area of surfactant molecule})$$

$$\text{division of (I) by (II): } \frac{v}{a} = \frac{l}{3} \quad \text{or} \quad \frac{v}{al} = \frac{1}{3}$$

- b) For cylindrical aggregates with radius  $l$  we consider a part of the cylinder with length  $b$  and the aggregation number  $N$ . Micelle volume  $V$  and micelle surface  $A$  are:

$$(I) \quad V = N v = \pi l^2 b$$

$$(II) \quad A = N a = 2\pi l b$$

$$\text{division of (I) by (II): } \frac{v}{a} = \frac{l}{2} \quad \text{or} \quad \frac{v}{al} = \frac{1}{2}$$

- c) For a flat bilayer with the thickness  $2l$  we consider a part of the size (area)  $x$  and aggregation number  $N$ . Micelle volume  $V$  and micelle surface  $A$  are:

$$(I) \quad V = N v = x \cdot 2l$$

$$(II) \quad A = N a = 2x$$

$$\text{Division of (I) by (II): } \frac{v}{a} = l \quad \text{or} \quad \frac{v}{al} = 1$$

$$31.6 \quad a) \quad \frac{v}{al} = \frac{0.35 \text{ nm}^3}{0.57 \text{ nm}^2 \times 1.67 \text{ nm}} \quad \frac{v}{al} = 0.37$$

$\frac{v}{al} > \frac{1}{3}$  cylindrical micelles form (note: slightly elongated micelles, "short cylinders")

For  $\frac{1}{3} < \frac{v}{al} < \frac{1}{2}$ , cylindrical micelles form.

The value calculated for the spherical geometry is an upper value. Concerning larger values of the packing parameter, the volume of the hydrophobic part of the molecule is too large to fit into a sphere. Cylinders (or slightly elongated micelles) can form, although the geometric conditions are not ideal. (Note also that the surfactant length given refers to the maximum extension of the hydrocarbon chain: conformations with shorter extensions may form, but there is no conformation with longer lengths.)

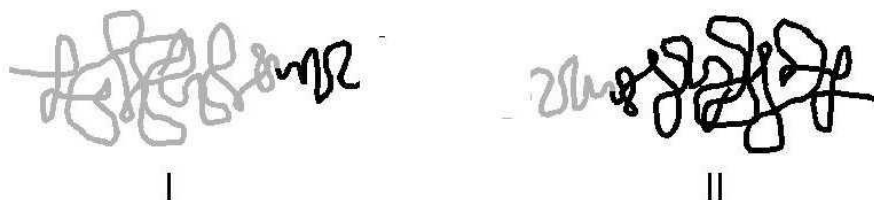
- b) Spherical micelles. Note: After the addition of a base, protolysis increases, the charges on the head groups (on average) increase and thus the effective head group area increases (electrostatic repulsion). Hence, the value of the packing parameter  $v \cdot (a_l)^{-1} = 0.37$  calculated in a) decreases. Since 0.37 is not much higher than the limit for spherical micelles, the regime of spherical aggregates can be reached.
-

## THEORETICAL PROBLEM 32

### *Self-assembly of Amphiphilic Block Copolymers*

Block copolymers are polymers consisting of two chemically different polymeric blocks that are covalently attached one to the other. Amphiphilic block copolymers consist of a hydrophilic and a hydrophobic block. Such molecules behave in analogy to low-molecular mass surfactants, but they can form larger aggregates in a size range from 5 nm to several  $\mu\text{m}$ , so that they allow further applications.

Block copolymers can vary in the relative lengths of their blocks. In the illustration below, the hydrophobic parts are black and the hydrophilic parts are grey. Note that the polymers are flexible chains.



**32.1** Which of these block copolymers do you expect to form spherical micelles, vesicles (bilayers), or which of them will show phase separations when given into a) water and b) toluene?

Two block copolymers consisting of poly(vinylpyridine) (PVP) and polystyrene (PS),  $\text{PVP}_{23}\text{-b-PS}_{122}$  (**A**) and  $\text{PVP}_{45}\text{-b-PS}_{122}$  (**B**), form "inverse" spherical micelles in toluene (PVP inside, PS outside). Aggregation numbers are determined via membrane osmometry. The solutions contain only micelles while monomers have been removed (which is possible for block copolymers). Here, we regard the solutions as ideal so that the van't Hoff equation is valid:

$$\Pi V = n R T.$$

$\Pi$  is the osmotic pressure.

The solutions of **A** and **B**, both with concentrations of  $c = 8.000 \text{ g dm}^{-3}$  are analyzed. The heights of the solvent columns above the solvent in osmotic equilibrium with the polymer-containing solutions are 11.02 mm and 2.48 mm for polymer **A** and polymer **B**, respectively.

( $\rho(\text{solvent}) = 0.866 \text{ g cm}^{-3}$  and  $T = 298.15 \text{ K}$ ).

**32.2** What are the aggregation numbers  $N$  of the two samples?

Colloidal metal particles are of high interest due to their special optical, electric and magnetic properties, applications as catalysts etc. Block copolymer micelles in organic solvent can be used as confined reaction compartments ("nanoreactors") for the preparation of such small metallic particles.

Two polymers **C** and **D** in toluene have the following properties

( $R$  is the micelle radius and  $N$  is the aggregation number):

**C:** PVP<sub>123</sub>-b-PS<sub>118</sub> with  $R = 25$  nm,  $N = 310$

**D:** PVP<sub>63</sub>-b-PS<sub>122</sub> with  $R = 21$  nm,  $N = 123$

Tetrachlorogoldacid-tri-hydrate ( $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$ , "gold acid") is added to the polymer solution and the mixture is stirred for several hours. While the gold compound is normally insoluble in toluene, the yellow colour of the solution indicates that it has solubilized within the micelles.

Two experiments are made with each polymer: a) the addition of 0.01 g and b) the addition of 0.05 g of  $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$  to 10 cm<sup>3</sup> of polymer solution ( $c(\text{polymer}) = 10 \text{ g dm}^{-3}$ ). In all cases, the total amount of added  $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$  is solubilized.

In a second step, a reducing agent such as hydrazine or sodium borohydride (sodium boranate) is added. The solution turns red or blue indicating the formation of metallic gold nanoparticles.

The micelle size does not change after the solubilization of  $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$  and reduction.

**32.3** Write down the reaction equations for the two reductions.

It is observed that one gold particle is formed in each micelle. Gold particles are spherical and show a narrow size distribution. There is no redistribution of gold during the process of particle formation, but  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  that has solubilized inside one micelle (by uniform distribution among the micelles) forms one particle.

$$\rho(\text{Au}) = 19.3 \text{ g cm}^{-3}$$

**32.4** Which gold particle diameters do you expect for the four experiments with the two polymers and the two given amounts of added gold acid ?

**32.5** Why is one gold particle per micelle preferentially formed instead of multiple smaller particles inside one micelle ?

## SOLUTION OF PREPARATORY PROBLEM 32

32.1

	in water	in toluene
I	spherical micelles	phase separation
II	phase separation	spherical micelles

32.2  $M(\text{PVP-monomer}) = 105.15 \text{ g mol}^{-1}$        $M(\text{PS-monomer}) = 104.16 \text{ g mol}^{-1}$   
 $M(\text{A}) = 15125.97 \text{ g mol}^{-1}$        $M(\text{B}) = 17439.27 \text{ g mol}^{-1}$

The molar mass of the micelles  $M(\text{micelle})$  can be obtained from the osmosis experiment. Notice that the molar concentration  $c_{\text{mo}}$  ( $\text{mol dm}^{-3}$ ) refers to the mass concentration  $c_{\text{ma}}$  ( $\text{g dm}^{-3}$ ):

$$c_{\text{mo}} = \frac{c_{\text{ma}}}{M(\text{micelle})} \quad \text{and} \quad c_{\text{mo}} = \frac{n}{V}, \quad n = c_{\text{mo}} \cdot V$$

$$\Pi V = n R T \qquad \Pi V = c_{\text{mo}} \cdot V R T$$

$$M(\text{micelle}) = \frac{c_{\text{ma}} R T}{\Pi} M(\text{micelle})$$

The osmotic pressure is counterbalanced by the pressure of the solvent column above the solution, thus  $\Pi = \rho g h$ .

$$M(\text{micelle}) = \frac{c_{\text{ma}} R T}{\rho g h}$$

$$\text{micelle A: } h = 11.02 \text{ mm} \quad \Pi = 93.62 \text{ Pa} \qquad M(\text{micelle A}) = 211820 \text{ g mol}^{-1}$$

$$\text{micelle B: } h = 2.48 \text{ mm} \quad \Pi = 21.07 \text{ Pa} \qquad M(\text{micelle B}) = 941231 \text{ g mol}^{-1}$$

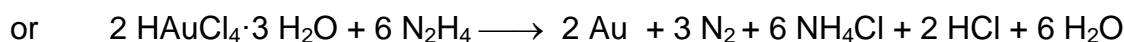
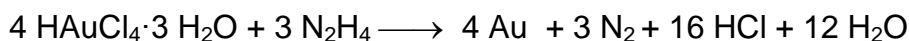
Note: In a real experiment, ideal behaviour can not be assumed. Instead, the osmotic pressures of solutions of different concentrations are measured. By extrapolation of  $\Pi \cdot c_{\text{ma}}^{-1}$  towards zero concentration the molar mass is obtained. Thus membrane osmometry is a convenient tool for molar mass determination of polymers and colloids.

The aggregation number  $N$  is obtained from the molar mass of the micelles and block copolymers

$$N(A) = \frac{M(\text{micelle A})}{M(A)} = \frac{211820 \text{ g mol}^{-1}}{15125.97 \text{ g mol}^{-1}} \quad N(A) = 14$$

$$N(B) = \frac{M(\text{micelle B})}{M(B)} = \frac{941231 \text{ g mol}^{-1}}{17439.27 \text{ g mol}^{-1}} \quad N(B) = 54$$

**32.3** Reduction with hydrazine: hydrazine can react to give nitrogen or nitrogen and  $\text{NH}_3$ .



Reduction with sodium borohydride:



**32.4**  $M(C) = 25224.33 \text{ g mol}^{-1}$

$M(D) = 19331.97 \text{ g mol}^{-1}$

$M(\text{micelle C}) = N \times M(C)$

$M(\text{micelle D}) = N \times M(D)$

$M(\text{micelle C}) = 7819542.3 \text{ g mol}^{-1}$

$M(\text{micelle D}) = 2377832.31 \text{ g mol}^{-1}$

$$c_{\text{mo}}(\text{micelle}) = \frac{c_{\text{ma}}(\text{polymer})}{M(\text{micelle})}$$

$c_{\text{mo}}(\text{micelle C}) = 1.2788 \times 10^{-6} \text{ mol dm}^{-3}$

$c_{\text{mo}}(\text{micelle D}) = 4.2055 \times 10^{-6} \text{ mol dm}^{-3}$

When  $M(\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}) = 393.84 \text{ g mol}^{-1}$  the molar concentration of  $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$  for the two cases a) and b) is:

a)  $c_{\text{mo}}(\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}) = 2.5391 \times 10^{-6} \text{ mol dm}^{-3}$

b)  $c_{\text{mo}}(\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}) = 0.0127 \text{ mol dm}^{-3}$

Hence, we can calculate the equivalents of  $\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$  that have been added per micelle, i.e. the number of gold ions per micelle  $z(\text{Au, micelle})$ :

$$z(\text{Au, micelle}) = \frac{c(\text{HAuCl}_4 \times 3 \text{H}_2\text{O})}{c_{\text{mo}}(\text{micelle})} \quad (\text{I})$$

We obtain the gold colloid mass  $m(\text{Au, colloid})$  and by its volume  $V$  the radius  $r$  and diameter  $d$  of the spherical gold colloid

$$m(\text{Au, micelle}) = \frac{z(\text{Au, micelle}) \times M(\text{Au})}{N_{\text{a}}} \quad m(\text{Au, colloid}) = m(\text{Au, micelle})$$

$$V(\text{Au, colloid}) = \frac{4}{3} \pi r^3 \quad \text{and} \quad V(\text{Au, colloid}) = \frac{m(\text{Au, colloid})}{\rho(\text{Au})}$$

$$r = \left( \frac{3 \times m(\text{Au, colloid})}{4 \pi \rho(\text{Au})} \right)^{\frac{1}{3}} \quad \text{and} \quad d = 2 \left( \frac{3 z(\text{Au, micelle}) M(\text{Au})}{4 \pi \rho(\text{Au}) N_{\text{a}}} \right)^{\frac{1}{3}} \quad (\text{II})$$

$$M(\text{Au}) = 196.97 \text{ g mol}^{-1} \text{ and } \rho(\text{Au}) = 19.3 \text{ g cm}^{-3}.$$

Equations (I) and (II) lead to

	polymer C a) 0.01g Au-acid	polymer C b) 0.05g Au-acid	polymer D a) 0.01g Au-acid	polymer D b) 0.05g Au-acid
z (Au, micelle)	1985	9931	604	3019
d	4.0 nm	6.8 nm	2.7 nm	4.6 nm

**32.5** The surface of a gold colloid is energetically unfavourable, because the surface atoms have fewer neighbours and thus contribute less crystallization energy than inner “bulk” gold atoms (surface tension is based on the same phenomenon, so that reasoning based on surface tension is correct as well ). The total surface area of larger particles is smaller. Therefore, particles tend to become as large as possible (by direct growth or coagulation) to decrease the ratio of surface area to volume.

Additional notes:

1. This is the reason why e.g. metallic gold forms as a macroscopic precipitate rather than colloids if you reduce gold ions in an aqueous solution without any additives. In the block copolymer micelles, however, growth is restricted due to compartmentalization.
2. Many small gold colloids inside one micelle can form if the inner polymer block has functional groups that attach to the surface of the gold with a gain in energy: the colloids are "stabilized". If a fast reduction creates many nuclei inside one micelle, multiple small gold colloids can be stabilized. Further, small colloids are often kinetically stabilized, because the activation energy for their coagulation is higher than the thermal energy.

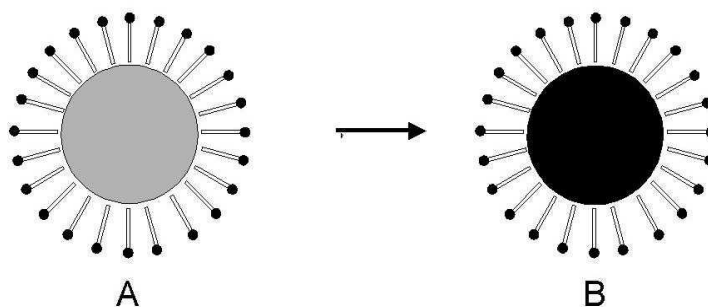


## THEORETICAL PROBLEM 33

### *Microemulsions*

Small polymer particles are of interest for many reasons, ranging from their use as coatings, effective support for catalysts due to their large surface area, to more "smart" applications such as biomedical carriers.

Well-defined spherical polymer particles within the size range from 10 nm to 200 nm can be synthesized by the method of microemulsion polymerization: a microemulsion consists of small oil droplets having surfactant layers on their surfaces and being dispersed in water. The system is in thermodynamic equilibrium. By using a monomer as an oil phase polymerization takes place resulting in small polymer particles in the volume of the initial oil droplet. The size of the droplets is controlled by the ratio of surfactant to oil.



A: microemulsion droplet with liquid monomer inside

B: polymerized microemulsion: polymer particle covered with surfactant

You would like to synthesize small polystyrene spheres, using a mixture of styrene (vinylbenzene) and p-divinylbenzene (mass ratio 10:1) as a monomer and cetyltrimethylammoniumbromide as a surfactant. A hydrophobic starter is added so that a radical polymerization takes place within the droplets.

Density of monomer, polymer and surfactant:  $1\text{g}\cdot\text{cm}^{-3}$

Length of surfactant  $b = 2\text{ nm}$ .

The surfactant is assumed to be a dense layer on the oil surface where hydrocarbon tails do not penetrate the oil phase.

**33.1** What is the function of p-divinylbenzene?

**33.2** Calculate the mass ratio of surfactant to monomer you have to use in order to produce polymer particles with sizes of  $d = 20 \text{ nm}$ ,  $d = 40 \text{ nm}$  and  $d = 120 \text{ nm}$  ( $d$  = diameter of the particle without surfactant).

**33.3** Calculate the total surface area of 1 g of polystyrene particles (after removal of the surfactant) for the three samples.

You would like to produce particles with an enzyme function by incorporating an enzyme into the polymer particle.

**33.4** Which kind of enzyme would you choose for this purpose?

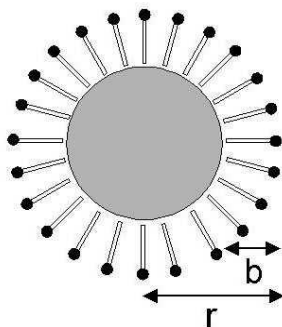
	true	false
a) a hydrophilic enzyme	<input type="checkbox"/>	<input type="checkbox"/>
b) a hydrophobic enzyme	<input type="checkbox"/>	<input type="checkbox"/>
c) an amphiphilic enzyme with the active center in the hydrophilic part	<input type="checkbox"/>	<input type="checkbox"/>
d) an amphiphilic enzyme with the active center in the hydrophobic part	<input type="checkbox"/>	<input type="checkbox"/>

---

## SOLUTION OF PREPARATORY PROBLEM 33

**33.1** It's a crosslinker. The resulting particle is a small spherical polymer network.

**33.2** The geometric conditions can be described as follows:



When  $r$  is the radius of the total microemulsion droplet,  $b$  the length of the surfactant molecule and  $r - b$  the radius of the polymer particle, you obtain:

$$V(\text{monomer}) = \frac{4\pi(r-b)^3}{3} \quad \text{and} \quad V(\text{surfac.}) = \frac{4\pi r^3}{3} - \frac{4\pi(r-b)^3}{3}$$

$$S = \frac{m(\text{surfac.})}{m(\text{monomer})} = \frac{V(\text{surfac.})}{V(\text{monomer})} = \frac{r^3}{(r-b)^3} - 1$$

to obtain particles with diameter  $d$  and  $r = 0.5 d + 2 \text{ nm}$

$d$	$r$	$S$
20 nm	12 nm	0.73
40 nm	22 nm	0.33
120 nm	62 nm	0.10

**33.3** The surface of a spherical particle is:

$$A(\text{particle}) = A(\text{monomer droplet}) = 4\pi(r-b)^2$$

For 1 g of polystyrene, i. e.  $1 \text{ cm}^3$  of polymer, the particle number is

$$N = \frac{1 \text{ cm}^3}{V(\text{particle})} = \frac{3 \times 1 \text{ cm}^3}{4\pi(r-b)^3} \quad \text{and the total surface of 1 g of polystyrene particles is:}$$

$$A(1 \text{ g polystyrene}) = N \times A(\text{monomer droplet}) = \frac{3 \times 1 \text{ cm}^3}{4\pi(r-b)^3} 4\pi(r-b)^2 = \frac{3 \text{ cm}^3}{(r-b)}$$

$d$	$A(\text{monomer droplet})$	$A(1 \text{ g of polystyrene})$
20 nm	$1257 \text{ nm}^2$	$3.0 \times 10^{20} \text{ nm}^2 = 300 \text{ m}^2$
40 nm	$5026 \text{ nm}^2$	$1.5 \times 10^{20} \text{ nm}^2 = 150 \text{ m}^2$
120 nm	$45239 \text{ nm}^2$	$5.0 \times 10^{19} \text{ nm}^2 = 50 \text{ m}^2$

**33.4** c) is true, the others are false.

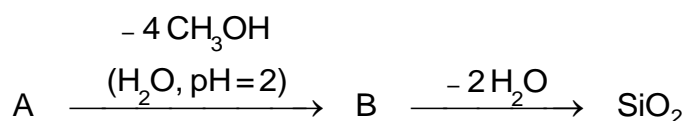
An amphiphilic enzyme should be included into the interface of the microemulsion particle. With the active centre in the hydrophilic part, it will be located towards the hydrophilic, aqueous phase and the enzyme may remain active.

## THEORETICAL PROBLEM 34

### Silica Nanostructures

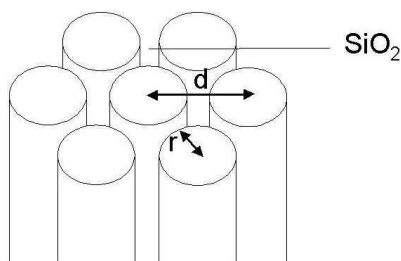
Porous silicates are important as ion exchangers, molecular sieves and catalysts in petrochemistry. Classic zeolites are silicates having defined channels with diameters of 0.4 nm to 1.5 nm. Materials with larger pore diameters are needed to accept larger molecules and make them react. Surfactants or block copolymers are used as "templates" for the production of amorphous silicates with pore sizes of 1.6 nm to 50 nm.

The production of  $\text{SiO}_2$  is carried out according to the following equation:



**34.1** Write down the formulas of A and B.

When this reaction is carried out in the presence of surfactants, silica-organic hybrid materials form. The organic component can be removed by combustion or dissolution and pure minerals with pores can be obtained. In the following example, X-ray scattering detects hexagonal pore structures.



The table contains the scattering angles  $2\theta$  of the first diffraction peaks (wavelength  $\lambda = 0.15$  nm) and the relative mass loss  $w$  after the removal of the surfactants.

surfactant	$2\theta$	$w$
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	$2.262^\circ$	37.2 %
$\text{C}_{14}\text{H}_{29}\text{N}(\text{CH}_3)_3\text{Cl}$	$2.046^\circ$	47.6 %
$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$	$1.829^\circ$	54.4 %
$\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3\text{Cl}$	$1.719^\circ$	60.0 %

$$\rho(\text{SiO}_2) = 2.2 \text{ g}\cdot\text{cm}^{-3}, \rho(\text{surfact.}) = 1 \text{ g cm}^{-3}$$

- 34.2** a) Calculate the pore distance  $d$  using Bragg's law for the diffraction peaks.  
b) What are the radii  $r$  of the pores? Calculate.

(Disregard possible end caps of cylindrical pores.)

In another experiment, hexagonal pore structures form by using surfactants of different chain lengths but the same surfactant mass concentrations.

- 34.3** How do a) pore diameter and b) pore distance depend on the tail lengths of the surfactants? Answer qualitatively and explain.

The specific surface  $A_{\text{sp}}$  (surface area per mass) of porous materials can be determined by gas adsorption experiments. The Langmuir adsorption isotherm can be derived from a kinetic consideration of adsorption and desorption in a monolayer.

- 34.4** a) Show that the relation between pressure  $p$ , volume of adsorbed gas  $V_{\text{ads}}$  and maximum adsorbable volume  $V^*$  can be expressed as

$$\frac{p}{V_{\text{ads}}} = \frac{1}{K V^*} + \frac{p}{V^*} \quad (K = \text{constant})$$

Concerning the adsorption of  $\text{N}_2$  to 1 g silica material at 77 K, the following volumes as functions of pressure are adsorbed. The volumes have been normalized to standard pressure. The area of one adsorbed  $\text{N}_2$  molecule is  $A(\text{N}_2) = 0.16 \text{ nm}^2$ .

$\begin{array}{c} p \\ \text{surfactant} \end{array}$	1.30 $\times 10^5 \text{ Pa}$	2.60 $\times 10^5 \text{ Pa}$	4.00 $\times 10^5 \text{ Pa}$	5.30 $\times 10^5 \text{ Pa}$	6.60 $\times 10^5 \text{ Pa}$	8.00 $\times 10^5 \text{ Pa}$
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	4.6	8.2	11.9	14.5	16.7	19.0
$\text{C}_{14}\text{H}_{29}\text{N}(\text{CH}_3)_3\text{Cl}$	6.0	11.5	16.0	19.0	23.1	25.5
$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$	7.8	14.0	19.0	24.0	28.0	31.3
$\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3\text{Cl}$	8.1	14.7	20.8	25.5	29.0	34.0

(volumes  $V_{\text{ads}}$  in  $\text{cm}^3$ )

- 34.5** Calculate the specific surfaces  $A_{\text{sp}}$  ( $\text{m}^2 \text{ g}^{-1}$ ) of the materials.

Imagine you don't have an x-ray machine to measure the pore distances in 34.2.

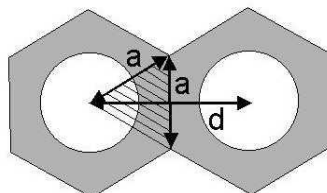
- 34.6** Calculate the pore radii from mass loss (in 34.2) and the specific surfaces  $A_{\text{sp}}$  determined in 34.5 without using the pore distance  $d$ .

## SOLUTION OF PREPARATORY PROBLEM 34

34.1  $A = \text{Si}(\text{OCH}_3)_4$ ,  $B = \text{Si}(\text{OH})_4$

34.2 a) Bragg:  $n \lambda = 2 d \sin \theta$ , with  $n = 1$ , results see table below

$$\text{b) } w = \frac{\rho(\text{surfact.}) \times V(\text{surfact.})}{\rho(\text{SiO}_2) \times V(\text{SiO}_2) + \rho(\text{surfact.}) \times V(\text{surfact.})}$$



$V(\text{surfact.}) = V(\text{pore})$  and  $V(\text{SiO}_2)$  can be calculated for a structure of height  $l$ :

$$V(\text{pore}) = \pi r^2 l$$

$$V(\text{SiO}_2) = 6 \cdot A(\text{triangle}) \cdot l - \pi r^2 l$$

$$\text{with } A(\text{triangle}) = a \cdot \frac{1}{2} \times \frac{1}{2} d \text{ and } \left(\frac{1}{2} a\right)^2 + \left(\frac{1}{2} d\right)^2 = a^2 \Leftrightarrow a = \frac{1}{\sqrt{3}} d$$

$$V(\text{SiO}_2) = 0.5 \sqrt{3} d^2 l - \pi r^2 l$$

$$r = \left( \frac{w \times \rho(\text{SiO}_2) \sqrt{3} d^2}{2 \times (1 - w) \times \rho(\text{surfact.}) \times \pi + 2 w \times \rho(\text{SiO}_2) \times \pi} \right)^{\frac{1}{2}}$$

surfactant	$d$	$r$
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	3.80 nm	1.50 nm
$\text{C}_{14}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	4.20 nm	1.80 nm
$\text{C}_{16}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	4.70 nm	2.10 nm
$\text{C}_{18}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	5.00 nm	2.30 nm

34.3 Increasing tail length leads to a) an increase in diameter and b) an increase in pore distance (the same total volume of surfactants but more surfactant molecules per pore, i.e. fewer pores and larger pore distances).

34.4 a) In equilibrium the rate of adsorption ( $k_{\text{ads}}(n^* - n_{\text{ads}})p$ ) is equal to the rate of desorption ( $k_{\text{des}} n_{\text{ads}}$ ):

$$k_{\text{des}} n_{\text{ads}} = (k_{\text{ads}}(n^* - n_{\text{ads}})p)$$

where  $n^*$  = maximum adsorbable amount (in mol dm<sup>-3</sup>)

and  $n_{\text{ads}}$  = adsorbed amount (in mol dm<sup>-3</sup>)

$$\frac{n_{\text{ads}}}{n^* - n_{\text{ads}}} = \frac{k_{\text{ads}}}{k_{\text{des}}} p \quad \text{or} \quad \frac{V_{\text{ads}}}{V^* - V_{\text{ads}}} = \frac{k_{\text{ads}}}{k_{\text{des}}} p \quad \text{and with} \quad \frac{k_{\text{ads}}}{k_{\text{des}}} = K$$

$$\frac{p}{V_{\text{ads}}} = \frac{1}{KV} + \frac{p}{V^*}$$

b) Linear regression of  $p V_{\text{ads}}^{-1}$  versus  $p$  yields the slope  $(V^*)^{-1}$ .

$$A_{\text{sp}} = \frac{n^* \times A(\text{N}_2) N_a}{m(\text{SiO}_2)} \quad \text{and} \quad A_{\text{sp}} = \frac{V^* p_0}{RT m(\text{SiO}_2)} A(\text{N}_2) \cdot N_a \quad \text{with} \quad m(\text{SiO}_2) = 1 \text{ g}$$

surfactant	$V^* (\text{cm}^3)^{-1}$	$A_{\text{sp}} (\text{m}^2 \text{g}^{-1})^{-1}$	$r (\text{nm})^{-1}$
$\text{C}_{12}\text{H}_{25}\text{N}(\text{CH}_3)_3\text{Cl}$	49.0	747.1	1.6
$\text{C}_{14}\text{H}_{29}\text{N}(\text{CH}_3)_3\text{Cl}$	67.5	1029.1	1.8
$\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$	77.3	1178.6	2.0
$\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3\text{Cl}$	86.5	1318.8	2.3

$$\text{c) } w = \frac{\rho(\text{surfac.}) \times V(\text{pore})}{m(\text{SiO}_2) + \rho(\text{surfac.}) \times V(\text{pore})} \Leftarrow \frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{w}{\rho(\text{surfac.}) \times (1 - w)} \quad (\text{I})$$

$$A_{\text{sp}} = \frac{2 \pi r l}{m(\text{SiO}_2)} \quad \Leftarrow \quad m(\text{SiO}_2) = \frac{2 \pi r l}{A_{\text{sp}}} \quad (\text{II})$$

$$\frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{\pi r^2 l}{m(\text{SiO}_2)} \quad \text{and with (II)} \quad \frac{V(\text{pore})}{m(\text{SiO}_2)} = \frac{A_{\text{sp}} r}{2} \quad (\text{III})$$

$$(\text{I}) - (\text{III}) \quad r = \frac{2 w}{\rho(\text{surfac.}) \times (1 - w) \times A_{\text{sp}}} \quad , \text{ values see table above.}$$

(Note: X-ray scattering is still necessary to detect the hexagonal structure.)



## PRACTICAL PREPARATORY PROBLEMS

### PREPARATORY PROBLEM 35 (PRACTICAL)

#### *Preparation and Volumetric Determination of Strontium Peroxide Octahydrate*

##### Introduction

Peroxo compounds play an important role in many areas including e. g. perborates or percarbonates in the detergent industry or peroxo compounds for the whitening of a variety of products. Barium peroxide is one of the best-known peroxides. It can be prepared by the oxidation of barium oxide with oxygen in a reversible reaction. However, the peroxide content of BaO<sub>2</sub> is always lower than that calculated. Because of the reversibility of this reaction, barium peroxide provides a means of storage of elemental oxygen and several years ago, it was the only source of oxygen gas.

The peroxide content of such compounds can be determined by reaction with an excess of acid to give dihydrogen peroxide followed by a titration with a standard solution of potassium permanganate. This quantitative method is widely used in all areas where peroxides are of importance.

This practical exercise involves the preparation of strontium peroxide, determination of the strontium content by a complexometric titration and determination of the peroxide content by manganometric analysis.

##### List of chemicals

- Ammonia, aqueous solution,  $w(\text{NH}_3) = 0.25$
- EDTA disodium salt, aqueous solution,  $c(\text{Na}_2\text{EDTA}) = 0.1 \text{ mol dm}^{-3}$
- Ethanol,  $w(\text{C}_2\text{H}_5\text{OH}) = 0.96$
- Hydrogen peroxide, aqueous solution,  $w(\text{H}_2\text{O}_2) = 0.03$
- Methyl red, solid
- Naphthol green B, solid
- Perchloric acid, aqueous solution,  $w(\text{HClO}_4) = 0.10$
- Phthalein purple, solid
- Potassium permanganate, aqueous solution,  $c(\text{KMnO}_4) = 0.1 \text{ mol dm}^{-3}$
- Strontium chloride hexahydrate, solid

#### Procedure 1: Preparation of strontium peroxide

5.0 g of strontium chloride hexahydrate are dissolved in about 2.5 cm<sup>3</sup> of distilled water and 25 cm<sup>3</sup> of dihydrogen peroxide ( $w(\text{H}_2\text{O}_2) = 0.03$ ) are added. A solution of 3.5 cm<sup>3</sup> of ammonia ( $w(\text{NH}_3) = 0.25$ ) in 50 cm<sup>3</sup> of distilled water is added to the mixture to give strontium peroxide octahydrate on standing. The precipitate is filtered off, and dried at about 150 °C. In this procedure, the octahydrate transforms nearly completely into the anhydrous compound. An extremely small amount of water remains in the product and the peroxide content is slightly lower than calculated for  $\text{SrO}_2$ . At higher temperatures, strontium peroxide decomposes rapidly. Note: calcium peroxide can be prepared similarly.

Record the yield of the product in g.

#### Procedure 2: Manganometric determination of the peroxide content

About 100 mg of the product prepared in procedure 1 (record the exact weight) are transferred into a 300 cm<sup>3</sup> Erlenmeyer flask and the contents dissolved in 5 cm<sup>3</sup> of perchloric acid. The volume of the solution is increased to about 100 cm<sup>3</sup> by addition of water. The determination of the peroxide content is performed by titration with potassium permanganate solution ( $c(\text{KMnO}_4) = 0.02 \text{ mol dm}^{-3}$ ), until the solution is slightly pink in colour. At the beginning, the solution has to be titrated slowly because of the slow rate of reaction. The latter can be accelerated by the addition of a small amount of a manganese(II) compound.

Record the volume of the potassium permanganate solution used in the titration in cm<sup>3</sup>.

#### Procedure 3: Complexometric determination of the strontium content

About 100 mg of the product prepared in procedure 1 (record the exact weight) are transformed into a 300 cm<sup>3</sup> Erlenmeyer flask and the contents dissolved in 5 cm<sup>3</sup> of perchloric acid. The solution is made up to a volume of 50 cm<sup>3</sup> and 15 cm<sup>3</sup> of ammonia solution, 60 cm<sup>3</sup> of ethanol and 2 cm<sup>3</sup> of phthalein purple indicator are added. The resulting deep purple solution is titrated with disodium EDTA solution ( $c(\text{Na}_2\text{EDTA}) = 0.1 \text{ mol dm}^{-3}$ ) until the solution is intense light-green in colour.

Record the volume of the  $\text{Na}_2\text{EDTA}$  solution in cm<sup>3</sup>.

Preparation of the phthalein purple indicator

100 mg of phthalein purple, 5 mg of methyl red and 50 mg of naphthol green B are dissolved in 2 cm<sup>3</sup> of ammonia solution. The solution is filled up to a volume of 100 cm<sup>3</sup>. The indicator is stable for up to a period of one week.

- 35.1** Calculate the yield (%) of the product based on the theoretical yield of strontium chloride hexahydrate.
- 35.2** Calculate the content of the liberated dihydrogen peroxide in percent for the manganometric analysis and compare this value with the theoretical value of SrO<sub>2</sub>.
- 35.3** Calculate the strontium peroxide content in percent determined by the manganometric analysis.
- 35.4** Calculate the strontium peroxide content in percent determined by the complexometric determination
- 35.5** Write down the equation of the formation of SrO<sub>2</sub> from SrCl<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub>.
- 35.6** Write down the equation for the reaction of permanganate anions with dihydrogen peroxide in an acidic solution
- 35.7** Why will the reaction in the manganometric analysis proceed faster if a manganese(II) salt is added to the mixture?
-

## SOLUTION OF PREPARATORY PROBLEM 35

35.1 From the experiment

35.2 From the experiment: 1 cm<sup>3</sup> of KMnO<sub>4</sub> solution ( $c = 0.02 \text{ mol dm}^{-3}$ ) corresponds to 1.701 mg of H<sub>2</sub>O<sub>2</sub>.

35.3 From the experiment: 1 cm<sup>3</sup> of KMnO<sub>4</sub> ( $c = 0.02 \text{ mol dm}^{-3}$ ) solution corresponds to 6.031 mg of SrO<sub>2</sub>.

35.4 From the experiment: 1 cm<sup>3</sup> of Na<sub>2</sub>EDTA solution ( $c = 0.1 \text{ mol dm}^{-3}$ ) corresponds to 12.062 mg of SrO<sub>2</sub>.

35.5  $\text{SrCl}_2 + \text{H}_2\text{O}_2 + 2 \text{NH}_3 \longrightarrow \text{SrO}_2 + 2 \text{NH}_4\text{Cl}$

35.6  $2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ \longrightarrow 2 \text{Mn}^{2+} + 5 \text{O}_2 + 8 \text{H}_2\text{O}$

35.7 Manganese(II) cations act as a catalyst.

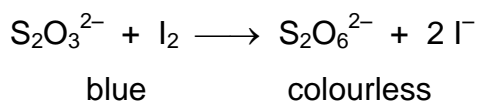
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## PREPARATORY PROBLEM 36 (PRACTICAL)

### *Preparation and Iodometric Determination of Potassium Iodate*

#### Introduction

Iodometric analysis is one of the most important volumetric procedures, because concentrations of both oxidizing and reducing agents, can be accurately determined using this approach. The reaction between thiosulfate dianions and elemental iodine in a neutral or acidic solution is the basis of this method.



For the determination of oxidizing agents an excess of potassium iodide and a small amount of an acid are added to the sample solution. The iodine formed in this reaction is titrated with sodium thiosulfate solution.

In contrast a back titration is typically performed for the determination of reducing agents in which a well defined excess of an iodine solution is added to the sample solution and the unreacted iodine is titrated with thiosulfate solution. Potassium iodate is used as a titrimetric standard for the standardization of the thiosulfate solution, because of its high stability and the fact that it can be produced in a very pure state. If an excess of potassium iodide is added to a well defined amount of potassium iodate in an acidic solution, an equivalent amount of iodine will be generated which can be titrated with sodium thiosulfate solution.

The practical exercise involves the preparation of potassium iodate and the determination of its purity by iodometric titration.

#### List of chemicals

- Acetic acid, aqueous sol. ,  $w(\text{H}_3\text{CCOOH}) = 0.05$
- Ethanol,  $w(\text{C}_2\text{H}_5\text{OH}) = 0.96$
- Hydrochloric acid,  $c(\text{HCl}) = 2 \text{ mol dm}^{-3}$
- Potassium iodide, solid
- Potassium permanganate, solid
- Sodium thiosulfate, aqueous sol.,  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol dm}^{-3}$

Procedure 1: Preparation of potassium iodate

6 g of potassium permanganate are dissolved in 150 cm<sup>3</sup> of hot distilled water. 3 g of potassium iodide dissolved in a small amount of distilled water are added to the solution. The reaction mixture is heated on a boiling water bath for 30 min. The unreacted potassium permanganate is removed by the addition of ethanol. During this procedure, the supernatant liquid becomes colourless.

The resulting precipitate of manganese(IV) oxide is filtered off and the filtrate is acidified by the addition of acetic acid. The solution is concentrated by heating on a water bath until the product begins to crystallize. The solution is allowed to cool to room temperature. The crystalline product is filtered off and washed with a small amount of ethanol. More product can be isolated by further concentration of the mother liquor. The product can be recrystallized from water and dried at 110°C.

Record the yield of the product in g

Procedure 2: Iodometric determination of the purity of the isolated potassium iodate.

If a 25 mL burette is to be used in the determination take about 60 mg of the product prepared in procedure 1 (record the exact weight) and dissolve it in about 100 cm<sup>3</sup> of distilled water. Add 1 g of potassium iodide to the solution and slightly acidify with dilute hydrochloric acid. The solution is titrated with sodium thiosulfate solution ( $c(\text{Na}_2\text{S}_2\text{O}_3) = 0.1 \text{ mol dm}^{-3}$ ) until it becomes colourless. Just before the end point 2 - 3 cm<sup>3</sup> of starch solution are added as an indicator.

Record the volume of the sodium thiosulfate solution used in cm<sup>3</sup>

Preparation of the starch solution:

About 2 g of starch are suspended in 3 cm<sup>3</sup> of distilled water and the suspension vigorously stirred. The mixture is added to 300 cm<sup>3</sup> of boiling water and heated for about two min. Any undissolved starch should be removed by decanting.

The starch solution should be prepared as required, however, it can be kept for a longer period by the addition of a small amount of a mercury(II) iodide solution.

**36.1** Calculate the yield (%) of the product.

**36.2** Calculate the purity of your product in a percentage.

**36.3** Give the equation for the reaction between iodate and iodide anions in an acidic solution.

- 36.4** What name is given to the redox reaction in 36.3?
- 36.5** Why should an iodometric determination not be performed in an alkaline solution ?
- 36.6** What is the expected trend in oxidising ability on going from fluorine to iodine?  
Give the explanation for this trend.
- 36.7** How can the following ions be determined iodometrically? In each case give the appropriate equation:
- a) iron(III) cations
  - b) copper(II) cations
  - c) sulfide anions
-

## SOLUTION OF PREPARATORY PROBLEM 36

**36.1** From experiment

**36.2** From experiment: 1 cm<sup>3</sup> of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution 0.1 mol dm<sup>-3</sup> corresponds to 3.576 mg of KIO<sub>3</sub>.

**36.3**  $\text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \longrightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O}$

**36.4** It is a comproportionation reaction.

**36.5** In a basic solution, tetrathionate dianions are oxidized to sulfate dianions.

**36.6** Oxidising ability increases from fluorine to iodine, because the ionization energy and electron affinity decrease and the ionic radii increase in this direction.

**36.7** a) After adding an excess of potassium iodide, iron(III) cations can be titrated directly with sodium thiosulfate solution, because an equivalent amount of iodine is produced:  $\text{Fe}^{3+} + 2 \text{I}^- \longrightarrow 2 \text{Fe}^{2+} + \text{I}_2$

b)  $\text{Cu}^{2+} + 2 \text{I}^- \longrightarrow \text{CuI} + \frac{1}{2} \text{I}_2$

c) A well defined excess of iodine solution must be added for the titration of sulfide. The unreacted iodine is subsequently titrated with thiosulfate solution (back titration).  $\text{S}^{2-} + \text{I}_2 \longrightarrow \text{S} + 2 \text{I}^-$



## PREPARATORY PROBLEM 37 (PRACTICAL)

### *Qualitative Analysis of Anions in an Unknown Mixture*

#### Introduction

Besides the quantitative analysis of chemical compounds, the qualitative analysis of unknown substances or mixtures of substances in order to identify the cations and/or anions is also an important procedure in analytical chemistry. Cations have to be separated prior to identification, however, this is not the case for anions.

In this exercise, the anions in an analytical sample are to be identified. Some of these anions can be identified by direct analysis of the solid sample, however, for other it is necessary to identify them in the filtrate of a soda extract. Several reagents are provided that can either be used in the initial identification of the anions present, or to perform the necessary confirmation tests for a particular anion.

The reactions of the anions with the reagents that are available, as far as is necessary for your analysis, are described below.

#### List of potential anions:

acetate,  $\text{H}_3\text{CCOO}^-$

nitrate,  $\text{NO}_3^-$

carbonate,  $\text{CO}_3^{2-}$

oxalate,  $\text{C}_2\text{O}_4^{2-}$

chloride,  $\text{Cl}^-$

perchlorate,  $\text{ClO}_4^-$

chromate,  $\text{CrO}_4^{2-}$

sulphate,  $\text{SO}_4^{2-}$

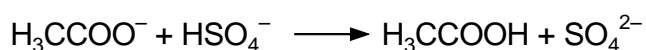
#### Preparation of the soda extract

One spatulaful of the sample (about 1 g) is mixed with 2 – 3 times the amount of sodium carbonate. The mixture is suspended in water and heated for 10 minutes. After cooling, the residue is filtered off and washed with water. The filtrate is used in the anion identification. It is always a good idea to use blind samples for comparison and to check the purity of soda.

#### **Selected reactions of the anions that may be present:**

##### **Acetate**

Theory: Acetate anions react with potassium hydrogensulfate to form acetic acid:

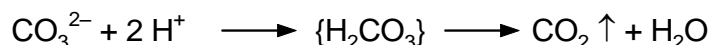


Dilute sulfuric acid also forms acetic acid upon reaction with acetate anions.

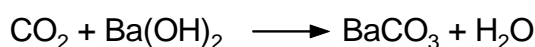
**Procedure:** The solid sample is grinded with four times the amount of potassium hydrogensulfate in a mortar. In the presence of acetate anions, there is the characteristic smell of acetic acid.

### Carbonate

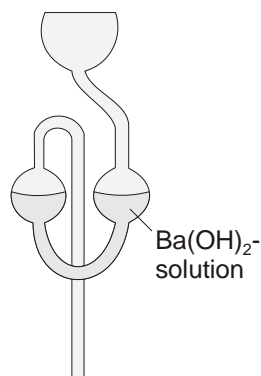
**Theory:** Carbonate anions react with dilute hydrochloric acid to form unstable carbonic acid that decomposes into water and carbon dioxide:



Carbon dioxide reacts with barium hydroxide to form barium carbonate:



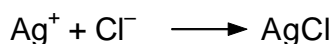
**Procedure:** In a test tube, dilute hydrochloric acid is added to a small amount of the sample. The test tube is closed immediately connected to a fermentation tube filled with freshly prepared barium hydroxide solution. The test tube is gently heated. In the presence of carbonate anions, white flakes of barium carbonate are observed in the solution in the fermentation tube within 3 - 5 minutes.



Schematic representation of a fermentation tube

### Chloride

**Theory:** Chloride anions in a nitric acid solution react with silver nitrate to form silver chloride:



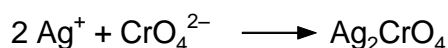
Silver chloride is soluble in concentrated ammonia solution. It is insoluble in concentrated nitric acid.

**Procedure:** An aqueous solution of silver nitrate is added to 5 cm<sup>3</sup> of the soda extract acidified with dilute nitric acid. In the presence of chloride anions, white silver chloride

precipitates from solution. The latter decomposes into elementary silver within a few hours if it is exposed to sunlight.

### Chromate

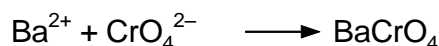
Theory: Chromate anions react with silver nitrate in a neutral or dilute nitric acid solution to form silver chromate:



Silver chromate is soluble in acids and ammonia solution.

Procedure: An aqueous solution of silver nitrate is added to 5 cm<sup>3</sup> of the soda extract that is acidified with dilute nitric acid. In the presence of chromate anions, reddish brown silver chromate precipitates from the solution.

Theory: Chromate anions react with barium chloride in an acetic acid solution buffered by ammonium acetate to form barium chromate:



Barium chromate is soluble in strong mineral acids.

Procedure: A spatulaful of ammonium acetate is added to 5 cm<sup>3</sup> of the soda extract that has been acidified with acetic acid. An aqueous solution of barium chloride is added and the mixture boiled for 2 minutes. In the presence of chromate anions, yellow barium chromate precipitates from the solution.

Concentrated, yellow coloured, chromate containing solutions form orange coloured dichromates upon acidification with dilute sulfuric acid. The addition of more highly concentrated sulfuric acid leads to the formation of dark coloured oligo- and polychromates.

### Nitrate

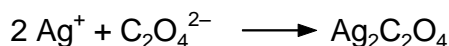
Theory: Nitrate anions are reduced to nitrogen monoxide (NO) by iron(II) sulfate in solutions acidified with sulfuric acid. Nitrogen monoxide reacts with iron(II) cations to form the brownish nitrosyl complex  $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ .

Procedure: 2.5 cm<sup>3</sup> of an iron(II) sulfate solution acidified with sulfuric acid is added to 2.5 cm<sup>3</sup> of the soda extract. After mixing, the test tube is brought into a skew position and concentrated sulfuric acid is poured carefully along the inner surface. In the presence of

nitrate anions, a brownish ring forms at the phase boundary between the solution and the sulfuric acid.

### **Oxalate**

Theory: In a neutral solution, oxalate anions react with silver nitrate solution to form silver oxalate:



Silver oxalate is sparingly soluble in acetic acid. It is soluble in nitric acid and ammonia solution.

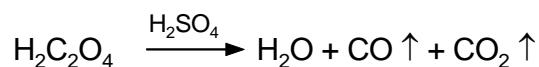
Procedure: An aqueous solution of silver nitrate is added to 5 cm<sup>3</sup> of the soda extract neutralized with acetic acid. In the presence of oxalate anions, a white precipitate of silver oxalate is formed.

Theory: Oxalate anions react in an ammoniacal or acetic acid solution that is buffered by sodium acetate, with calcium chloride to form calcium oxalate:



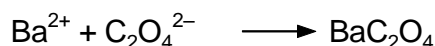
Calcium oxalate is insoluble in dilute acetic acid. It is soluble in strong mineral acids. Calcium oxalate is oxidized to carbon dioxide by potassium permanganate in an acidic solution. In this reaction, the manganese(VII) cations are reduced to manganese(II) cations.

Oxalates and oxalic acid decompose by reaction with concentrated sulfuric acid into carbon monoxide and carbon dioxide:



Procedure: 5 cm<sup>3</sup> of the soda extract are acidified with acetic acid. Ammonia solution is added until the mixture is slightly ammoniacal followed by the addition of an aqueous solution of calcium chloride. In the presence of oxalate anions, white calcium oxalate precipitates from solution. The precipitate is filtered off and dissolved in sulfuric acid. A solution of potassium permanganate is added dropwise to the solution. The potassium permanganate solution rapidly decolourizes and a gas is formed.

Theory: In a neutral solution, oxalate anions react with barium chloride to form barium oxalate:

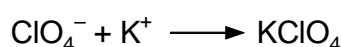


Barium oxalate dissolves in dilute acetic acid.

Procedure: An aqueous solution of barium chloride is added to 5 cm<sup>3</sup> of the soda extract neutralized with dilute hydrochloric acid. In the presence of oxalate anions, white barium oxalate precipitates from the solution.

### Perchlorate

Theory: In a solution slightly acidified with nitric acid, perchlorate anions react with potassium nitrate to form potassium perchlorate:



Potassium perchlorate is insoluble in cold water and cold dilute acid.

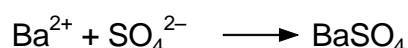
Procedure: An aqueous solution of potassium nitrate is added to 5 cm<sup>3</sup> of the soda extract slightly acidified with nitric acid. In the presence of perchlorate anions, a white precipitate of potassium perchlorate forms.

Theory: In a neutral and slightly alkaline solution perchlorate anions are reduced by iron(II) hydroxide (formed by the reaction of iron(II) sulfate with sodium hydroxide) to chloride anions.

Procedure: 4 cm<sup>3</sup> of an aqueous iron(II) sulfate solution are added to 5 cm<sup>3</sup> of the soda extract acidified with dilute nitric acid. Dilute sodium hydroxide solution is added until some iron(II) hydroxide begins to precipitate from solution or the solution is slightly alkaline. The mixture is boiled for a few minutes and the resulting precipitate is filtered off. In the presence of perchlorate anions, the filtrate of the reaction contains chloride anions, which can be confirmed by reaction with silver nitrate in a solution acidified with nitric acid .

### Sulfate

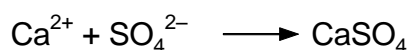
Theory: In an acidic solution acidified with hydrochloric acid sulfate anions react with barium chloride to form barium sulfate:



Barium sulfate is insoluble in concentrated hydrochloric acid and in concentrated nitric acid. It is sparingly soluble in hot concentrated sulfuric acid, 12 percent of barium sulfate dissolves.

Procedure: An aqueous solution of barium chloride is added to 5 cm<sup>3</sup> of the soda extract acidified with dilute hydrochloric acid. In the presence of sulfate anions white barium sulfate precipitates from the solution.

Theory: In an acidic solution acidified with hydrochloric acid, sulfate anions react with calcium chloride to form calcium sulfate:



Calcium sulfate dissolves in concentrated sulfuric acid and concentrated hydrochloric acid.

Procedure: An aqueous solution of calcium chloride is added to 5 cm<sup>3</sup> of the soda extract acidified with dilute hydrochloric acid. In the presence of sulfate anions, white calcium sulfate precipitates from the solution. The precipitation is not quantitative!

- 37.1** Which anions are present in your sample?
- 37.2** Give the equations of the reaction of nitrate anions with iron(II) cations and of the subsequent formation of the nitrosyl complex.
- 37.3** Why does the brownish coloured complex form directly at the phase boundary between the solution and concentrated sulfuric acid?
- 37.4** Write the equation of the reaction of permanganate anions with oxalate anions in an acidic solution.
- 37.5** Write the equation of the reaction of perchlorate anions with iron(II) hydroxide in a neutral solution.

#### List of chemicals

- acetic acid, aqueous solution,  $w(\text{H}_3\text{CCOOH}) = 0.99$
- acetic acid, aqueous solution,  $w(\text{H}_3\text{CCOOH}) = 0.05$
- ammonia, aqueous solution,  $w(\text{NH}_3) = 0.25$
- ammonium acetate, solid
- barium chloride, aqueous solution,  $c(\text{BaCl}_2) \sim 1.5 \text{ mol dm}^{-3}$
- barium hydroxide, aqueous solution,  $w(\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}) \sim 0.02$
- calcium chloride, aqueous solution,  $c(\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}) = 1 \text{ mol dm}^{-3}$
- hydrochloric acid,  $w(\text{HCl}) = 0.36$
- hydrochloric acid,  $c(\text{HCl}) = 2 \text{ mol dm}^{-3}$
- iron(II) sulfate, aqueous solution,  $c(\text{FeSO}_4) = 1 \text{ mol dm}^{-3}$
- nitric acid, aqueous solution,  $w(\text{HNO}_3) = 0.65$

- nitric acid, aqueous solution,  $c(\text{HNO}_3) = 2 \text{ mol dm}^{-3}$
- potassium hydrogensulfate, solid
- potassium nitrate, aqueous solution, saturated
- potassium permanganate, aqueous solution,  $c(\text{KMnO}_4) = 0.02 \text{ mol dm}^{-3}$
- silver nitrate, aqueous solution,  $c(\text{AgNO}_3) = 0.2 \text{ mol dm}^{-3}$
- sodium acetate, solid
- sodium carbonate, solid
- sodium hydroxide, aqueous solution,  $w(\text{NaOH}) \sim 0.05$
- sulfuric acid, aqueous solution, (95-97 %)
- sulfuric acid, aqueous solution,  $c(\text{H}_2\text{SO}_4) = 2 \text{ mol dm}^{-3}$

### Preparation of the sample:

To avoid interferences in the qualitative determinations only certain selected counter ions should be present in the analytical sample. The following salts guarantee the determination of anions without any interference:  $\text{LiCl}$ ,  $\text{LiClO}_4$ ,  $\text{Na}(\text{OOCCH}_3)$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{FeCl}_2$ ,  $\text{FeSO}_4$ ,  $\text{CoCl}_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{CoSO}_4$ ,  $\text{NiCl}_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{NiSO}_4$ . Certain other salts can be used. The salts must not form sparingly soluble residues. If salts are to be used that are not mentioned in the following table, then the hazard and safety data sheets for the compounds must first be consulted.

aluminium(III) chloride,  $\text{AlCl}_3 \cdot 6 \text{ H}_2\text{O}$

aluminium(III) sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot x \text{ H}_2\text{O}$

cobalt(II) chloride,  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$

cobalt(II) nitrate,  $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$

cobalt(II) sulfate,  $\text{CoSO}_4 \cdot 7 \text{ H}_2\text{O}$

iron(II) chloride,  $\text{FeCl}_2 \cdot 4 \text{ H}_2\text{O}$

iron(II) sulfate,  $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$

lithium chloride,  $\text{LiCl}$

lithium perchlorate,  $\text{LiClO}_4$

nickel(II) chloride,  $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$

nickel(II) nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$

nickel(II) sulfate,  $\text{NiSO}_4 \cdot 6 \text{ H}_2\text{O}$

potassium carbonate,  $\text{K}_2\text{CO}_3$

potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$

potassium nitrate,  $\text{KNO}_3$

potassium sulfate,  $\text{K}_2\text{SO}_4$

sodium acetate,  $\text{NaH}_3\text{CCOO}$

sodium carbonate,  $\text{Na}_2\text{CO}_3$

sodium chloride,  $\text{NaCl}$

sodium nitrate,  $\text{NaNO}_3$

sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$

sodium perchlorate,  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$

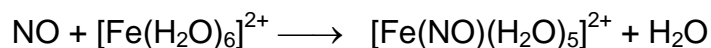
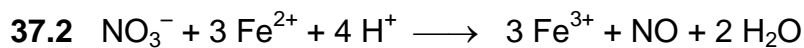
sodium sulfate,  $\text{Na}_2\text{SO}_4$

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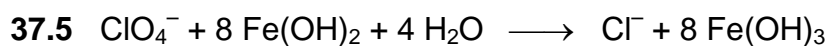
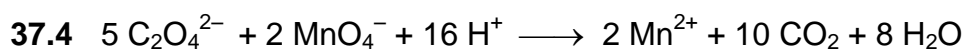


## SOLUTION OF PREPARATORY PROBLEM 37

**37.1** From the experiment



**37.3** The hydroxide anions produced during the formation of the nitrosyl complex are removed by sulfuric acid. This is the reason why the equilibrium is shifted towards the right side of the equation.

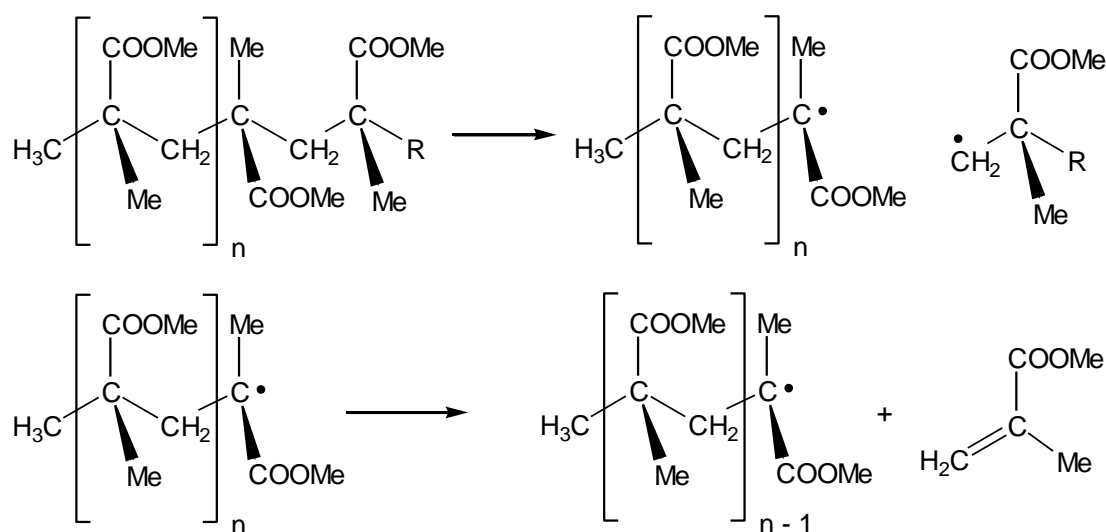


## PREPARATORY PROBLEM 38 (PRACTICAL)

### Recycling of Polymethylmethacrylate

#### Introduction

The regeneration of monomers from plastic waste followed by their repolymerization is an ideal recycling method, especially when the plastic waste is dirty, variously coloured or contains filling materials. Unfortunately, only a few polyolefins depolymerize into their monomers when heated. One example is polymethylmethacrylate (PMMA, Plexiglas), a plastic that starts to depolymerize into its monomers at 150 °C. At temperatures between



300 °C to 350 °C, the reaction is quantitative, the polymer chains are decomposed consecutively and the formation of the fragments is not statistical:

In the case of polymethylmethacrylate, the reformation of monomers proceeds in a high yield, as during the pyrolytic degradation tertiary radicals are formed from the quaternary carbon atoms. These are more stable and chemically less reactive than the corresponding secondary and primary radicals. Hence, degradation is the preferential reaction compared to other radical reactions such as recombination. Subsequent polymerization of the purified monomer gives a product that cannot be distinguished from the starting material.

#### Equipment

- Bunsen burner
- 2 small test tubes (diameter ca. 3 cm)
- rubber stopper that fits to the test tube with a hole bored through a right-angled bent

- glass tube (inner diameter ca. 0.5 cm) that is passed through the hole of the stopper
- test tube (diameter ca. 2.0 cm)
- rubber stopper that fits to the test tube with a hole bored through
- a straight glass tube (reflux condenser, inner diameter ca. 0.5 cm) that is passed through the hole of the stopper
- ice water bath (for cooling)
- distillation apparatus with thermometer and 50 cm<sup>3</sup> distillation flask
- sand bath on heating plate or heating mantle (50 cm<sup>3</sup>)
- stand

### Chemicals

- Polymethylmethacrylate (pulvarized), 30 g, or
- Polymethylmethacrylate-waste, 30 g, (for example covers of rear lamps that have been pulvarized)
- dibenzoylperoxide (C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>), 0.6 g

The experiment should be carried out in a fume hood. Avoid inhaling methyl methacrylate produced in the experiment and do not allow it to come into contact with the skin.

### Procedure

Fill a weighed test tube with small pieces of polymethylmethacrylate-waste to about one third and weigh the filled tube. Set up the apparatus shown in figure 1. The apparatus should be clamped to a stand.

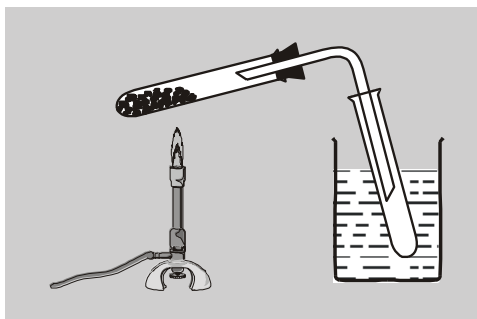


Figure 1: Experiment set-up for the pyrolysis of polymethylmethacrylate.

Heat the test tube containing the plastic waste carefully with a Bunsen burner (move the Bunsen burner continually to ensure uniform heating of the plastic and to prevent the

liquid foaming). If bubbles are formed in some parts of the melt, heat more strongly but do not overheat. Overheating causes effervescence of the melt and the resulting vapour can no longer be condensed. In the cooled test tube a fruity smelling liquid is formed which can have a variety of colours, depending on the nature of the dyes carried over with it.

Transfer the liquid to a distillation flask, add boiling chips and support the flask on a sand bath arranged in a way that the level of the sand is about the same height as the condensate. Distill under atmospheric pressure and collect the methyl methacrylate. The product is a colourless liquid. Determine the boiling point of methyl methacrylate.

Place 8 g of the purified methyl methacrylate into a large, carefully dried test tube, add 0.6 g of dibenzoylperoxide and mix the two components using a glass rod. Place a rubber stop containing a straight piece of glass tubing, that will act as a condenser, in the neck of the test tube and clamp it to a stand. Heat the mixture cautiously with a small Bunsen flame till an exothermic reaction takes place. Within minutes, a hard and bubbly plastic is formed.

Disposal:

Test tubes that were used for the depolymerization can be reused in the same experiment, as any plastic residual in them will not interfere with any subsequent reaction.

Sources of error

In some cases, the repolymerization does not readily take place. If there is no observable reaction, the mixture should be heated in a water bath for about 10 minutes.

- 38.1** Determine the experimental yield of the isolated methyl methacrylate in g.
- 38.2** Determine the theoretical yield of methyl methacrylate in g.
- 38.3** Calculate the yield as a percentage of the theoretical yield.
- 38.4** Determine the refractive index of the isolated pure methyl methacrylate.
- 38.5** What is the boiling temperature of methyl methacrylate under standard pressure?
- 38.6** Write down the polymerization reaction using the decomposition of dibenzoyl peroxide as the initial step.

## SOLUTION OF PREPARATORY PROBLEM 38

38.1 From experiment.

38.2 30 g polymethylmethacrylate = 30 g methyl methacrylate ( $M = 100 \text{ g mol}^{-1}$ )  
theoretical yield: 30 g (0.3 mol) methyl methacrylate.

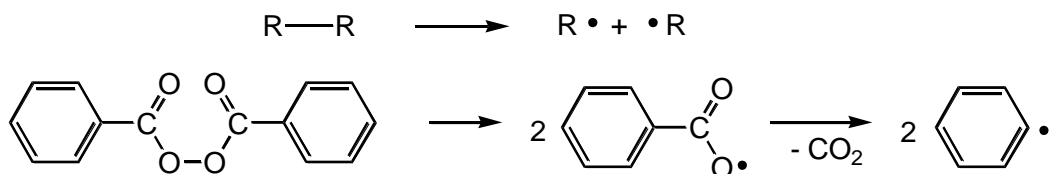
38.3 From experiment.

38.4 Refractive index of methyl methacrylate:  $n_D = 1.4142$ .

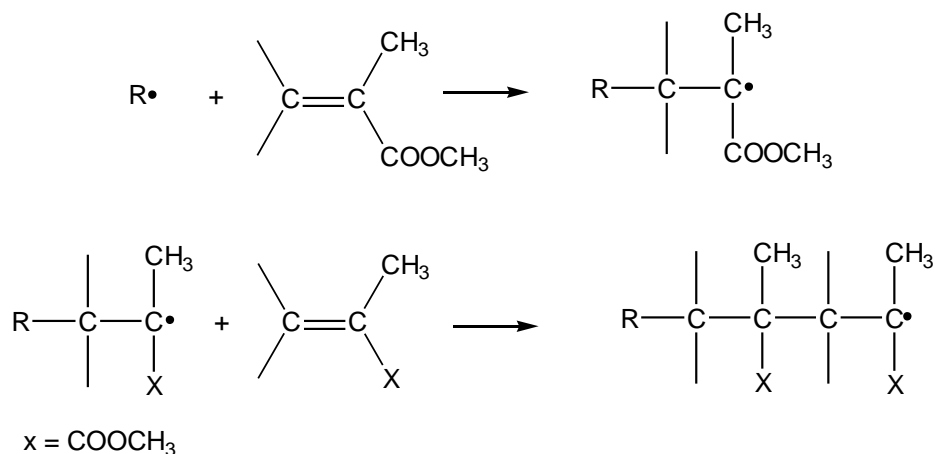
38.5 Boiling point of methyl methacrylate: b.p. = 100 – 101 °C.

38.6 Polymerization reaction of methyl methacrylate:

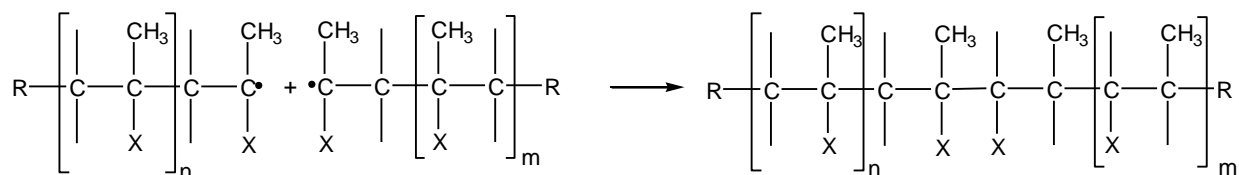
1. Initial step: decomposition dibenzoylperoxide



2. Chain initiation and chain extension:



3. Chain termination (other chain terminations are possible):



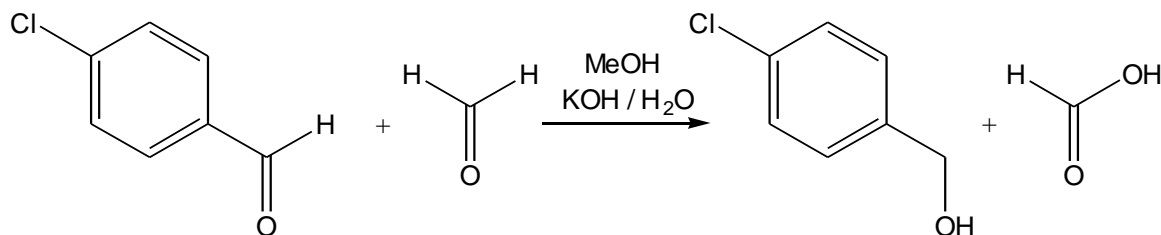
## PREPARATORY PROBLEM 39 (PRACTICAL)

### *Synthesis of para-Chlorobenzyl Alcohol – an Example of the Cannizzaro Reaction*

#### Introduction

The Italian scientist Stanislao Cannizzaro (1826-1910) was a professor at the Technical Institute of Alessandria (1851) and subsequently held professorships at Genoa (1855), Palermo (1861), and Rome (1871). In Rome, he also became a member of the senate and of the council of public instruction. He is known for his discovery of cyanamide, for obtaining alcohols from aldehydes – an organic reaction named after him – and for distinguishing between molecular and atomic weights.

The Cannizzaro reaction is a base-catalyzed disproportionation reaction of aromatic or aliphatic aldehydes with no  $\alpha$ -hydrogens to the corresponding acid and alcohol. In this disproportionation reaction, one molecule of aldehyde oxidizes another to the acid and is itself reduced to the primary alcohol. Aldehydes with an  $\alpha$ -hydrogen do not react in this manner, since for these aldehydes the aldol condensation is much faster.



In cases where two different aldehydes are used, the reaction is called a crossed Cannizzaro reaction. In the present reaction of *para*-chlorobenzaldehyde with formaldehyde, the latter reduces the sooner to the corresponding alcohol, here *p*-chlorobenzylalcohol, and is itself oxidized to formic acid.

#### Equipment

- three-necked flask (250 cm<sup>3</sup>)
- reflux condenser
- dropping funnel
- internal thermometer
- magnetic stirrer with heating plate
- magnetic stirrer bar
- water bath on heating plate
- beaker (500 cm<sup>3</sup> and 250 cm<sup>3</sup>)

- heating mantle (250 cm<sup>3</sup>) or sand bath on heating plate
- glass rod
- vacuum filter (Ø 5 cm) or Hirsch funnel
- vacuum filtration apparatus
- Bunsen burner
- chromatography tank
- test tubes
- capillary tubes

#### List of Chemicals

- para-chlorobenzaldehyde
- methanol
- ethanol
- potassium hydroxide
- distilled water
- ethyl acetate
- formalin (aqueous formaldehyde solution, 37 %)
- light petroleum ether (boiling range 40 – 70 °C)
- TLC plates (silica gel 60 F254)

#### Procedure

Place 28.1 g of para-chlorobenzaldehyde into a 250 cm<sup>3</sup> three-necked, round bottomed flask containing a magnetic stirrer bar and fitted with a reflux condenser, an internal thermometer, and a dropping funnel that contains a solution of 33.7 g of potassium hydroxide in 25 cm<sup>3</sup> of water. Add 60 cm<sup>3</sup> of methanol and 21 g of formalin. Support the flask in a water bath arranged in a way that the level of the water in the bath is at about the same height as the reaction mixture. Stir and heat the solution. When the internal temperature rises to 65 °C, remove the heating source and add the solution of potassium hydroxide dropwise. Ensure that the temperature remains between 65 °C and 75 °C. If necessary, cool the flask with a cold water bath. When the reagent has been added, heat the reaction mixture for 40 minutes at 70 °C followed by further 20 minutes under reflux. If necessary, use a heating mantle or a sand bath instead of the water bath. Allow the reaction mixture to cool down to ambient temperature, transfer the reaction mixture to an appropriate beaker and add 100 cm<sup>3</sup> of water to induce crystallization.

Collect the crude product via vacuum filtration. Wash the crude product with several small aliquots of cold distilled water. Reserve a small sample of the crude product for use in the TLC and for the determination of the melting point.

Recrystallize the crude product from an appropriate solvent, collect the purified crystals by vacuum filtration, dry the product and determine its melting point. In order to determine the appropriate solvent for the recrystallization, place small samples of the crude product in test tubes and recrystallize them from the following solvents:

- water
- water : ethanol (5 : 1)
- ethyl acetate : petroleum ether (1 : 5)

The procedure of the recrystallization from ethyl acetate / petroleum ether is different from standard recrystallization techniques. Dissolve the sample in ethyl acetate at room temperature and slowly add five times the volume of petroleum ether.

The purity of the crude product and of the recrystallized product are determined by thin-layer chromatography (silica gel 60 F254) using petroleum ether, ethyl acetate or a mixture of these two solvents as the eluting solvent. As a reference, run the starting material on the same plate.

#### Sources of Error

The starting material para-chlorobenzaldehyde is a solid that is most conveniently transferred in the liquid state by heating the whole storage bottle in a warm water bath. The melting point of para-chlorobenzaldehyde is 47.5 °C. If no crystals of the crude product form or an aqueous emulsion or an oily substance are formed, scratch the base and side of the beaker with a glass rod to initiate crystallization.

**39.1** Which is the most appropriate solvent or solvent mixture for the recrystallization?

**39.2** Describe the appearances and the colours of the crystals.

**39.3** Determine the melting points of both the dried crude and recrystallized products.

**39.4** Which is the most appropriate solvent or solvent mixture for the thin-layer chromatography (silica gel 60 F254) to obtain  $R_f$ -values between 0.3 and 0.7?

**39.5** Determine the respective  $R_f$ -values.

**39.6** Describe the reaction mechanism.



## SOLUTION OF PREPARATORY PROBLEM 39

**39.1** From the experiment.

**39.2** Colorless needles from water.

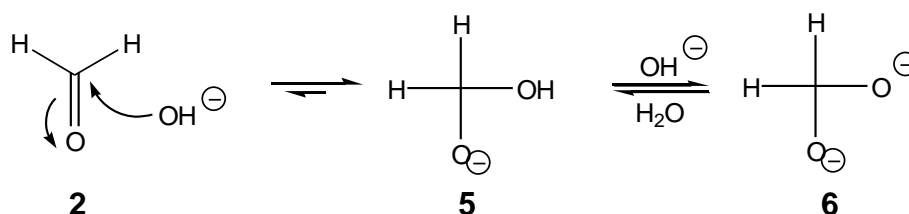
**39.3** Melting point of para-chlorobenzylalcohol: m.p. = 75 °C.

**39.4** From the experiment.

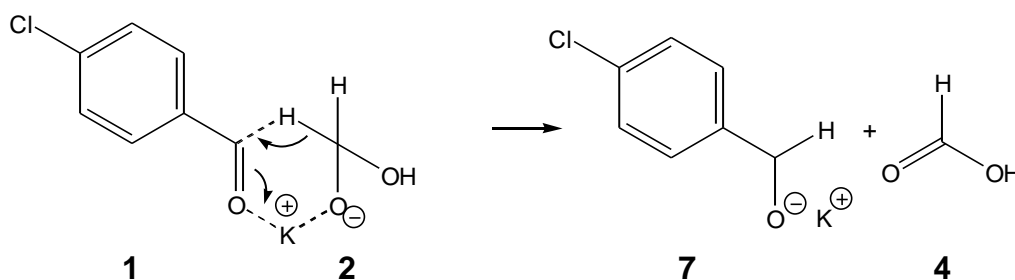
**39.5** From the experiment.

**39.6** Reaction mechanism:

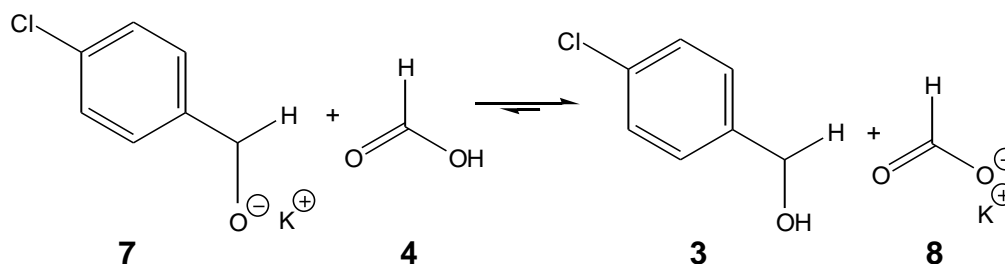
The mechanism of the Cannizzaro reaction involves a hydrid ( $\text{H}^-$ ) shift. In the first step a hydroxide ion ( $\text{OH}^-$ ) of the strong base adds to the formaldehyde **2** to give the tetrahedral anion **5**, which may lose a proton in the strong basic reaction mixture to give the dianion **6**.



The strong electron-donating character of the negative charged oxygen of **5** or much stronger in **6** forces the hydrogen to leave the anion or the dianion with its electron pair. This hydride transfer takes place, when **5** (or **6**) attacks an other molecule, which acts as a hydride acceptor, and runs through a cyclic transition state.



The final step is a rapid proton transfer from the acid **4** to alcoholat **7**.

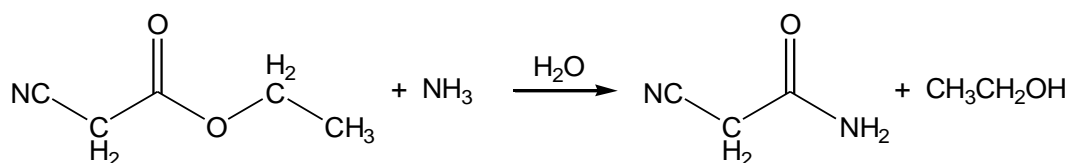


## PREPARATORY PROBLEM 40 (PRACTICAL)

### *Ammonolysis of an Activated Carboxylic Acid Ester: Synthesis of Cyano Acetamide*

#### Introduction

Unsubstituted amides are readily prepared by the ammonolysis of carboxylic acid derivatives, e.g. esters, as they are more reactive than the corresponding free acid. Thus, the reaction using carboxylic acid derivatives can be carried out under milder conditions. Esters are amongst the most reactive, particularly when the carbonyl group is further activated by electron-attracting groups. The latter are termed activated carboxylic acid esters. Cyanoacetic ethyl ester is an example of an activated carboxylic acid ester that readily reacts with ammonia easily to give the corresponding amide.



#### Equipment

- magnetic stirrer with heating plate
- magnetic stirrer bar
- Erlenmeyer flask (250 cm<sup>3</sup>)
- beaker (250 cm<sup>3</sup>)
- 2 pipettes (10 cm<sup>3</sup>) with pipette control
- Thermometer
- vacuum filter (Ø 5 cm) or Hirsch funnel
- dropping funnel
- vacuum filtration apparatus
- crystallizing dish or beaker
- graduated measuring cylinder
- balance (precision 0.01 g)
- spatula
- stand

#### List of Chemicals

- cyanoacetic ethyl ester
- aqueous ammonia (25 %)

- ethanol
- distilled water
- ice

### Procedure

Place 32.0 cm<sup>3</sup> (0.3 mol) of cyanoacetic ethyl ester into a 200 cm<sup>3</sup> Erlenmeyer flask equipped with a magnetic stirrer bar and an internal thermometer. Support a dropping funnel, containing 37.4 cm<sup>3</sup> (0.5 mol) of aqueous ammonia above the neck of the flask. Add the ammonia solution dropwise, being careful to ensure that the temperature remains between 30 and 35 °C. If necessary, cool the flask with cold water or an ice water bath. When the addition is complete, the reaction mixture is stirred for 30 minutes at room temperature.

Cool the reaction mixture to 0°C to induce crystallization. Collect the colourless crystals on a Hirsch funnel by vacuum filtration. Transfer the remaining crystals from the flask by adding small amounts of cold alcohol. Wash the crude product with several small aliquots of chilled ethanol. Reserve a small sample of the crude product for the determination of its melting point.

Transfer the crude product into a 250 cm<sup>3</sup> beaker and recrystallize it from 70 cm<sup>3</sup> of hot ethanol. Upon complete dissolution of the crude product the reaction mixture should be allowed to cool to room temperature and finally cooled in an ice bath. Collect the product by vacuum filtration and weigh the dried product.

- 40.1** Determine the experimental yield of the cyano acetamide product in g.
- 40.2** Calculate the theoretical yield of the pure amide in g.
- 40.3** Calculate the yield as a percentage of the theoretical yield.
- 40.4** Determine the melting point of the crude product and of the recrystallized product.

## SOLUTION OF PREPARATORY PROBLEM 40

**40.1** From the experiment.

**40.2** 32.0 cm<sup>3</sup> of cyanoacetic acid ethyl ester ( $\rho = 1.065 \text{ g cm}^{-3}$ ,  $M = 113.1 \text{ g mol}^{-1}$ ) =  
25.3 g (0.301 mol)

**40.3** From the experiment.

**40.4** Melting point of cyano acetamid: m.p. = 121–122 °C.