

36<sup>th</sup> International Chemistry Olympiad



**Preparatory Problems  
and  
Worked Solutions**

**Kiel, Germany**

**January, 2004**



# Preface

The problems have been designed to challenge and stimulate the students who take part in the 36<sup>th</sup> IChO in Kiel, Germany. They cover a wide range of subjects but most of them can be solved by applying a basic knowledge of chemistry. Problems and answers are very detailed to give students the opportunity to learn and to understand the background.

You will find the problems on the internet: [www.icho.de](http://www.icho.de) ... Chemistry (without solutions). The solutions will be published on the site at the end of May 2004.

On the same page (... Participation) you will find

- the regulations of the IChO
- the syllabus for the practical and the theoretical part
- the safety rules and recommendations set up by the International Jury
- the hazard warning symbols, their designations and their explanations, R-ratings and S-provisions.

## **A note to the mentors:**

The periodic table of elements and roughly the same list of constants and useful formulas as in the preparatory problems will be provided in the theoretical exam. If you want to have additional or different material please mail.

In the exams the students get a booklet with exam questions and separate answer sheets. Everything written in the boxes on the answer sheets will be marked but nothing else.

During the examination an official English version of the problems will be available on request but only for clarification.

Every answer which needs calculation can only be graded if the calculation is shown.

We place great importance on safety. On page 45 preceding the practical problems you will find a list of rules concerning safety precautions and procedures to be followed in Kiel. At the registration in Kiel, we will ask the headmentors to sign a form saying that the students in their teams know these rules and are trained and able to follow them.

Finally, despite proof reading efforts you will uncover some mistakes. Please let us know. We welcome any comments concerning the problems. ([Hampe@t-online.de](mailto:Hampe@t-online.de))

Welcome to the 36<sup>th</sup> IChO, welcome to Germany, welcome to Kiel.

Wolfgang Hampe

# 36<sup>th</sup> International Chemistry Olympiad

Kiel, Germany  
July 18 - 27, 2004

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# Periodic table of elements

with atom masses / u

<b>1</b> <b>H</b> 1.01																	<b>2</b> <b>He</b> 4.00
<b>3</b> <b>Li</b> 6.94	<b>4</b> <b>Be</b> 9.01											<b>5</b> <b>B</b> 10.81	<b>6</b> <b>C</b> 12.01	<b>7</b> <b>N</b> 14.01	<b>8</b> <b>O</b> 16.00	<b>9</b> <b>F</b> 19.00	<b>10</b> <b>Ne</b> 20.18
<b>11</b> <b>Na</b> 22.99	<b>12</b> <b>Mg</b> 24.31											<b>13</b> <b>Al</b> 26.98	<b>14</b> <b>Si</b> 28.09	<b>15</b> <b>P</b> 30.97	<b>16</b> <b>S</b> 32.07	<b>17</b> <b>Cl</b> 35.45	<b>18</b> <b>Ar</b> 39.95
<b>19</b> <b>K</b> 39.10	<b>20</b> <b>Ca</b> 40.08	<b>21</b> <b>Sc</b> 44.96	<b>22</b> <b>Ti</b> 47.88	<b>23</b> <b>V</b> 50.94	<b>24</b> <b>Cr</b> 52.00	<b>25</b> <b>Mn</b> 54.94	<b>26</b> <b>Fe</b> 55.85	<b>27</b> <b>Co</b> 58.93	<b>28</b> <b>Ni</b> 58.69	<b>29</b> <b>Cu</b> 63.55	<b>30</b> <b>Zn</b> 65.39	<b>31</b> <b>Ga</b> 69.72	<b>32</b> <b>Ge</b> 72.61	<b>33</b> <b>As</b> 74.92	<b>34</b> <b>Se</b> 78.96	<b>35</b> <b>Br</b> 79.90	<b>36</b> <b>Kr</b> 83.80
<b>37</b> <b>Rb</b> 85.47	<b>38</b> <b>Sr</b> 87.62	<b>39</b> <b>Y</b> 88.91	<b>40</b> <b>Zr</b> 91.22	<b>41</b> <b>Nb</b> 92.91	<b>42</b> <b>Mo</b> 95.94	<b>43</b> <b>Tc</b> 98.91	<b>44</b> <b>Ru</b> 101.07	<b>45</b> <b>Rh</b> 102.91	<b>46</b> <b>Pd</b> 106.42	<b>47</b> <b>Ag</b> 107.87	<b>48</b> <b>Cd</b> 112.41	<b>49</b> <b>In</b> 114.82	<b>50</b> <b>Sn</b> 118.71	<b>51</b> <b>Sb</b> 121.76	<b>52</b> <b>Te</b> 127.60	<b>53</b> <b>I</b> 126.90	<b>54</b> <b>Xe</b> 131.29
<b>55</b> <b>Cs</b> 132.91	<b>56</b> <b>Ba</b> 137.3	<b>57-71</b>	<b>72</b> <b>Hf</b> 178.49	<b>73</b> <b>Ta</b> 180.95	<b>74</b> <b>W</b> 183.84	<b>75</b> <b>Re</b> 186.21	<b>76</b> <b>Os</b> 190.23	<b>77</b> <b>Ir</b> 192.22	<b>78</b> <b>Pt</b> 195.08	<b>79</b> <b>Au</b> 196.97	<b>80</b> <b>Hg</b> 200.59	<b>81</b> <b>Tl</b> 204.38	<b>82</b> <b>Pb</b> 207.19	<b>83</b> <b>Bi</b> 208.98	<b>84</b> <b>Po</b> 208.98	<b>85</b> <b>At</b> 209.99	<b>86</b> <b>Rn</b> 222.02
<b>87</b> <b>Fr</b> 223	<b>88</b> <b>Rd</b> 226	<b>89-103</b>	<b>104</b> <b>Rf</b> 261	<b>105</b> <b>Db</b> 262	<b>106</b> <b>Sg</b> 263	<b>107</b> <b>Bh</b> 264	<b>108</b> <b>Hs</b> 265	<b>109</b> <b>Mt</b> 268									
			<b>57</b> <b>La</b> 138.91	<b>58</b> <b>Ce</b> 140.12	<b>59</b> <b>Pr</b> 140.91	<b>60</b> <b>Nd</b> 144.24	<b>61</b> <b>Pm</b> 144.92	<b>62</b> <b>Sm</b> 150.36	<b>63</b> <b>Eu</b> 151.96	<b>64</b> <b>Gd</b> 157.25	<b>65</b> <b>Tb</b> 158.93	<b>66</b> <b>Dy</b> 162.50	<b>67</b> <b>Ho</b> 164.93	<b>68</b> <b>Er</b> 167.26	<b>69</b> <b>Tm</b> 168.93	<b>70</b> <b>Yb</b> 173.04	<b>71</b> <b>Lu</b> 174.97
			<b>89</b> <b>Ac</b> 227	<b>90</b> <b>Th</b> 232	<b>91</b> <b>Pa</b> 231	<b>92</b> <b>U</b> 238	<b>93</b> <b>Np</b> 237	<b>94</b> <b>Pu</b> 244	<b>95</b> <b>Am</b> 243	<b>96</b> <b>Cm</b> 247	<b>97</b> <b>Bk</b> 247	<b>98</b> <b>Cf</b> 251	<b>99</b> <b>Es</b> 252	<b>100</b> <b>Fm</b> 257	<b>101</b> <b>Md</b> 258	<b>102</b> <b>No</b> 259	<b>103</b> <b>Lr</b> 262

## Constants and useful formulars

f	p	n	μ	m	k	M	G	T
femto 10 <sup>-15</sup>	pico 10 <sup>-12</sup>	nano 10 <sup>-9</sup>	micro 10 <sup>-6</sup>	milli 10 <sup>-3</sup>	kilo 10 <sup>3</sup>	mega 10 <sup>6</sup>	giga 10 <sup>9</sup>	tera 10 <sup>12</sup>

$$1 \text{ \AA} = 10^{-10} \text{ m}$$

Gas constant	R = 8.314 JK <sup>-1</sup> mol <sup>-1</sup>	Faraday constant	F = 96485 C mol <sup>-1</sup>
Standard pressure	p = 1.013·10 <sup>5</sup> Pa	Standard temperature	25°C = 298.15K
Avogadro number	N <sub>A</sub> = 6.022·10 <sup>23</sup> mol <sup>-1</sup>	Planck constant	h = 6.626·10 <sup>-34</sup> Js
Speed of light	c = 3.00·10 <sup>8</sup> ms <sup>-1</sup>		

$$\Delta G = \Delta H - T \cdot \Delta S$$

$$\Delta G = - nEF$$

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

$$\Delta G = \Delta G^0 + RT \cdot \ln Q \quad \text{with } Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{react.})}$$

$$\Delta H(T_1) = \Delta H^0 + \int_{298.15}^{T_1} C_p dT$$

if C<sub>p</sub> = constant:

$$\Delta H(T_1) = \Delta H^0 + (T_1 - 298.15 \text{ K}) \cdot C_p$$

Arrhenius equation

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

Perfect gas law

$$p \cdot V = n \cdot RT$$

for osmotic pressure  $\Pi$ :  $\Pi \cdot V = n \cdot RT$

Nernst equation

$$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{ox}}{c_{red}}$$

Bragg's law

$$n \cdot \lambda = 2d \cdot \sin \theta$$

Law of Lambert Beer

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

Energy of a photon

$$E = h \cdot c \cdot \lambda^{-1}$$

kinetic energy =  $\frac{1}{2} mv^2$

$$\rho = \frac{F}{A}$$

$$F = m \cdot a$$

$$V(\text{cylinder}) = \pi \cdot r^2 \cdot h$$

$$A(\text{sphere}) = 4\pi \cdot r^2$$

$$V(\text{sphere}) = \frac{4}{3} \pi \cdot r^3$$

$$1 \text{ J} = 1 \text{ Nm}$$

$$1 \text{ N} = 1 \text{ kg ms}^{-2}$$

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

$$1 \text{ W} = 1 \text{ J s}^{-1}$$



## 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 gcm<sup>-3</sup>.

Thermochemical data:

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

## 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  $C_p(T) = a + b \cdot T + c \cdot T^2$  and  $S(T) = d + e \cdot T + f \cdot T^2$ . The values of the constants a-f can be found in Table 2.

**2.5 Calculate the mole fraction of  $NH_3$  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	$\Delta_f H^0 \cdot (kJ mol^{-1})^{-1}$	$S^0 \cdot (J mol^{-1} K^{-1})^{-1}$	$C_p^0 \cdot (J mol^{-1} K^{-1})^{-1}$
$N_2 (g)$	0.0	191.6	29.1
$NH_3 (g)$	- 45.9	192.8	35.1
$H_2 (g)$	0.0	130.7	28.8

Table 2:

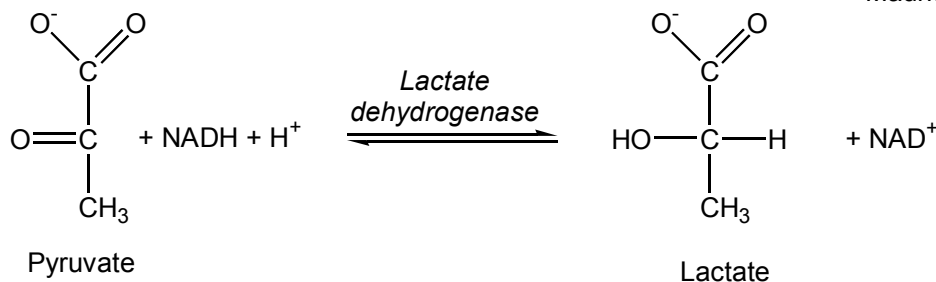
Chemical Substance	$a \cdot (J mol^{-1} K^{-1})^{-1}$	$b \cdot (J mol^{-1} K^{-2})^{-1}$	$c \cdot (J mol^{-1} K^{-3})^{-1}$	$d \cdot (J mol^{-1} K^{-1})^{-1}$	$e \cdot (J mol^{-1} K^{-2})^{-1}$	$f \cdot (J mol^{-1} K^{-3})^{-1}$
$N_2 (g)$	27.3	$5.2 \cdot 10^{-3}$	$-1.7 \cdot 10^{-9}$	170.5	$8.1 \cdot 10^{-2}$	$-2.3 \cdot 10^{-5}$
$NH_3 (g)$	24.2	$4.0 \cdot 10^{-2}$	$-8.2 \cdot 10^{-6}$	163.8	$1.1 \cdot 10^{-1}$	$-2.4 \cdot 10^{-5}$
$H_2 (g)$	28.9	$-5.8 \cdot 10^{-4}$	$1.9 \cdot 10^{-6}$	109.8	$8.1 \cdot 10^{-2}$	$-2.4 \cdot 10^{-5}$

### 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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  $\text{H}^+$ ) is 1 mol  $\text{L}^{-1}$ . Assume the following cellular concentrations at pH = 7: pyruvate 380  $\mu\text{mol L}^{-1}$ , NADH 50  $\mu\text{mol L}^{-1}$ , lactate 3700  $\mu\text{mol L}^{-1}$ ,  $\text{NAD}^+$  540  $\mu\text{mol L}^{-1}$ !

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

### 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  $\text{m}^2$  (typical of a single-family house in Central Europe) that consists of a brick layer with a thickness of  $d = 24 \text{ cm}$  and through the wall that consists, however, of a brick layer with a thickness of  $d = 36 \text{ cm}$ . 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:

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

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

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

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	$\lambda \cdot (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})^{-1}$
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

## 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  $p_c = 72.8 \cdot 10^5$  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 ml, 298 K, ideal gas).**

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

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

constants for CO<sub>2</sub>:  
 $a = 3.59 \cdot 10^5 \text{ Pa dm}^6 \text{ mol}^{-2}$   
 $b = 0.0427 \text{ dm}^3 \text{ mol}^{-1}$

**5.2 Calculate the pressures needed to achieve a density of 220 g dm<sup>-3</sup>, 330 g dm<sup>-3</sup>, and 440 g dm<sup>-3</sup> 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 Pd/Al<sub>2</sub>O<sub>3</sub> 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) ?**

## 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  $\text{S}_2\text{O}_8^{2-} + 2 \text{I}^- \rightarrow 2 \text{SO}_4^{2-} + \text{I}_2$  was determined as a function of the initial concentrations ( $c_0$ ) of the reactants at 25°C:

$c_0(\text{S}_2\text{O}_8^{2-})$ [mol·L <sup>-1</sup> ]	$c_0(\text{I}^-)$ [mol·L <sup>-1</sup> ]	$r_0$ [10 <sup>-8</sup> mol·L <sup>-1</sup> ·s <sup>-1</sup> ]
0.0001	0.010	1.1
0.0002	0.010	2.2
0.0002	0.005	1.1

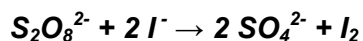
- 6.1** Draw the line-bond structure of the peroxodisulfate ion and determine the oxidation states of all atoms.
- 6.2** Write down the rate equation for the reaction shown above.
- 6.3** Write down the total order and the partial orders of the reaction shown above.
- 6.4** Prove that the rate constant of the reaction is 0.011 L·mol<sup>-1</sup>·s<sup>-1</sup>.

The activation energy of the reaction mentioned above is 42 kJ·mol<sup>-1</sup>.

- 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



assuming that there is an excess of thiosulfate ions relative to the peroxodisulfate ions and the iodide ions in the solution.

## 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.	
	$\text{H} \text{---} \text{H}$ $\dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots$		$\begin{array}{c} \text{H} \quad \text{H}_2\text{C}=\text{CH}_2 \quad \text{H} \\   \quad \quad \quad   \\ \dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots \end{array}$
	$\begin{array}{c} \text{H} \quad \quad \quad \text{H} \\   \quad \quad \quad   \\ \dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots \end{array}$		$\text{H}_3\text{C} \text{---} \text{CH}_3$ $\dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots$
	$\text{H}_2\text{C}=\text{CH}_2$ $\begin{array}{c} \text{H} \quad \quad \quad \text{H} \\   \quad \quad \quad   \\ \dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots \end{array}$		$\begin{array}{c} \text{H} \quad \quad \quad \text{H} \\   \quad \quad \quad   \\ \dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots \end{array}$
	$\begin{array}{c} \text{H} \quad \quad \quad \text{CH}_3 \\   \quad \quad \quad   \\ \dots \text{---} \text{O} \text{---} \dots \text{---} \text{Zn} \text{---} \dots \text{---} \text{O} \text{---} \dots \\ \quad \quad \quad   \\ \quad \quad \quad \text{CH}_2 \end{array}$		

$\theta(\text{H})$  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?**

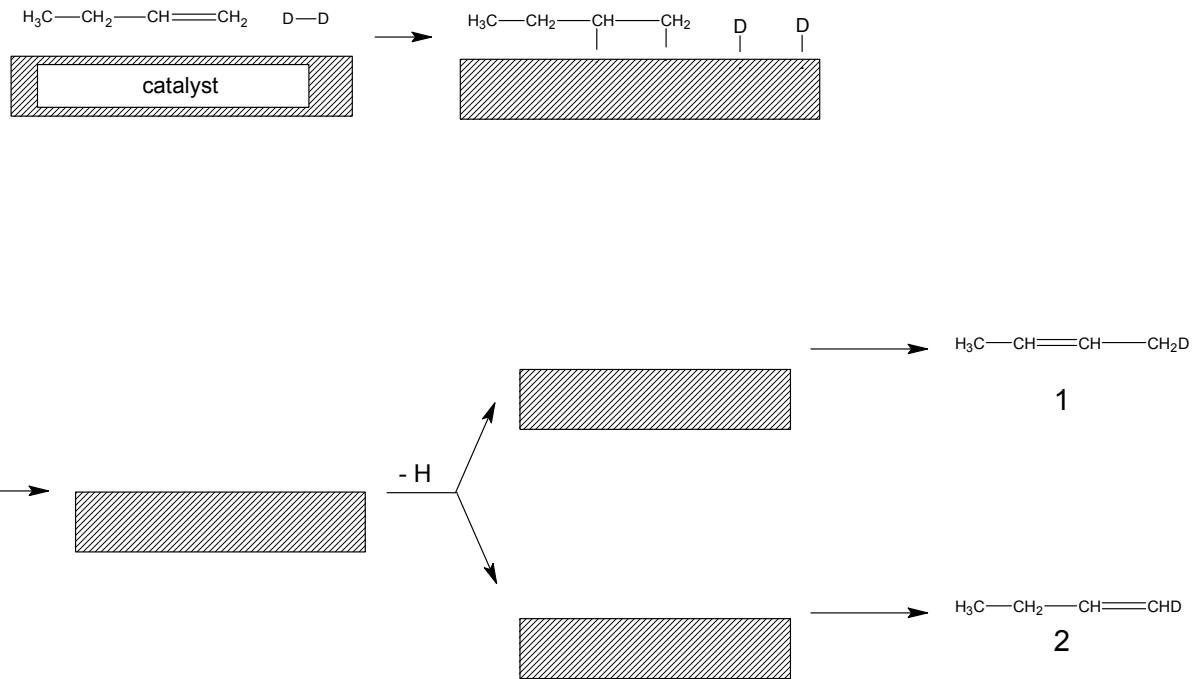
- (1)  $r = k \cdot \theta(\text{H})$
- (2)  $r = k \cdot \theta(\text{C}_2\text{H}_4)$
- (3)  $r = k \cdot \theta(\text{H}) \cdot \theta(\text{C}_2\text{H}_4)$
- (4)  $r = k \cdot \theta(\text{H}) \cdot \theta(\text{C}_2\text{H}_5)$

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.**



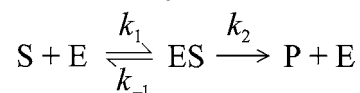
The fraction of surface sites that are occupied by adsorbed gas molecules ( $\theta$ ) may be described in a simple way by using the Langmuir isotherm:

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

**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.**

## Problem 8: Kinetics of an Enzymatic Reaction

The mechanism of an enzymatic reaction may be described as:

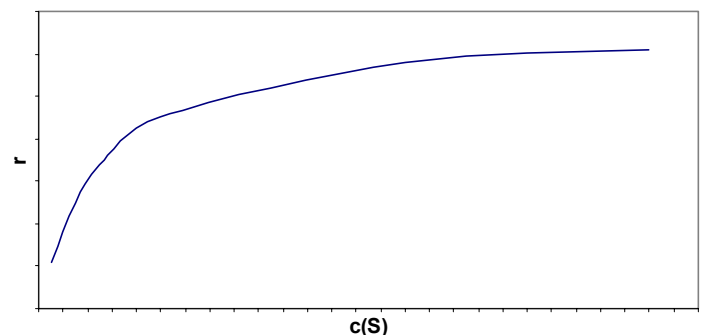


S is the substrate, E is the enzyme, ES is the complex formed by S and E, and P is the product.  $k_1$ ,  $k_{-1}$  and  $k_2$  are the rate constants of the elementary reactions.

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

$$r = \frac{dc(\text{P})}{dt} = k_2 c_{\text{T}}(\text{E}) \frac{c(\text{S})}{K_{\text{M}} + c(\text{S})}$$

$t$  is the time,  
 $c(\text{P})$  is the product concentration,  
 $c_{\text{T}}(\text{E})$  is the total enzyme concentration  
 and  $K_{\text{M}} = (k_{-1} + k_2)/k_1$ .





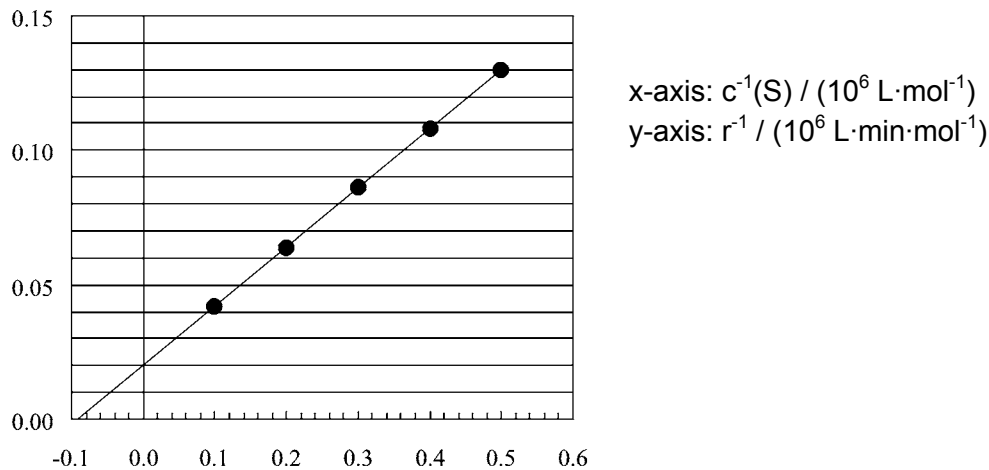
8.1 Determine the variables  $x$ ,  $y$  and  $z$  in the following rate equations:

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

8.2 Complete the following rate equation:

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

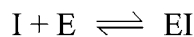
Penicillin (substrate) is hydrolyzed by  $\beta$ -lactamase (enzyme). The following data have been recorded when the total enzyme concentration was  $10^{-9} \text{ mol}\cdot\text{L}^{-1}$ .



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

If  $c(S) = 0.01 \cdot K_M$ , 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  $9.5 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  and the total enzyme concentration is  $8 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , 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
The rate of the enzymatic reaction, $r$ , is reduced by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
The maximum value of the rate $r$ is reduced by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
The concentration of the substrate $S$ is unaffected by the competitive inhibitor.	<input type="checkbox"/>	<input type="checkbox"/>
The activation energy of the <u>enzymatic</u> 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.

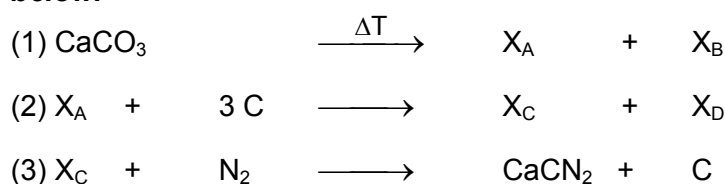
**8.6 Decide whether the following statements are true or false.**

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

### Problem 9: $\text{CaCN}_2$ – An Old but still Important Fertilizer

Calcium cyanamide ( $\text{CaCN}_2$ ) is a very versatile and powerful fertilizer. It can be produced easily from cheap and common chemicals such as  $\text{CaCO}_3$ . The thermal decomposition of  $\text{CaCO}_3$  leads to a white solid  $X_A$  and a colourless gas  $X_B$  which does not sustain combustion. A greyish solid  $X_C$  and a gas  $X_D$  form by the reduction of  $X_A$  with carbon.  $X_C$  and  $X_D$  can be further oxidized. The reaction of  $X_C$  with nitrogen finally leads to  $\text{CaCN}_2$ .

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



**9.2 What gas forms by the hydrolysis of  $\text{CaCN}_2$ ? Write down the equation of the reaction of  $\text{CaCN}_2$  with water.**

**9.3 In solid state chemistry the  $\text{CN}_2^{2-}$  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.**

### 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.

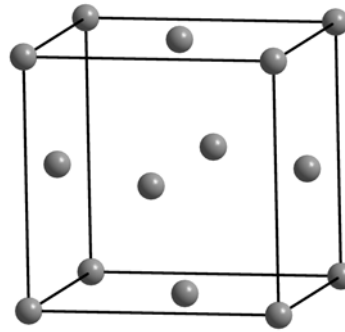
**10.1 Draw a two-dimensional model of a closed-packed assembly of spheres.**

**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

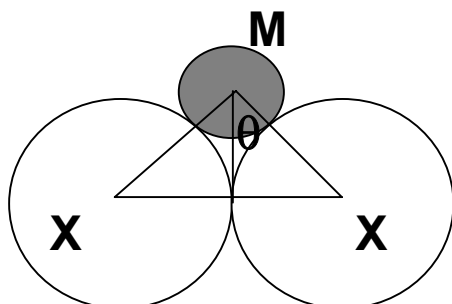
are  $0.225 \cdot r$  for a tetrahedral hole

and  $0.414 \cdot r$  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	cubeoctahedron	$1.0$	closed packed

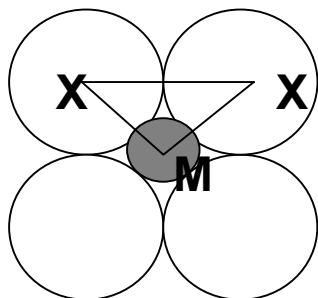
**10.6 Show that the ideal  $r_M/r_X$  value for the cation-anion and anion-anion contacts of a tetrahedral arrangement of anions around a cation is 0.225.**



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

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

**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.

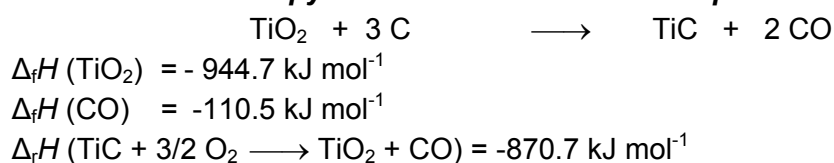
## Problem 11: Titanium carbide – A High-Tech Solid

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  $\text{TiO}_2$  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.

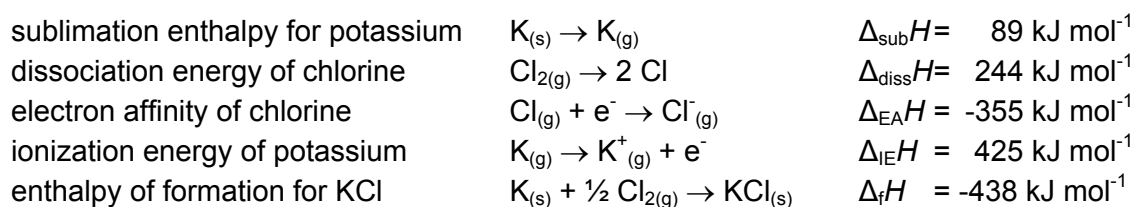
**11.2 Calculate the enthalpy of reaction of the technical production process of TiC:**



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.**



## 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)

- (I)  $\text{Ag(s) / AgCl (saturated) // Ag}^+ (\text{aq}, c = 0.01 \text{ mol L}^{-1}) / \text{Ag(s)}$   $U_1 = 0.170 \text{ V}$   
(II)  $\text{Pt / Ag}_n(\text{s, nanoclusters}), \text{Ag}^+ (\text{aq}, c = 0.01 \text{ mol L}^{-1}) // \text{AgCl (saturated) / Ag(s)}$   
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

- a) the  $\text{Ag}_{10}$  clusters and – in a second experiment – the  $\text{Ag}_5$  clusters, into an aqueous solution of  $\text{pH} = 13$  ?  
b) the  $\text{Ag}_{10}$  clusters and – in a second experiment – the  $\text{Ag}_5$  into an aqueous solution of  $\text{pH} = 5$   
c) both clusters together into an aqueous solution having a  $\text{pH}$  of 7 with  $c(\text{Cu}^{2+}) = 0.001 \text{ mol L}^{-1}$  and  $c(\text{Ag}^+) = 1 \cdot 10^{-10} \text{ mol L}^{-1}$  ? Calculate.  
What happens if the reaction proceeds (qualitatively)?

$$E^0(\text{Ag} / \text{Ag}^+) = 0.800 \text{ V}$$

$$E^0(\text{Cu} / \text{Cu}^{2+}) = 0.345 \text{ V}$$

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

## 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  $d$ :

$$A = \log \frac{P_0}{P} = \varepsilon cd \quad \varepsilon \text{ is the molar absorptivity (also called extinction coefficient).}$$

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  $c = 4 \cdot 10^{-6} \text{ mol L}^{-1}$  has a molar absorptivity of  $\varepsilon = 1.5 \cdot 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$ . 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?**

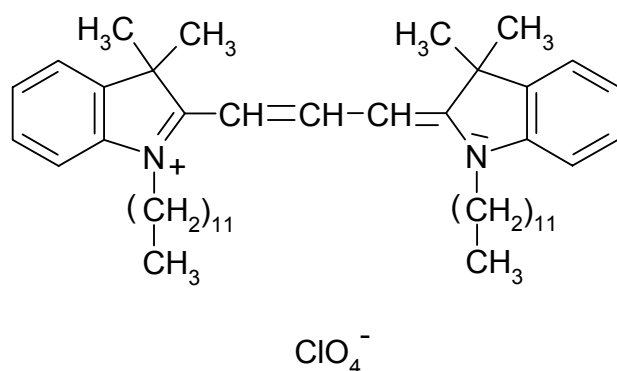
**13.4 Calculate the molecular absorption cross section in units of  $\text{\AA}^2$ .**

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?**

## 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 ( $\text{diIC}_{12}$ ). In this experiment, dye molecules are spread on a sample surface and localized according to their fluorescence signals. The structure of  $\text{diIC}_{12}$  is shown below.



**14.1 Indicate which part of the  $\text{diIC}_{12}$  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  $\mu\text{L}$  of a solution of  $\text{diIC}_{12}$  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  $3 \cdot 10^{10}$  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  $\text{diIC}_{12}$  molecule absorbs  $2.3 \cdot 10^5$  photons per second under the described conditions. Calculate the absorption cross section of the  $\text{diIC}_{12}$  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  $\text{diIC}_{12}$  (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  $\text{diIC}_{12}$  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  $\mu\text{m}$

## Problem 15: Infrared Spectroscopy of Tetrahedral Molecules

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

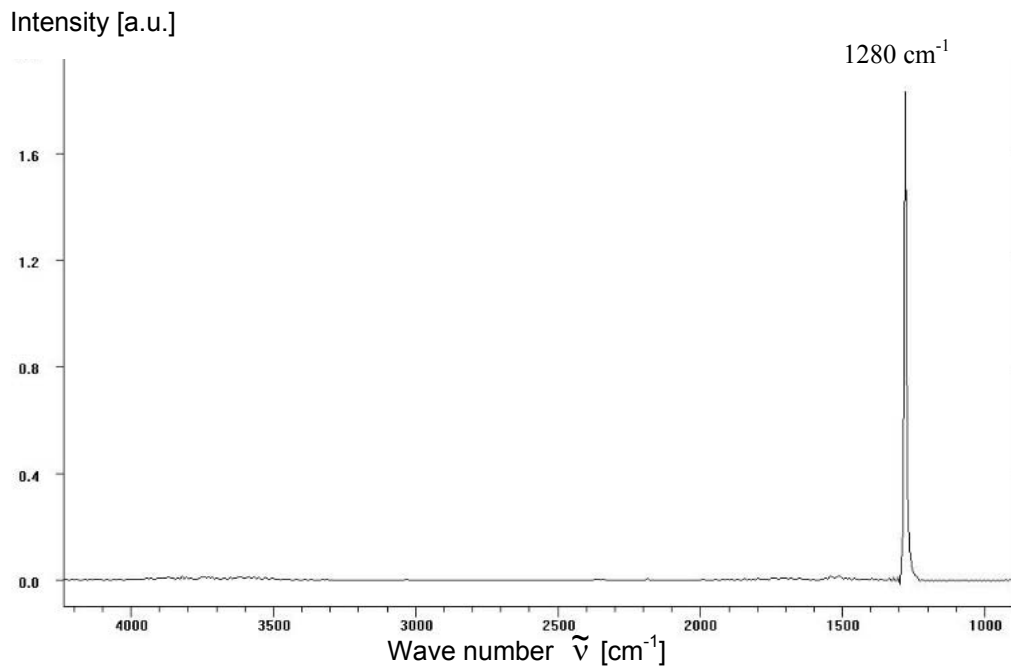
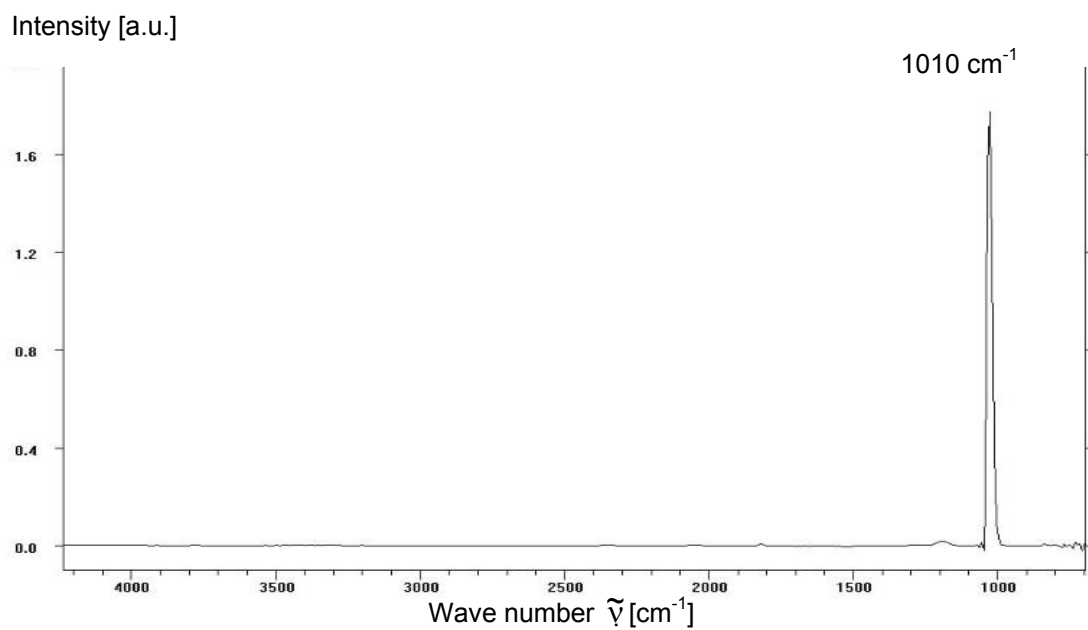


Fig. 2: IR spectrum of  $\text{SiF}_4$ , intensity vs. wavenumber  $\tilde{\nu}$  in  $\text{cm}^{-1}$



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

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

**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  $-1222 \text{ kJmol}^{-1}$  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?**

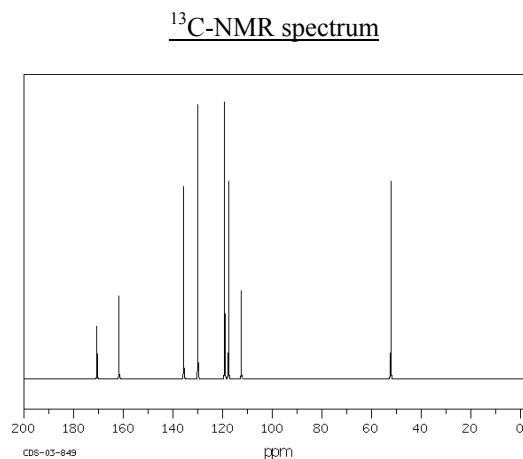
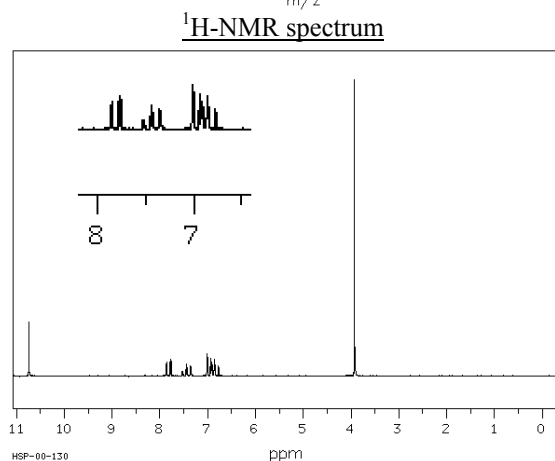
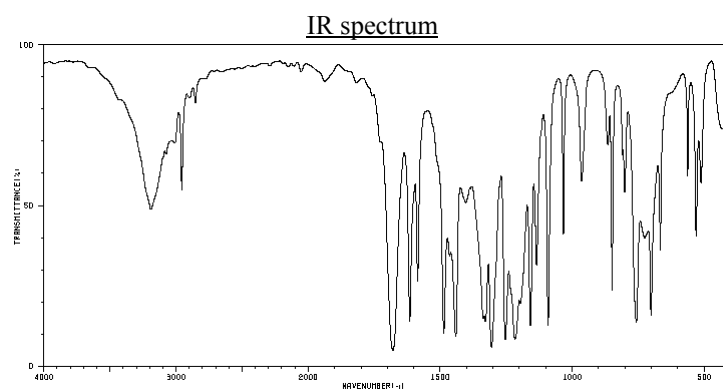
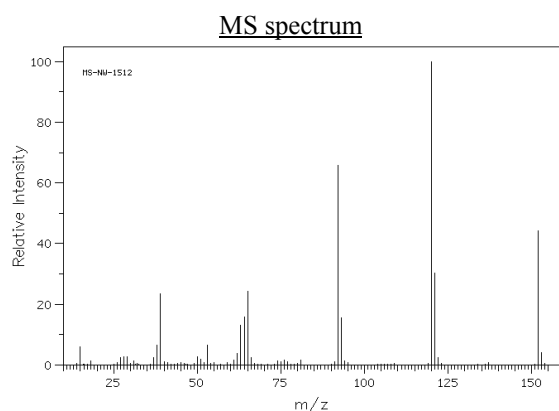
The enthalpies of vaporization of carbon and silicon are  $717 \text{ kJmol}^{-1}$  and  $439 \text{ kJmol}^{-1}$ .

**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.**

## 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:



- 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  $\text{-OH}$  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 $\text{C}\equiv\text{C-H}$
		<b>m</b>				C-H in $\text{C}=\text{C-H}$
		<b>w</b>				C-H in $\text{C}\div\text{C-H}$
		<b>s</b>				C-H (alkanes)
				<b>w</b>		$\text{C}\equiv\text{C}$
					<b>m</b>	$\text{C}=\text{C}=\text{C}$
					<b>w</b>	$\text{C}=\text{C}$
					<b>s</b>	$\text{C}\div\text{C}\div\text{C}$
					<b>s</b>	$\text{C}=\text{O}$

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  $^1\text{H-NMR}$  spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).**

Simplified table of  $^{13}\text{C-NMR}$  chemical shifts:

C=O	$\text{C}\div\text{C}, \text{C}=\text{C}$	$\text{C}\equiv\text{C}$		O-C	CH, $\text{CH}_2$ , $\text{CH}_3$													
200 ppm	180	170	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  $^{13}\text{C-NMR}$  spectrum to moieties that you expect in the unknown substance (consider 16.3 and 16.4).**

Simplified table of  $^1\text{H-NMR}$  chemical shifts:

OH, COOH, CHO		$\text{C}\div\text{CH}$	$\text{C}=\text{CH}$	$\text{OCH}_x$	CH	$\text{CH}_2$	$\text{CH}_3$			
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

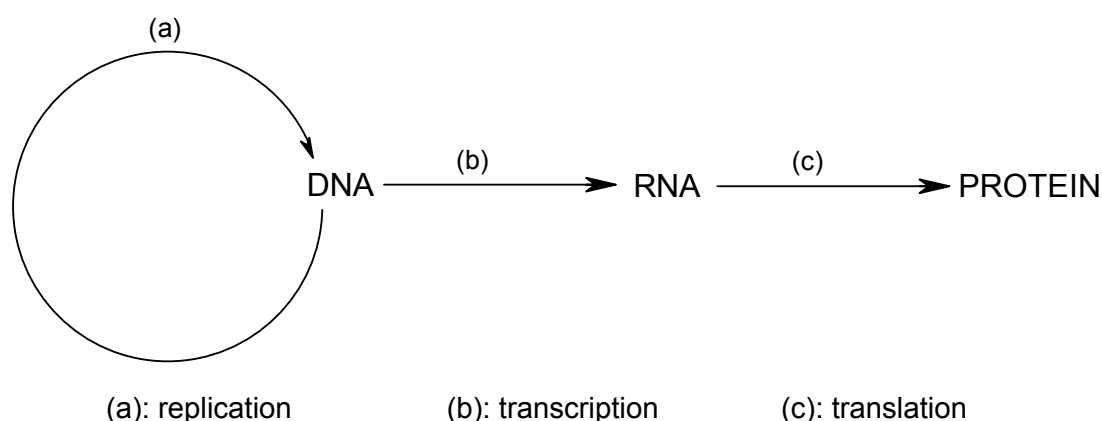
splitting of the signals at 6.8, 6.9, 7.5, and 7.8 ppm in the  $^1\text{H-NMR}$  spectrum and the  $-\text{O-H}$  band in the IR spectrum.

**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  $^1\text{H-NMR}$  spectrum and the signals at 52 and 161 ppm in the  $^{13}\text{C-NMR}$  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  $-\text{O-H}$  band.**

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

## Problem 17: DNA, RNA, Proteins

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



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'-monophosphate (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-Va – L-Gly indicating the charges at the isoelectric point.**

## 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.

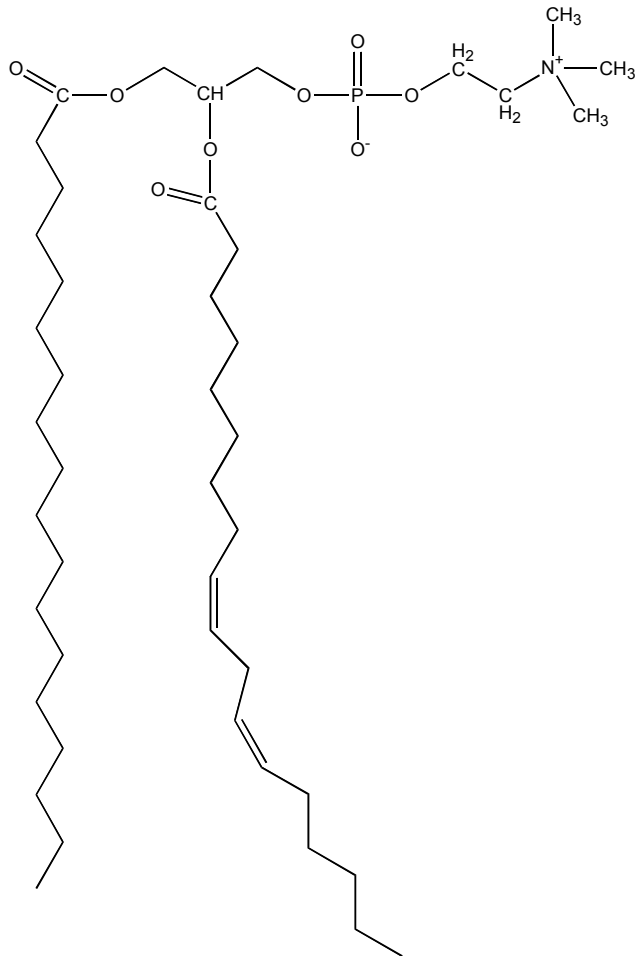
- 18.4 What is the oxidation product of the respiratory chain?  
How is the free energy stored at the inner mitochondrial membrane independently of chemical bonds, and how is it used for the synthesis of ATP?**
- 18.5 Write down the molecular formula of the overall oxidation reaction of a fatty acid in these three reaction cascades.  
What roles do A and B play in these reaction cascades?**

## Problem 19: Lipids

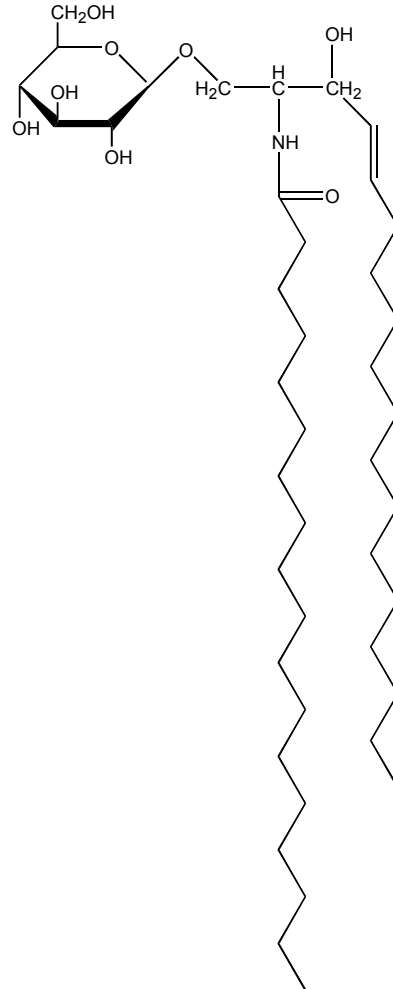
Lipids are important components of our nutrition, and they fulfill a variety of important roles in the body - although we do not always want to be reminded of their presence!

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.**

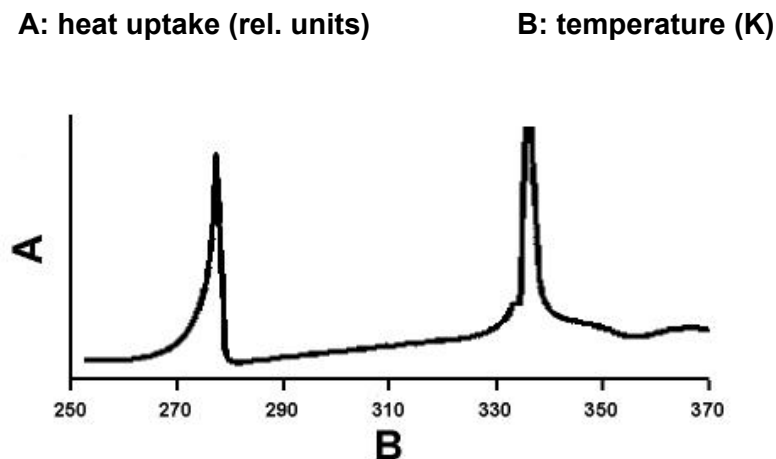
Lipids are substances that are soluble in organic solvents like chloroform, but hardly soluble in water.

**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**

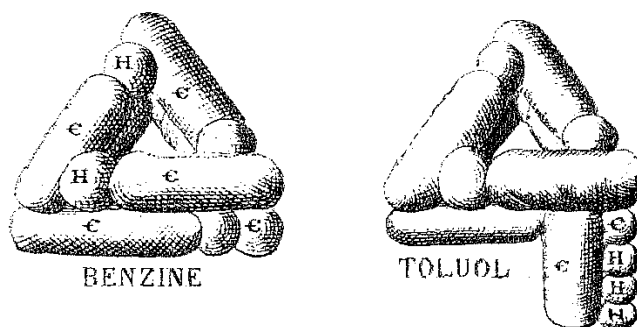
**a) cholesterol**

**b) esters of cholesterol with fatty acids**

**be incorporated into lipoproteins?**

## **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:



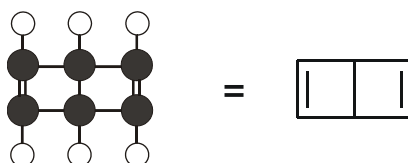
However, at that time it was already known that there is only one isomer of *ortho* di-substituted benzenes. If benzene had alternating single and double bonds there would be two isomers, one with a double bond between the substituents and one with a single bond. Kekulé solved this contradiction by assuming 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.**

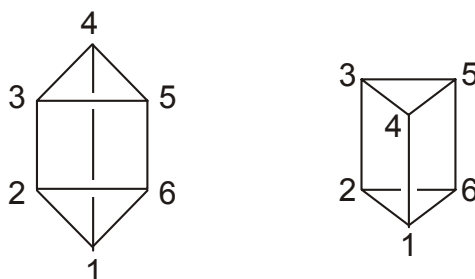
**20.2 Draw the structures of all conceivable disubstituted benzene isomers bearing two identical substituents ( $C_6H_4R_2$ ).**

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

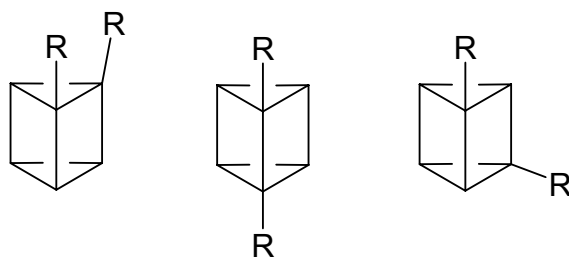


**20.3 How many isomers of Dewar benzene will be conceivable if it is substituted with two identical substituents? Draw the structures.**

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):



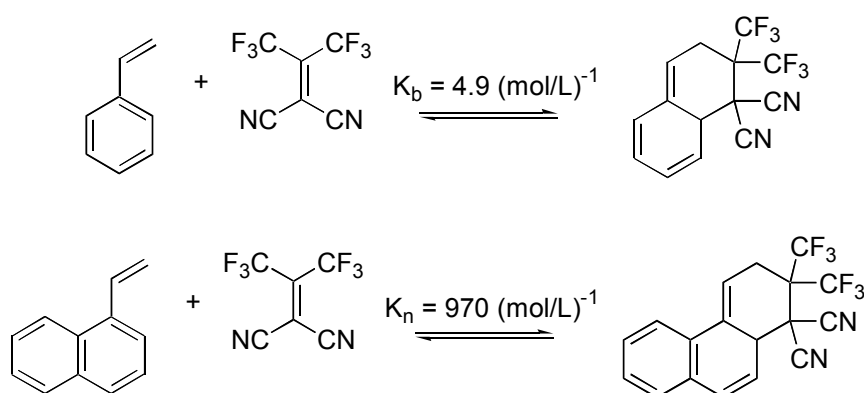
According to Prof. Ladenburg, the benzene model is in agreement with the fact that there are three disubstituted benzene isomers:



Ladenburg was wrong. The list above is not complete.

**20.4 There is a 4<sup>th</sup> 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.

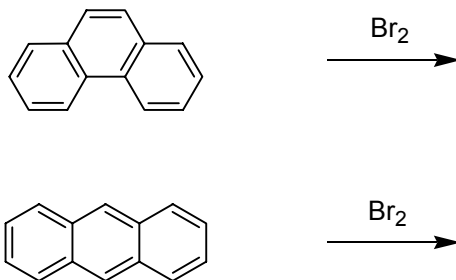
**20.5 Calculate the free enthalpies of reaction  $\Delta_r G$  for both reactions.**

**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)?

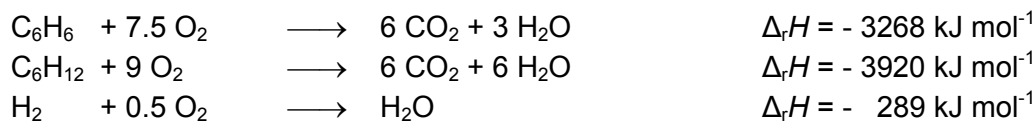


**20.8 Fill in the structures of the reaction products.**



## 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.

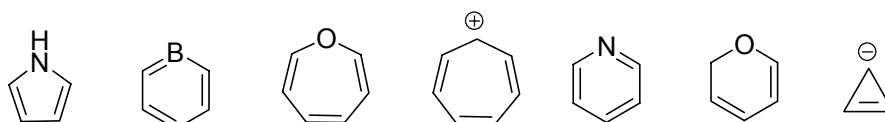
**21.2** Calculate the expected enthalpy of hydrogenation of a six-membered ring with three double bonds and compare it with the value obtained in 74.1. What is the reason for this difference?

## 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.



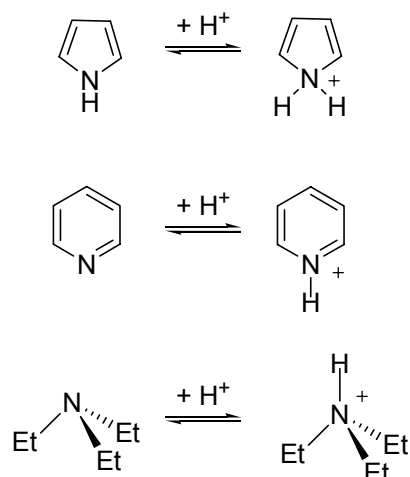
**22.2** Which compounds are aromatic?

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

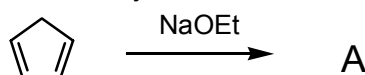
**22.3** Which of the following two compounds would you expect to have a greater dipole moment? Support your answer by writing the corresponding (plausible) resonance structures.



**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.

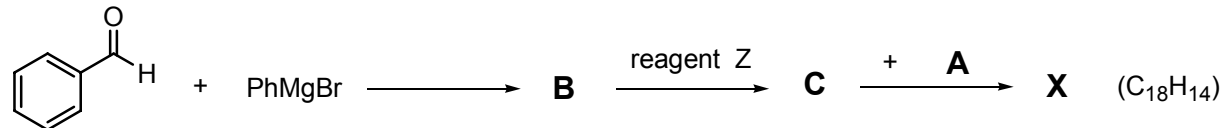


**22.5** Write down a structure for compound A.

**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.

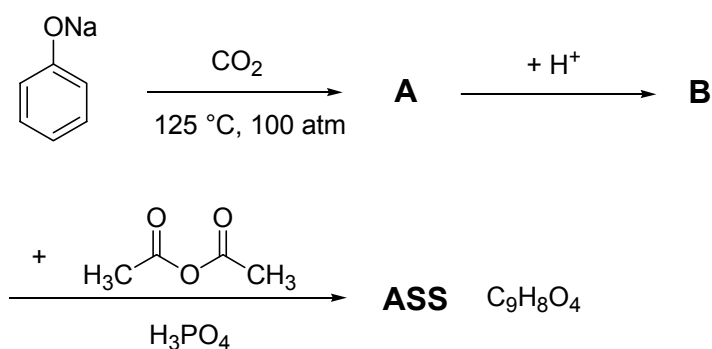
**22.9** Suggest a plausible reagent Z.

**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.

## 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<sup>®</sup> by a German company in 1899. Now, billions of tablets are sold each year. Acetylsalicylic acid can be synthesized according to the following scheme:



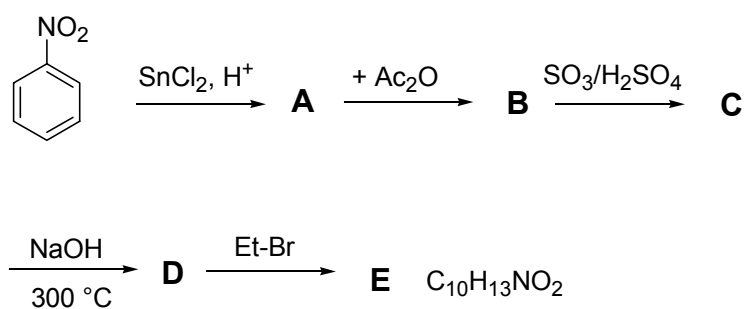
**23.1 Give structural formulas for A, B and ASS.**

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

	true	false	no decision possible
<b>ASS</b> 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"/>

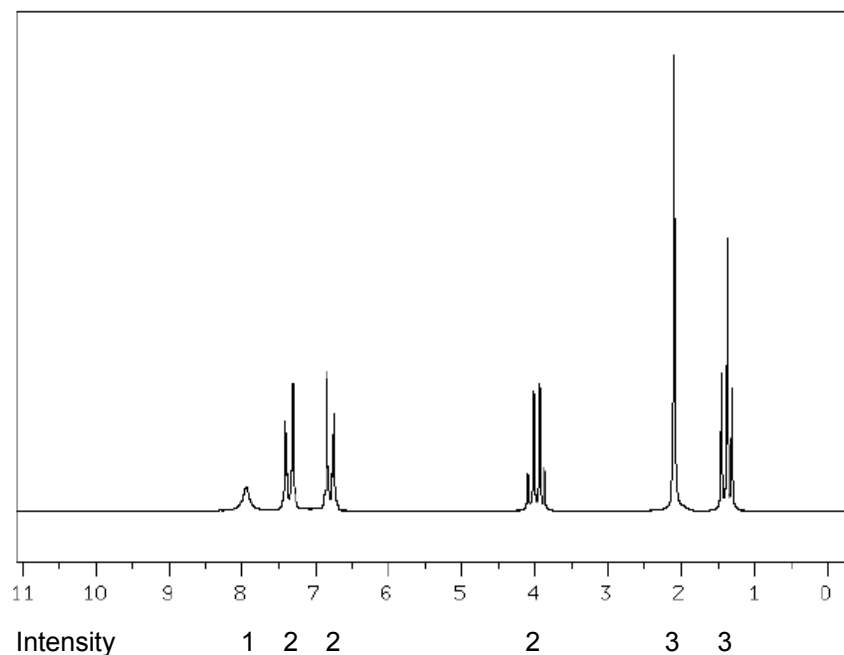
**Phenacetin:**

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 <sup>1</sup>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 <sup>1</sup>H-NMR chemical shifts on page 24)**

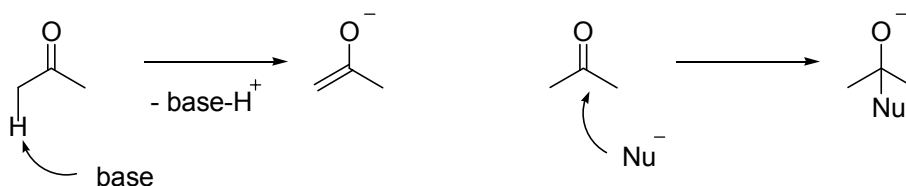


**23.4** If you compare acetylsalicylic acid (ASS) and phenacetin (E), which of the following statements are true, false or can not be evaluated?

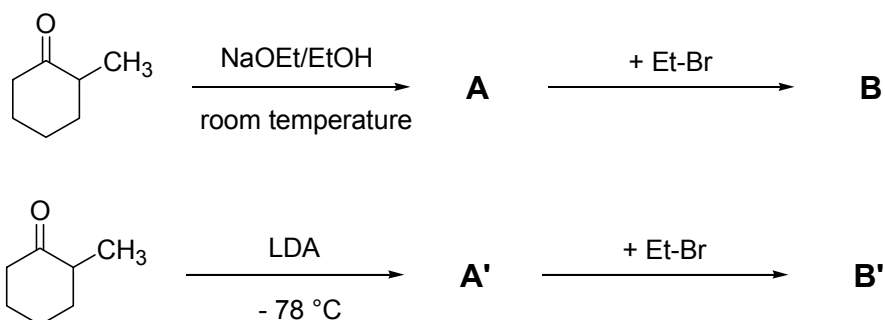
	true	false	no decision possible
At pH = 9 phenacetin is more polar than acetyl salicylic acid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Both compounds can be deprotonated by NaHCO <sub>3</sub>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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 R <sub>f</sub> value for phenacetin is larger than for acetylsalicylic acid	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

## 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):

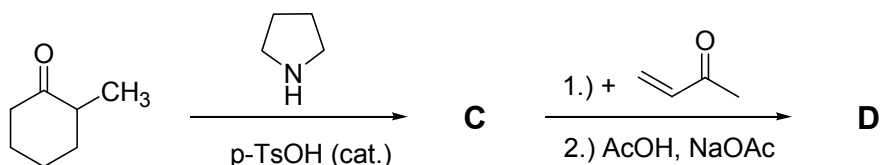


LDA: lithium diisopropyl amide,  $\text{Pr}_2\text{NLi}$ , a strong non-nucleophilic base

**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.

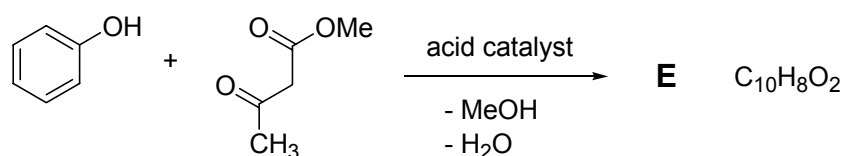


**24.3 Write down the mechanism of the formation of enamine C. What about regiochemistry here?**

**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).**

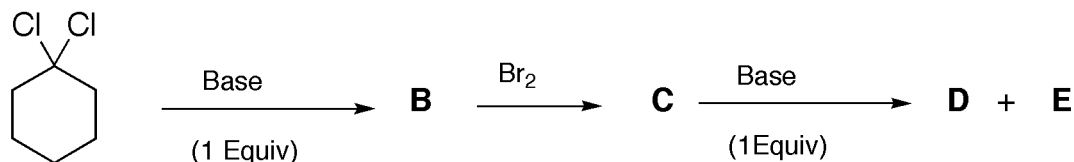
Consider the following reaction sequence for the synthesis of a coumarin derivative (nowadays solid phase bound acids such as Nafion H or Amberlyst are used as acid catalysts).



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

## 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.



**A**

- 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**.

## Problem 26: Chiral Compounds

There are a number of compounds with the molecular formula  $\text{C}_4\text{H}_8\text{O}$  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.

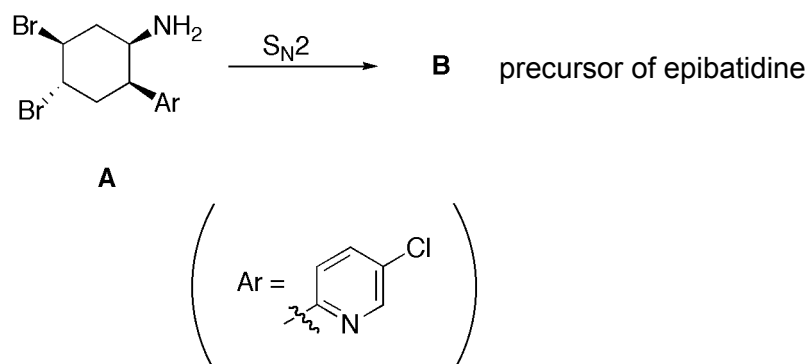
## Problem 27: Monosaccharides

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  $\text{NaBH}_4$ .

- 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.

## 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  $S_N2$  reaction.



28.1 Mark all asymmetric stereocenters in **A** by an \*.

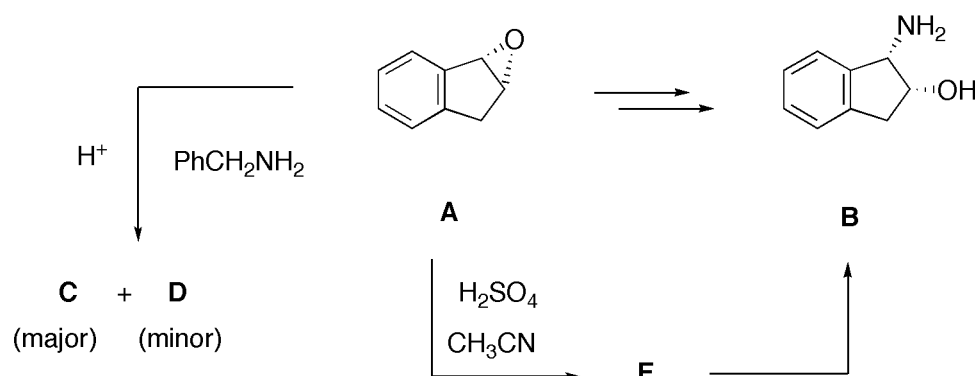
28.2 Determine the absolute configuration of **A** according to the CIP (R/S) nomenclature at all stereocenters.

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**.

## 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.

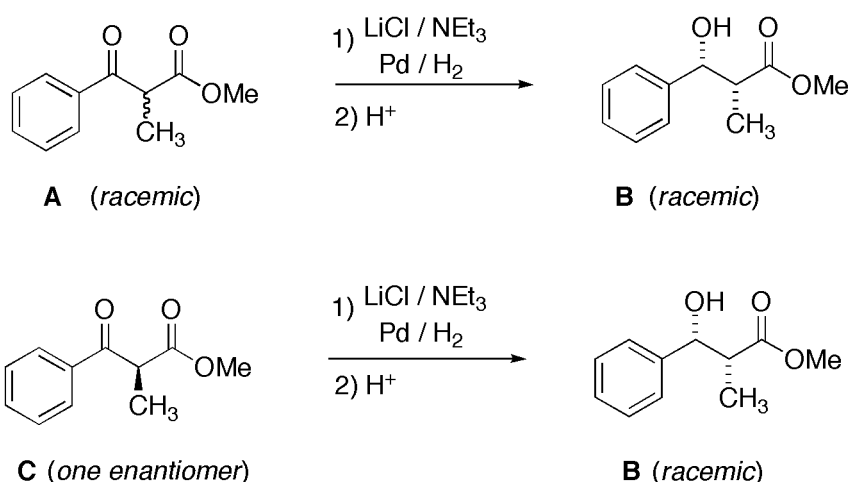
29.2 After the treatment of **A** with concentrated  $H_2SO_4$  and acetonitrile under thermodynamic conditions, only **E** formed that was subsequently hydrolyzed to **B**. Draw the structure of **E** and a mechanism leading to this compound. Take into account stereochemical and regiochemical issues.

### 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.

E. g., *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.



## 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.

$c_0 \cdot (\text{gL}^{-1})^{-1}$	0.5	0.75	1	1.5
$c_1 \cdot (\text{gL}^{-1})^{-1}$	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.

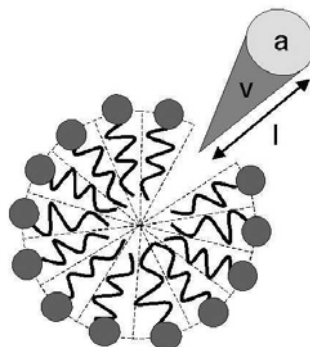
There is the general aggregation equilibrium of  $N$  molecules of  $A$  in an aggregate  $B$  with the equilibrium constant  $K$ .  $c(A)$  and  $c(B)$  are the molar concentrations of monomers and aggregates, and  $c_0$  the total concentration of monomers in the solution.

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

$N = 50$  and  $K = 10^{90} \text{ L}^{49} \text{ mol}^{-49}$  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):

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

**31.6 a)** Which shape do SDS micelles in aqueous solution have? Calculate.

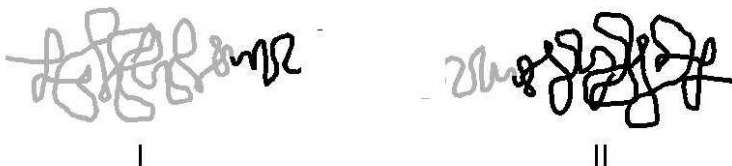
(Hint: Are the ideal values calculated in 31.5 lower or upper values?)

**b)** What do you think will form after the addition of base?

## 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), PVP<sub>23</sub>-b-PS<sub>122</sub> (**A**) and PVP<sub>45</sub>-b-PS<sub>122</sub> (**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:

$$\Pi V = nRT.$$

$\Pi$  is the osmotic pressure.

The solutions of **A** and **B**, both with concentrations of  $c = 8.000 \text{ gL}^{-1}$  are analyzed. The heights of the solvent columns above the solvent in osmotic equilibrium with the polymer-containing solutions are 11.02 mm for polymer **A** and 2.48 mm for polymer **B**. ( $\rho(\text{solvent}) = 0.866 \text{ g}\cdot\text{cm}^{-3}$  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  $R = 25 \text{ nm}$ ,  $N = 310$

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

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 mL of polymer solution ( $c(\text{polymer}) = 10 \text{ gL}^{-1}$ ). 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.

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

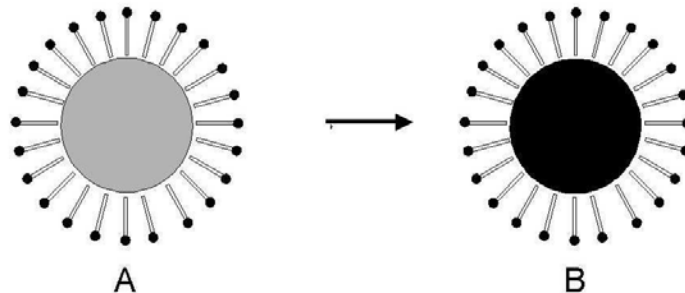
### **32.4 Which gold particle diameters do you expect for the four experiments with the two polymers and the two given amounts of added gold acid ?**

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

## 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.

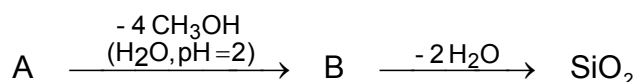
33.4 Which kind of enzyme would you choose for this purpose?

- |   | 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"/> |

## Problem 34: Silica Nanostructures

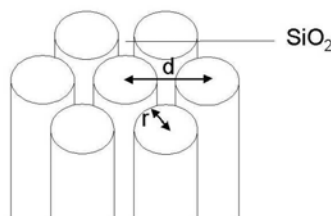
Porous silicates are important as ion exchangers, molecular sieves and catalysts in petrochemistry. Classic zeolites are silicates having defined channels with diameters of 0.4 nm to 1.5 nm. Materials with larger pore diameters are needed to accept larger molecules and make them react. Surfactants or 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  $\lambda = 0.15 \text{ nm}$ ) 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 %

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

### 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  $V_{ads}$  and maximum adsorbable volume  $V^*$  can be expressed as**

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

Concerning the adsorption of  $N_2$  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  $N_2$  molecule is  $A(N_2) = 0.16 \text{ nm}^2$ .

surfactant \ p	1.30 $\cdot 10^5 \text{ Pa}$	2.60 $\cdot 10^5 \text{ Pa}$	4.00 $\cdot 10^5 \text{ Pa}$	5.30 $\cdot 10^5 \text{ Pa}$	6.60 $\cdot 10^5 \text{ Pa}$	8.00 $\cdot 10^5 \text{ Pa}$
$C_{12}H_{25}N(CH_3)_3Cl$	4.6	8.2	11.9	14.5	16.7	19.0
$C_{14}H_{29}N(CH_3)_3Cl$	6.0	11.5	16.0	19.0	23.1	25.5
$C_{16}H_{33}N(CH_3)_3Cl$	7.8	14.0	19.0	24.0	28.0	31.3
$C_{18}H_{37}N(CH_3)_3Cl$	8.1	14.7	20.8	25.5	29.0	34.0

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

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

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

**34.4 c) Calculate the pore radii from mass loss (in 34.2) and the specific surfaces  $A_{sp}$  determined in b) without using the pore distance  $d$ .**

## Notes for the Practical Problems:

In the practical preparatory problems we have not included specific details of handling or disposal of laboratory materials and waste as regulations vary greatly from country to country.

We take it for granted that the students are able to perform basic experimental techniques such as titration, filtration, recrystallisation, distillation.

As mentioned in the preface we attach great importance to safety.

**The rules below have to be followed during laboratory work at the 36<sup>th</sup> IChO in Kiel.**

- The students have to bring their own laboratory coats.
- When the students enter the labs they must familiarise themselves with the locations of emergency exits  
safety shower, fire blanket and eye wash.
- Laboratory coats, eye protections and closed shoes must be worn at all times in the laboratories. Long hair has to be tied.
- Coats and bags are forbidden in the laboratory. They have to be deposited in the cloakroom.
- Eating, drinking or smoking in the laboratory or tasting any chemicals are strictly forbidden.
- Pipetting by mouth is strictly forbidden.
- All potentially dangerous materials will be labelled by international symbols. Each student is responsible for recognizing these symbols and knowing their meaning.
- Do not dispose of chemicals down the sink. Follow all disposal rules provided by the organizer.
- Do not hesitate to ask an instructor if you have any questions concerning safety issues.

A brief instruction will be given on the day preceding the examination.

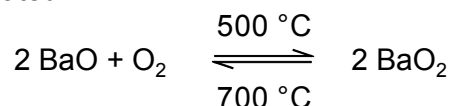
Apologies for all the do's and don't's - we guarantee that the students will still be allowed to perform the experiments and we hope they will enjoy it!

## Problem 35: 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 peroxy 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

reagent	concentration	R phrases	S phrases
ammonia	w(NH <sub>3</sub> ) = 25 %	34-50	26-36/37/39-45-61
EDTA disodium salt	c(Na <sub>2</sub> EDTA) = 0.1 mol L <sup>-1</sup>		
ethanol	w(C <sub>2</sub> H <sub>5</sub> OH) = 96 %	11	7-16
hydrogen peroxide	w(H <sub>2</sub> O <sub>2</sub> ) = 3%	34	3-26-36/37/39-45
methyl red	solid		
naphthol green B	solid		
perchloric acid	w(HClO <sub>4</sub> ) = 10%	10-35	23.2-26-36/37/39-45
phthalein purple	solid		
potassium perman- ganate	c(KMnO <sub>4</sub> ) = 0.1 mol L <sup>-1</sup>		
strontium chloride hexahydrate	solid		

### Procedure 1: Preparation of strontium peroxide

5.0 g of strontium chloride hexahydrate are dissolved in about 2.5 mL of distilled water and 25 mL of dihydrogen peroxide (w(H<sub>2</sub>O<sub>2</sub>) = 3%) are added. A solution of 3.5 mL of ammonia (w(NH<sub>3</sub>) = 25%) in 50 mL 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 SrO<sub>2</sub>. 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 mL Erlenmeyer flask and the contents dissolved in 5 mL of perchloric acid. The volume of the solution is increased to about 100 mL by addition of water. The determination of the peroxide content is performed by titration with potassium permanganate solution ( $c(\text{KMnO}_4) = 0.02 \text{ mol}\cdot\text{L}^{-1}$ ), 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 mL.

### **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 mL Erlenmeyer flask and the contents dissolved in 5 mL of perchloric acid. The solution is made up to a volume of 50 mL and 15 mL of ammonia solution, 60 mL of ethanol and 2 mL of phthalein purple indicator are added. The resulting deep purple solution is titrated with disodium EDTA ( $c(\text{Na}_2\text{EDTA}) = 0.1 \text{ mol L}^{-1}$ ) until the solution is intense light-green in colour.

Record the volume of the  $\text{Na}_2\text{EDTA}$  solution in mL

### **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 mL of ammonia solution. The solution is filled up to a volume of 100 mL. 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  $\text{SrO}_2$ .**
- 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  $\text{SrO}_2$  from  $\text{SrCl}_2$ ,  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$ .**
- 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?**

## **Problem 36: 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



becomes colourless. Just before the end point 2 - 3 mL of starch solution are added as an indicator.

Record the volume of the sodium thiosulfate solution used in mL

#### **Preparation of the starch solution:**

About 2 g of starch are suspended in 3 mL of distilled water and the suspension vigorously stirred. The mixture is added to 300 mL 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**

## **Problem 37: 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  $\text{H}_3\text{CCOO}^-$

carbonate  $\text{CO}_3^{2-}$

chloride  $\text{Cl}^-$

chromate  $\text{CrO}_4^{2-}$

nitrate  $\text{NO}_3^-$

oxalate  $\text{C}_2\text{O}_4^{2-}$

perchlorate  $\text{ClO}_4^-$

sulfate  $\text{SO}_4^{2-}$

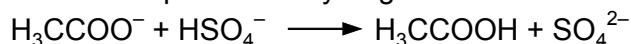
### Preparation of the soda extract

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:

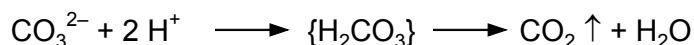


Dilute sulfuric acid also forms acetic acid upon reaction with acetate anions.

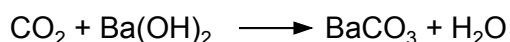
Procedure: The solid sample is grinded with four times the amount of potassium hydrogensulfate in a mortar. In the presence of acetate anions, there is the characteristic smell of acetic acid.

#### Carbonate

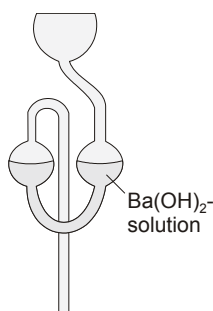
Theory: Carbonate anions react with dilute hydrochloric acid to form unstable carbonic acid that decomposes into water and carbon dioxide:



Carbon dioxide reacts with barium hydroxide to form barium carbonate:



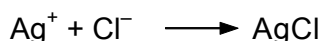
Procedure: In a test tube, dilute hydrochloric acid is added to a small amount of the sample. The test tube is closed immediately connected to a fermentation tube filled with freshly prepared barium hydroxide solution. The test tube is gently heated. In the presence of carbonate anions, white flakes 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:

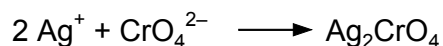


Silver chloride is soluble in concentrated ammonia solution. It is insoluble in concentrated nitric acid.

Procedure: An aqueous solution of silver nitrate is added to 5 mL 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 mL 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 mL 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.

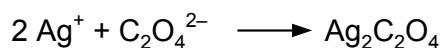
## Nitrate

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 mL of an iron(II) sulfate solution acidified with sulfuric acid is added to 2.5 mL 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

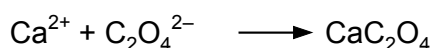
Theory: In a neutral solution, oxalate anions react with silver nitrate solution to form silver oxalate:



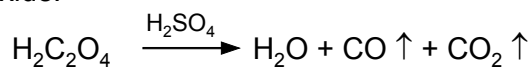
Silver oxalate is sparingly soluble in acetic acid. It is soluble in nitric acid and ammonia solution.

Procedure: An aqueous solution of silver nitrate is added to 5 mL 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:

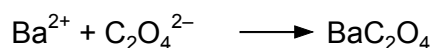


Calcium oxalate is insoluble in dilute acetic acid. It is soluble in strong mineral acids. Calcium oxalate is oxidized to carbon dioxide by potassium permanganate in an acidic solution. In this reaction, the manganese(VII) cations are reduced to manganese(II) cations. Oxalates and oxalic acid decompose by reaction with concentrated sulfuric acid into carbon monoxide and carbon dioxide:



Procedure: 5 mL 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:

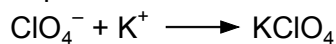


Barium oxalate dissolves in dilute acetic acid.

Procedure: An aqueous solution of barium chloride is added to 5 mL 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.

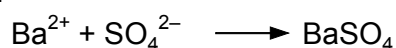
Procedure: An aqueous solution of potassium nitrate is added to 5 mL of the soda extract slightly acidified with nitric acid. In the presence of perchlorate anions, a white precipitate of potassium perchlorate forms.

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 mL of an aqueous iron(II) sulfate solution are added to 5 mL 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**

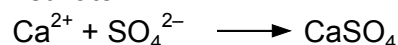
Theory: In an acidic solution acidified with hydrochloric acid sulfate anions react with barium chloride to form barium sulfate:



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 mL 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 mL 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

reagent	concentration	R phrases	S phrases
acetic acid	w(H <sub>3</sub> CCOOH) = 99%	10-35	23-26-45
acetic acid	w(H <sub>3</sub> CCOOH) = 5%		
ammonia	w(NH <sub>3</sub> ) = 25%	34-50	26-36/37/39-45-61
ammonium acetate	solid		
barium chloride	c(BaCl <sub>2</sub> · 2 H <sub>2</sub> O) ~ 1.5 mol L <sup>-1</sup>	20/22	28
barium hydroxide	w(Ba(OH) <sub>2</sub> · 8 H <sub>2</sub> O) ~ 2 %	20/22-34	26-36/37/39-45
calcium chloride	c(CaCl <sub>2</sub> · 2 H <sub>2</sub> O) = 1 mol L <sup>-1</sup>	36	22-24
hydrochloric acid	w(HCl) = 36%	34-37	26-45
hydrochloric acid	c(HCl) = 2 mol L <sup>-1</sup>	34	26-36/37/39-45
iron(II) sulfate	c(FeSO <sub>4</sub> · 7 H <sub>2</sub> O) = 1 mol L <sup>-1</sup>	22	24/25
nitric acid	w (HNO <sub>3</sub> ) = 65%	8-35	23-26-36-45
nitric acid	c (HNO <sub>3</sub> ) = 2 mol L <sup>-1</sup>	8-35	23-26-36-45
potassium hydrogen-sulfate	solid	34-37	26-36/37/39-45
potassium nitrate	saturated	36/38	26
potassium perman-ganate	c(KMnO <sub>4</sub> ) = 0.02 mol L <sup>-1</sup>	52/53	61
silver nitrate	c(AgNO <sub>3</sub> ) = 0.2 mol L <sup>-1</sup>	34-51/53	26-36/37/39-45-61
sodium acetate	solid		

sodium carbonate	solid	36	22-26
sodium hydroxide	w(NaOH) ~ 5 %	35	26-37/39-45
sulfuric acid	w(H <sub>2</sub> SO <sub>4</sub> ) = 95-97 %	35	26-30-45
sulfuric acid	c(H <sub>2</sub> SO <sub>4</sub> ) = 2 mol L <sup>-1</sup>	35	26-30-45

### 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: LiCl, LiClO<sub>4</sub>, Na(OOCCH<sub>3</sub>), Na<sub>2</sub>CO<sub>3</sub>, NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, NaClO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, AlCl<sub>3</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, FeCl<sub>2</sub>, FeSO<sub>4</sub>, CoCl<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, CoSO<sub>4</sub>, NiCl<sub>2</sub>, Ni(NO<sub>3</sub>)<sub>2</sub>, NiSO<sub>4</sub>. 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.

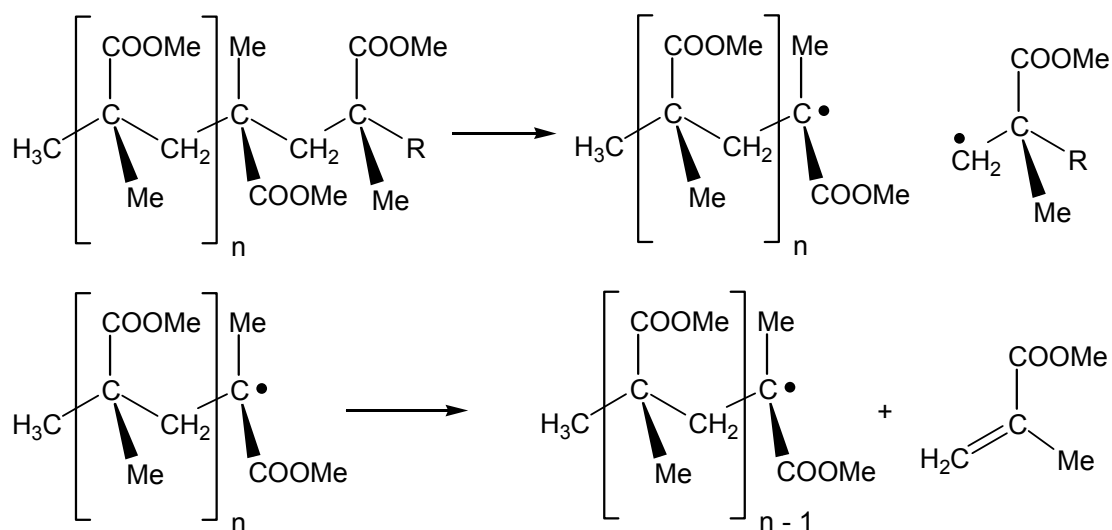
salt	formula	R phrases	S phrases
aluminium chloride	AlCl <sub>3</sub> · 6 H <sub>2</sub> O	36/38	
aluminium sulfate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · x H <sub>2</sub> O		24/25
cobalt(II) chloride	CoCl <sub>2</sub> · 6 H <sub>2</sub> O	49-22-42/43-50/53	53-22-45-60-61
cobalt(II) nitrate	Co(NO <sub>3</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O	22-20-43	36/37
cobalt(II) sulfate	CoSO <sub>4</sub> · 7 H <sub>2</sub> O	49-22-42/43-50/53	53-22-45-60-61
iron(II) chloride	FeCl <sub>2</sub> · 4 H <sub>2</sub> O	22-38-41	26-39
iron(II) sulfate	FeSO <sub>4</sub> · 7 H <sub>2</sub> O	22	24/25
lithium chloride	LiCl	22-36/38	
lithium perchlorate	LiClO <sub>4</sub>	8-22-36/37/38	17-26-36
nickel(II) chloride	NiCl <sub>2</sub> · 6 H <sub>2</sub> O	25-43-50/53	24-37-45-61
nickel(II) nitrate	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O	8-22-43	24-37
nickel(II) sulfate	NiSO <sub>4</sub> · 6 H <sub>2</sub> O	22-40-42/43-50/53	22-36/37-60-61
potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	36/37/38	22-26
potassium dichromate	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	49-46-21-25-26-37/38- 41-43-50/53	53-45-60-61
potassium nitrate	KNO <sub>3</sub>	36/38	26
potassium sulfate	K <sub>2</sub> SO <sub>4</sub>		
sodium acetate	NaH <sub>3</sub> CCOO		
sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	36	22-26
sodium chloride	NaCl		
sodium nitrate	NaNO <sub>3</sub>	8-22-36	22-24-41
sodium oxalate	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	21/22	24/25
sodium perchlorate	NaClO <sub>4</sub> · H <sub>2</sub> O	9-22	13-22-27
sodium sulfate	Na <sub>2</sub> SO <sub>4</sub>		



## Problem 38: 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 mL distillation flask

sand bath on heating plate or heating mantle (50 mL)

stand

## Chemicals

30 g Polymethylmethacrylate (pulvarized) or

30 g Polymethylmethacrylate-waste (for example covers of rear lamps that have been pulvarized)

0.6 g dibenzoylperoxide ( $C_{14}H_{10}O_4$ )

## Safety measurements: Hazard Symbols and Safety Codes

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.

methyl methacrylate                      irritant Xi, highly flammable F

R 11, 37/39, 43; S 24, 37, 46

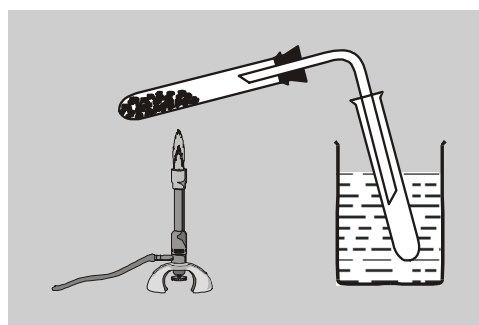
dibenzoylperoxide

irritant Xi, explosive E

R 2, 36, 43; S 3, 7, 14, 24, 26, 36/37/39

## 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?**

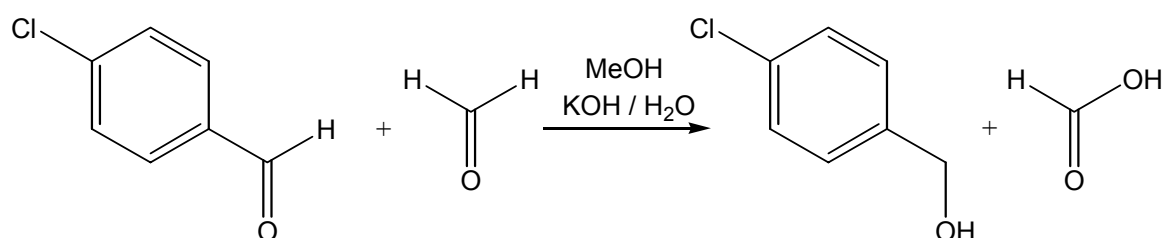
**38.6 Write down the polymerization reaction using the decomposition of dibenzoyl-peroxide as the initial step.**

## Problem 39: 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.

### List of Equipment

three-necked flask (250 mL)

dropping funnel

magnetic stirrer with heating plate

reflux condenser

internal thermometer

magnetic stirrer bar

water bath on heating plate	beaker (500 mL and 250 mL)
heating mantle (250 mL) 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

<i>para</i> -chlorobenzaldehyde	methanol
potassium hydroxide	ethanol
distilled water	ethyl acetate
formalin (aqueous formaldehyde solution, 37%)	
light petroleum ether (boiling range 40-70°C)	
TLC plates (silica gel 60 F254)	

### Safety measurements: Hazard Symbols and Safety Codes

<i>para</i> -chlorobenzaldehyde	harmful Xn, dangerous for the environment N, R 22, 36/38; S 22, 26, 37/39
methanol	highly flammable F, toxic T R 11, 23/25; S 7, 16, 37/39
potassium hydroxide	corrosive C R 22, 35; S 26, 36/37/39, 45
ethanol	highly flammable F R 11; S 7, 16
ethyl acetate	highly flammable F, irritant Xi R 11, 36, 66,67; S 16, 26, 33
formalin (37%)	toxic T R 23/24/25, 34, 39, 40, 43; S 26, 36/37/45, 51
light petroleum ether	highly flammable F, harmful Xn, dangerous for the environment N, R 11, 20, 38, 48, 51/53, 62, 65, 67; S 26, 36/37/45, 51
<i>para</i> -chlorobenzylalcohol	harmful Xn, dangerous for the environment N, R 22, 36/38, 51, 53; S 23, 26, 61

### Procedure

Place 28.1 g of *para*-chlorobenzaldehyde into a 250 mL 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 mL of water. Add 60 mL 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 mL 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:

1. water
2. water : ethanol (5 : 1)
3. 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?**

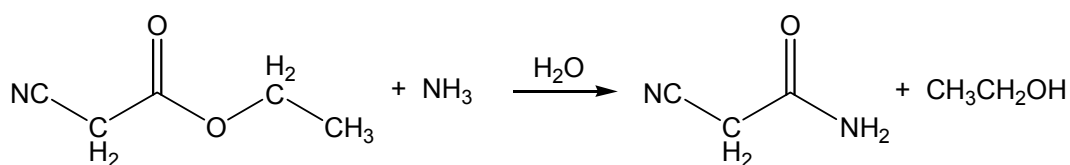
**39.5 Determine the respective  $R_f$ -values.**

**39.6 Describe the reaction mechanism.**

## **Problem 40: Ammonolysis of an activated carbonic 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.



### List of Equipment

magnetic stirrer with heating plate  
 Erlenmeyer flask (250 mL)  
 2 pipettes (10 mL) with pipette control  
 vacuum filter (Ø 5 cm) or Hirsch funnel  
 vacuum filtration apparatus  
 graduated measuring cylinder  
 spatula,

magnetic stirrer bar  
 beaker (250 mL)  
 thermometer  
 dropping funnel  
 crystallizing dish or beaker  
 balance (precision 0.01 g)  
 stand

### List of Chemicals

cyanoacetic ethyl ester  
 ethanol  
 ice

aqueous ammonia (25 %)  
 distilled water

### Safety measurements: Hazard Symbols and Safety Codes

aqueous ammonia (25 %)	corrosive C, dangerous for the environment N R 34, 50; S 26, 36/37/39, 45, 61
ethanol	highly flammable F R 11; S 7,16

### Procedure

Place 32.0 mL (0.3 mol) of cyanoacetic ethyl ester into a 200 mL Erlenmeyer flask equipped with a magnetic stirrer bar and an internal thermometer. Support a dropping funnel, containing 37.4 mL (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 mL beaker and recrystallize it from 70 mL 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.**

## **Avoiding culture shock or The German way of life**

People of different countries have different ways of doing things. So, to avoid culture shock, it's important to be prepared before you visit another country. Here are some notes students made after their year in Germany. This list is supposed to help you while you stay in Germany.

- Germans close room doors and pull shades.
- They worry about their health. (There's something wrong with them if they don't.)
- They get up early – and go to bed early.
- They have small refrigerators. (You shouldn't raid them.)
- There is more fresh food, less processed stuff.
- Meals are social events (so hold back with your fork until everybody is there.)
- If guests want more food, they take it. (Don't wait to be asked or you'll wait for ever.)
- Germans absolutely love mineral water.
- They would never visit other people's home without an invitation.
- They bring flowers when they visit friends. (Uneven number, no red or white roses unless in love.)
- They shake hands any time they meet people.
- They don't stand in line. (You have to push your way to the front of stores and onto trains.)
- Few people use credit cards for shopping.
- There are often restroom attendants. (They expect money.)
- Weekends are totally dead.
- German families go for long walks on Sundays.
- Germans don't waste time on polite phrases – they say what they mean.