36th

8 theoretical problems
2 practical problems

THE THIRTY-SIXTH
INTERNATIONAL CHEMISTRY OLYMPIAD
18–27 JULY 2004, KIEL, GERMANY

THEORETICAL PROBLEMS

PROBLEM 1

Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

The thermodynamic properties and the composition of natural gas can be found in Table 1.

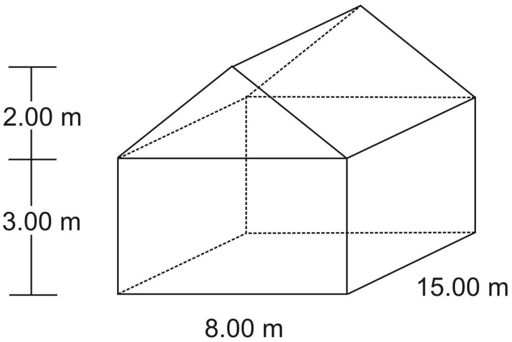
1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

a) Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).

b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m^3 of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of $\rho = 1.00$ kg dm^{-3} and air behaving like an ideal gas.



1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C and the energy which is required to heat the initial amount of air (21.0 % of O_2, 79.0 % of N_2) to 30.0 °C at a pressure of 1.013×10^5 Pa.

In February, the outside temperature is about 5 °C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is 1.00 W K^{-1} m^{-1}.

1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0 °C during the party (12 hours).

1.00 m^3 of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0$ (kJ mol^{-1})$^{-1}$	S^0 (J mol^{-1} K^{-1})$^{-1}$	C_p^0 (J mol^{-1} K^{-1})$^{-1}$
CO_2 (g)	0.0024	-393.5	213.8	37.1
N_2 (g)	0.0134	0.0	191.6	29.1
CH_4 (g)	0.9732	-74.6	186.3	35.7
C_2H_6 (g)	0.0110	-84.0	229.2	52.5
H_2O (l)	-	-285.8	70.0	75.3
H_2O (g)	-	-241.8	188.8	33.6
O_2 (g)	-	0.0	205.2	29.4

Equation:

$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$

J energy flow E along a temperature gradient (wall direction z) per area A and time Δt

d wall thickness

λ_{wall} heat conductivity

ΔT difference in temperature between the inside and the outside of the house

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SOLUTION

1.1 Chemical equations:

a) methane: $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$

b) ethane: $2\,C_2H_6 + 7\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O$

Thermodynamic data for the equations:

$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)]$ kJ mol^{-1} = -802.5 kJ mol^{-1}

$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2]$ J mol^{-1} K^{-1} = -5.3 J mol^{-1} K^{-1}

$\Delta G^0 = -802.5\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (-5.3\ \text{J mol}^{-1}\ \text{K}^{-1}) = -800.9\ \text{kJ mol}^{-1}$

Methane: $\Delta H^0 = -802.5\ \text{kJ mol}^{-1}$; $\Delta S^0 = -5.3\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -800.9\ \text{kJ mol}^{-1}$

$\Delta H^0 = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)]\ \text{kJ mol}^{-1} = -2856.8\ \text{kJ mol}^{-1}$

$\Delta S^0 = [6\times188.8 + 4\times213.8 - 2\times229.2 - 7\times205.2]\ \text{J mol}^{-1}\ \text{K}^{-1} = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G^0 = -2856.8\ \text{kJ mol}^{-1} - 298.15\ \text{K} \times (93.2\ \text{J mol}^{-1}\ \text{K}^{-1}) = -2884.6\ \text{kJ mol}^{-1}$

Ethane: $\Delta H^0 = -2856.8\ \text{kJ mol}^{-1}$; $\Delta S^0 = +93.2\ \text{J mol}^{-1}\ \text{K}^{-1}$; $\Delta G^0 = -2884.6\ \text{kJ mol}^{-1}$

1.2 a) Amount of methane and ethane in 1 m^3 natural gas:

$m = \rho \times V = 0.740\ \text{g dm}^{-3} \times 1000\ \text{dm}^3 = 740\ \text{g}$

$M_{av} = \sum_i x(i)M(i) = (0.0024 \times 44.01\ \text{g mol}^{-1}) + (0.0134 \times 28.02\ \text{g mol}^{-1})$

$+ (0.9732 \times 16.05\ \text{g mol}^{-1}) + (0.011 \times 30.08\ \text{g mol}^{-1}) = 16.43\ \text{g mol}^{-1}$

$n_{tot} = m\ (M_{av})^{-1} = 740\ \text{g} \times (16.43\ \text{g/mol})^{-1} = 45.04\ \text{mol}$

$n(i) = x(i) \cdot n_{tot}$

$n(CH_4) = x(CH_4) \times n_{tot} = 0.9732 \times 45.04\ \text{mol} = 43.83\ \text{mol}$

$n(C_2H_6) = x(C_2H_6) \times n_{tot} = 0.0110 \times 45.04\ \text{mol} = 0.495\ \text{mol}$

b) Energy of combustion, deviation:

$E_{comb.}(H_2O(g)) = \sum_i n(i)\Delta_c H^\circ(i) =$

$= 43.83\ \text{mol} \times (-802.5\ \text{kJ mol}^{-1}) + 0.495\ \text{mol} \times 0.5 \times (-2856.8\ \text{kJ mol}^{-1})$

$= -35881\ \text{kJ}$

$E_{comb.}(H_2O(g)) = -35881\ \text{kJ}$

Deviation from PUC

$E_{PUC}(H_2O(g)) = 9.981\ \text{kWh m}^{-3} \times 1\ \text{m}^3 \times 3600\ \text{kJ (kWh)}^{-1} = 35932\ \text{kJ}$

Deviation: $\Delta E = (E_{comb.}(H_2O(g)) - E_{PUC}(H_2O(g)) \times 100\ \% \times [E_{comb.}(H_2O(g))]^{-1}$

$= (35881\ \text{kJ} - 35932\ \text{kJ}) \times 100\ \% \times (35881\ \text{kJ})^{-1} = -0.14\%$

1.3 Energy for heating the water:

Volume of water: $V_{water} = 22.5\ \text{m}^3$

$n_{water} = V_{water}\ \rho_{water}\ (M_{water})^{-1} = 22.5\ m^3 \times 10^6\ g\ m^{-3} \times (18.02\ g\ mol^{-1})^{-1} = 1.249\times10^6\ mol$

$E_{water} = n_{water} \times C_p \times \Delta T = 1.249\times10^6\ mol \times 75.30\ J\ K^{-1}\ mol^{-1} \times 14\ K = 1316\ MJ$

Energy for heating the air:

Volume of the house is:

$V_{air} = (15\ m \times 8\ m \times 3\ m) + 0.5 \times (15\ m \times 8\ m \times 2\ m) = 480\ m^3$

$n_{air} = pV\ (RT)^{-1} = 1.013\times10^5\ Pa \times 480\ m^3 \times (8.314\ J\ (K\ mol)^{-1} \times 283.15\ K)^{-1} =$

$= 2.065\times10^4\ mol$

$C_p(air) = 0.21 \times 29.4\ J\ (K\ mol)^{-1} + 0.79 \times 29.1\ J\ (K\ mol)^{-1} = 29.16\ J\ (K\ mol)^{-1}$

$E_{air} = n_{air} \times C_p(air) \times \Delta T = 2.065\times10^4\ mol \times 29.17\ J\ (K\ mol)^{-1} \times 20\ K = 12.05\ MJ$

1.4 Energy for maintaining the temperature:

Surface area of the house:

$A_{house} = 3\ m \times 46\ m + 8\ m \times 2\ m + ((2\ m)^2 + (4\ m)^2)^{1/2} \times 2 \times 15\ m = 288.16\ m^2$

Heat conductivity: $\lambda_{wall} = 1\ J\ (s\ K\ m)^{-1}$

Energy flux along a temperature gradient (wall thickness d = 0.2 m)

$J = E_{loss}\ (A \times \Delta t)^{-1} = \lambda_{wall}\ \ \Delta T\ \ d^{-1}$

$E_{loss} = 288.16\ m^2 \times (12\cdot60\cdot60\ s) \times 1\ J\ (s\ K\ m)^{-1} \times 25\ K \times (0.2\ m)^{-1} = 1556\ MJ$

$E_{loss} = 1556\ MJ$

1.5 Total energy and costs:

Total energy: $E_{tot} = E_{water} + E_{air} + E_{loss} = 1316\ MJ + 12\ MJ + 1556\ MJ = 2884\ MJ$

2884 MJ corresponds to $2.884\times10^6\ kJ \times (3600\ s\ h^{-1} \times 9.981\ kJ\ s^{-1}\ m^{-3} \times 0.9)^{-1} = 89.18\ m^3$

Volume of gas: $V = 89.18\ m^3$

2884 MJ correspond to a cost of:

$0.40\ € \ m^{-3} \times 89.18\ m^3 = 35.67\ €$

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

$2.884 \cdot 10^6$ kJ × 0.137 € × (3600 s h^{-1} × 1 kJ s^{-1} h)$^{-1}$ = 109.75 €

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

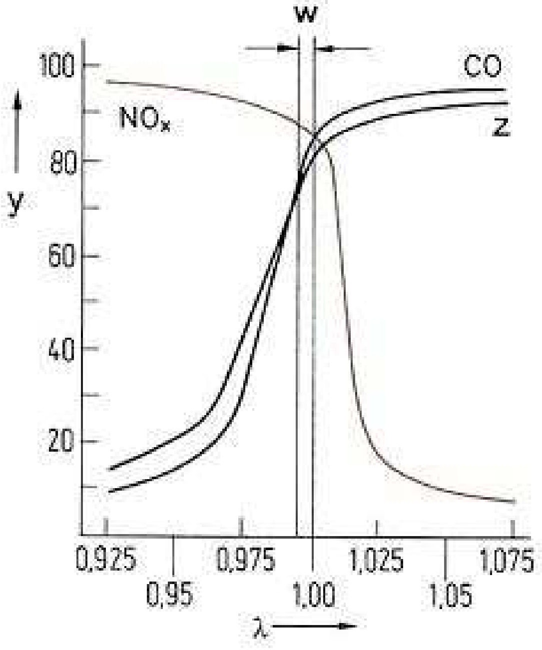
Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ-value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \dfrac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ-window

y: conversion efficiency (%)

z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with K = 0.85 kPa^{-1}.

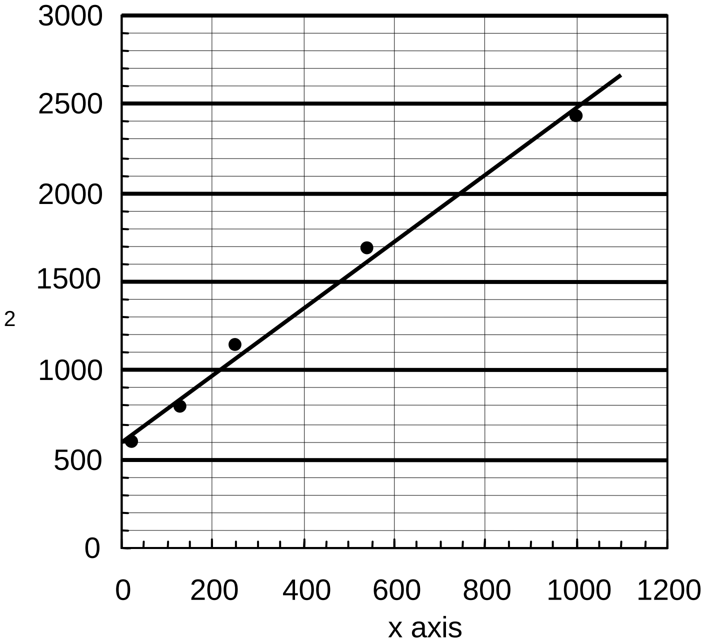
2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.

b) Determine the pressure p at which 15 % of the surface is covered.

c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k\,\theta$

Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).

d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,max}$ needed for a complete coverage of the metal surface and the product $K\,V_{a,max}$.

Hint: Set $\theta = V_a / V_{a,max}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,

$$CO\ (ads.) + 0.5\ O_2\ (ads.) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_{\substack{500\\0}}\ (ads.)$$

In a slow second step, CO_2 is then desorbed from the surface:

$$CO_2\ (ads.) \xrightarrow{k_2} CO_2\ (g)$$

2.4 Derive the formula for the reaction rate of the CO_2(g) - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_i = \frac{K_i \times p_i}{1+\sum_j K_j \times p_j}$$ j: relevant gas components

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SOLUTION

2.1 Reaction equations:

$2\ CO + O_2 \rightarrow 2\ CO_2$

$2\ NO + 2\ CO \rightarrow N_2 + 2\ CO_2$

$2\ C_8H_{18} + 25\ O_2 \rightarrow 16\ CO_2 + 18\ H_2O$

2.2 Questions concerning the λ probe:

	true	false	no decision possible
If the λ-value is in the range of the λ-window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ > 1, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	☒	☐	☐
With λ < 0.975, nitrogen oxides can be reduced poorly.	☐	☒	☐

2.3 a) Surface coverage:

$$\theta = \frac{0.85\ \text{kPa}^{-1} \times 0.65\ \text{kPa}}{1 + 0.85 \times 0.65}$$

θ = 0.356 or 35.6 %

b) Pressure at which 15 % of the surface is covered:

$$\theta = \frac{K \times p}{1 + K \times p} \quad \Leftrightarrow \quad K \times p = \theta + \theta \times K \times p \quad \Leftrightarrow \quad p \cdot (K - \theta \times K) = \theta \quad \Leftrightarrow$$

$$p = \frac{\theta}{K - \theta \times K}$$

θ = 0.15

p = 0.21 kPa

c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures	1
Order of the decomposition reaction at high gas pressures	0

Notes:

$$r = k \times \theta = k \, \frac{K \times p}{1 + K \times p},$$

p *low* $\Rightarrow \; p << \dfrac{1}{K} \Rightarrow r = k\,K\,p$ *reaction order 1.*

p *high* $\Rightarrow \; p >> \dfrac{1}{K} \Rightarrow r = k$ *reaction order 0.*

d) Gas volume $V_{a,max}$ and product $K \cdot V_{a,max}$:

$$\frac{1}{\theta} = \frac{1}{K\,p} + 1 = \frac{V_{a,max}}{V_a} \quad \Rightarrow \quad \frac{1}{K\,V_{a,max}} + \frac{p}{V_{a,max}} = \frac{p}{V_a}$$

Slope: $\dfrac{1}{V_{a,max}} = 1.9 \text{ cm}^{-3} \;\Rightarrow\; V_{a,max} = 0.53 \text{ cm}^3$

Intercept: $\dfrac{1}{K\;V_{a,max}} = 6 \times 10^2 \text{ Pa cm}^{-3} \;\Rightarrow\; K\,V_{a,max} = 1.7 \times 10^{-3} \text{ Pa}^{-1}\text{ cm}^3$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2\;\theta_{CO_2}$

The law of mass action for the first step of the mechanism is given by

$$\theta_{CO_2} = \frac{k_1}{k_{-1}} \cdot \theta_{co}\;\theta_{o_2}^{\frac{1}{2}}, \;\Rightarrow \qquad r = k_2\,\frac{k_1}{k_{-1}}\,\theta_{co}\;\theta_{o_2}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{CO} = \frac{K_{CO}\ p_{CO}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}} \text{ and } \theta_{O_2} = \frac{K_{O_2}\ p_{O_2}}{1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}}$$

$$r = k_2\ \frac{k_1}{k_{-1}}\ \frac{K_{CO}\ p_{CO}\left(K_{O_2}\ p_{O_2}\right)^{\frac{1}{2}}}{\left(1 + K_{CO_2}\ p_{CO_2} + K_{CO}\ p_{CO} + K_{O_2}\ p_{O_2}\right)^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these “compounds” was not known but they are still of great interest to solid state chemists.

Attempts to reduce $CaCl_2$ to CaCl have been made with

(a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl.

After an attempt to reduce $CaCl_2$ with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When $CaCl_2$ is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When $CaCl_2$ is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3.

3.4 a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.

b) What compound is formed by the reaction of $CaCl_2$ with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl. One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^0$ for CaCl
3	Triangular	0.155 – 0.225	BN	–663.8 kJ mol^{-1}
4	Tetrahedral	0.225 – 0.414	ZnS	–704.8 kJ mol^{-1}
6	Octahedral	0.414 – 0.732	NaCl	–751.9 kJ mol^{-1}
8	Cubic	0.732 – 1.000	CsCl	–758.4 kJ mol^{-1}

$\Delta_L H^0$(CaCl) is defined for the reaction $Ca^+(g) + Cl^-(g) \rightarrow CaCl(s)$

3.5 a) What type of structure is CaCl likely to have?

[$r(Ca^+) \approx 120$ pm (estimated), $r(Cl^-) \approx 167$ pm)]

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^0$ (CaCl) with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{fusion}H^0$(Ca)		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1.\ IE}H$(Ca)	$Ca \rightarrow Ca^+$	589.7 kJ mol^{-1}
ionization enthalpy	$\Delta_{2.\ IE}H$(Ca)	$Ca^+ \rightarrow Ca^{2+}$	1145.0 kJ mol^{-1}
heat of vaporization	$\Delta_{vap}H^0$(Ca)		150.0 kJ mol^{-1}
dissociation energy	$\Delta_{diss}H(Cl_2)$	$Cl_2 \rightarrow 2\ Cl$	240.0 kJ mol^{-1}

enthalpy of formation	$\Delta_f H^0(CaCl_2)$		-796.0 kJ mol^{-1}
electron affinity	$\Delta_{EA}H(Cl)$	$Cl + e^- \rightarrow Cl^-$	-349.0 kJ mol^{-1}

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and $CaCl_2$ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

(a) $CaCl_2 + Ca \rightarrow 2\ CaCl$

(b) $2\ CaCl_2 + H_2 \rightarrow 2\ CaCl + 2\ HCl$

(c) $4\ CaCl_2 + C \rightarrow 4\ CaCl + CCl_4$

3.2

Silvery metallic particles:	Ca
Colourless crystals:	$CaCl_2$

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and $CaCl_2$

3.3 Empirical formula:

100 % –(mass % Ca + mass % Cl) = mass % X

100 % –(52.36 % + 46.32 %) = 1.32 % X

mol % of Ca = 52.36 mass % / M(Ca)

= 52.36 mass % / 40.08 g mol^{-1} = 1.31 mol %

mol % of Cl = 46.32 mass % / M (Cl)

= 46.32 mass % / 35.45 g mol^{-1} = 1.31 mol %

mol % of X = 1.32 % X / M (H)

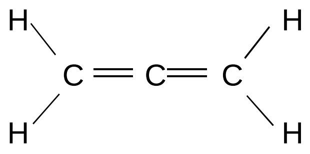
= 1.32 % X / 1.01 g mol^{-1} = 1.31 mol %

$n(Ca) : n(Cl) : n(H) = 1 : 1 : 1$

Empirical formula: CaClH

Notes: The reaction of $CaCl_2$ with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only:



$H-C\equiv C-CH_3$

b) Empirical formula of the compound formed:

$$Ca_3C_3Cl_2$$

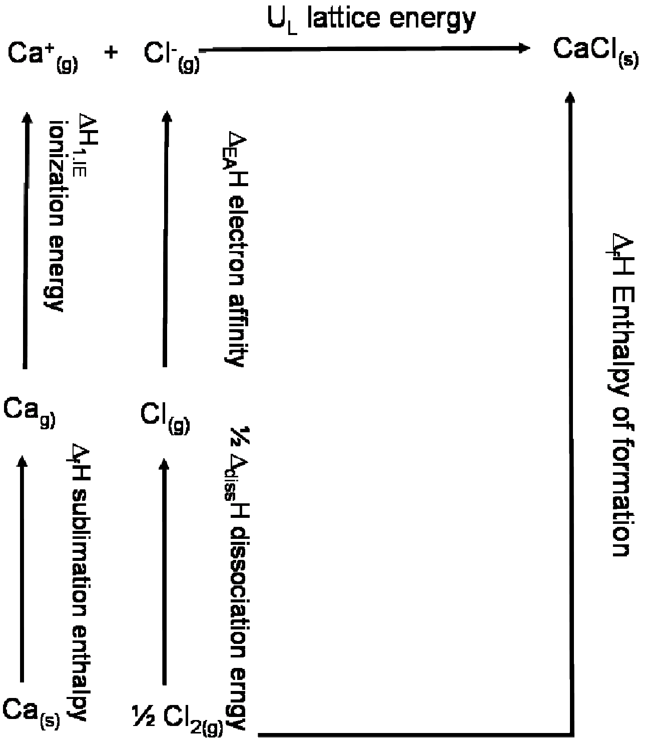
Notes: If the ratio of n(Ca) : n(Cl) = 1.5 : 1 [or better = 3 : 2 which can be rewritten as $CaCl_2 \cdot 2\ Ca^{2+} = Ca_3Cl_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $Ca_3C_3Cl_2$ will follow.

3.5 a) Structure type CaCl likely to have:

$r(Ca^+)/r(Cl^-)$ = 120 pm / 167 pm = 0.719

NaCl	CsCl	ZnS	BN	no decision possible
☒	☐	☐	☐	☐

b) $\Delta_f H^0$(CaCl) with a Born-Haber-cycle:



Summing up of all the single steps of the Born-Haber-cycle:

$\Delta_f H^0$ (CaCl) = $\Delta_{subl}H^0$(Ca) + $\Delta_{1.\ IE}H$(Ca) + ½ $\Delta_{diss}H(Cl_2)$ + $\Delta_{EA}H$(Cl) + $\Delta_L H$(CaCl)

= (159.3 + 589.7 + 120 – 349.0 – 751.9) kJ mol^{-1}

= –231.9 kJ mol^{-1}

3.6 Stability to disproportionation:

2 CaCl → $CaCl_2$ + Ca

$\Delta H = \Delta_f H^0(CaCl_2) - 2\,\Delta_f H^0(CaCl)$ = –796.0 kJ mol^{-1}+ 463.8 kJ mol^{-1} = –332.2 kJ mol^{-1}

Disproportionation:	yes	no	no decision possible, more information needed
	☐	☒	☐

PROBLEM 4

Determining atomic masses

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is m(Ag) : m(Y) = 11.88 : 1. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S. To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond (N m^{-1}= kg s^{-2})

μ reduced mass in AB_4, which is given by $\mu = \frac{3\,m(A)\,m(B)}{3\,m(A) + 4\,m(B)}$

m(A), m(B) - the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1}. The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1}. The bond enthalpy of a C-H bond in methane is 438.4 kJ mol^{-1}. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be 450.2 kJ mol^{-1}.

4.3 Determine the force constant *k* of a C-H bond using Hooke's law.

Estimate the force constant *k* of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:

1) $X + 2\ H_2 \rightarrow XH_4$

2) $2\ X + 3\ H_2 \rightarrow X_2H_6$

i) $5.0\ \text{g} = [n_1(X) + n_2(X)] \cdot M(X)$

ii) $5.628\ \text{g} =$

$= n_1(XH_4)\times[M(X) + 4\times1.01\ \text{g mol}^{-1}] + n_2(X_2H_6)y \times [2\ M(X) + 6\times1.01\ \text{g mol}^{-1}]$

iii) $n_1(XH_4) = 2\ n_2(X_2H_6)$

iii,i) → i') $2\ n_1(X) \times M(X) = 5.0\ \text{g}$

iii,ii) → ii') $n_1(X) \times [2M(X) + 7.07\ \text{g mol}^{-1}] = 5.628\ \text{g}$

i',ii') → vi) $(5.0\ \text{g}) \times [2\ M(X)]^{-1} = (5.628\ \text{g}) \times [2\ M(X) + 7.07\ \text{g mol}^{-1}]^{-1}$

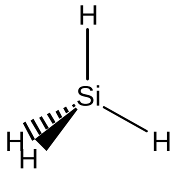
$M(X) = 3.535\ \text{g mol}^{-1} \times (5.628\ \text{g})^{-1} \times [(5.0\ \text{g})^{-1} - (5.628\ \text{g})^{-1}]^{-1}$

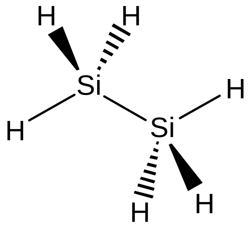
$M(X) = 28.14\ \text{g mol}^{-1}$

Atomic mass of X: $M(X) = 28.14\ \text{g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:





4.2 Atomic mass of Y and empirical formula of Argyrodite:

$Ag_aY_bS_{0.5\cdot a + 2\cdot b}$ + b H_2 → 0.5a Ag_2S + b YS + b H_2S

i) 10 g $= n(Ag_aY_bS_{0.5\cdot a+2\cdot b}) \times$ [a 107.87 g mol^{-1} + b M(Y) +

+ (0.5 a + 2 b) × 32.07 g mol^{-1}]

ii) $n(H_2) = \dfrac{pV(H_2)}{RT}$ $n(H_2) = \dfrac{100\ \text{kPa} \times 0.295 \times 10^{-3}\ \text{m}^3}{8.314\ \text{J K}^{-1}\text{mol}^{-1} \times 400\ \text{K}}$

$n(H_2) = 8.871 \times 10^{-3}$ mol $n(Ag_aY_bS_{0.5\cdot a + 2\cdot b}) = b^{-1} \times 8.871\cdot 10^{-3}$ mol

iii) $11.88 = \dfrac{a \times 107.87\ \text{g mol}^{-1}}{b \times M(\text{Y})}$ a 107.87 g mol^{-1} = 11.88 × b × M(Y)

ii,i) → ii')

b ×10 g × $(8.871\cdot 10^{-3}\ \text{mol})^{-1}$ =

= a 107.87 g mol^{-1} + b M(Y) + (0.5 a + 2 b) ×32.07 g mol^{-1}

b 1127 g mol^{-1} = a 107.87 g mol^{-1} + b M(Y) + (0.5 a + 2 b) ×32.07 g mol^{-1}

iii,ii')→iv)

b·1127 g mol^{-1} = 11.88·b·M(Y) + b·M(Y) + (0.5·a + 2b)·32.07 g mol^{-1}

b·1127 g mol^{-1} =

$= 11.88\ b\ M(\text{Y}) + b\ M(\text{Y}) + \left(0.5\ \dfrac{11.88 \times b \times M(Y)}{107.87\ \text{gmol}^{-1}} + 2\ b\right) \times 32.07\ \text{g mol}^{-1}$

M(Y) = 72.57 g mol^{-1} → iii a : b = 8 : 1

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

$$k(\text{C-H}) = [2\pi\, c\ \tilde{\nu}\,(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3\,M(\text{C}) \times M(\text{H})}{3\,M(\text{C}) + 4\,M(\text{H})}$$

$$= [2\pi \times\ 3{\cdot}10^{10}\ \text{cm s}^{-1} \times 3030\ \text{cm}^{-1}]^2 \frac{1}{6.022 \times 10^{23}\ \text{mol}^{-1}} \times \frac{3 \times 12.01 \times 1.01}{3 \times 12.01 + 4 \times 1.01}\ \text{g mol}^{-1}$$

k(C-H) = 491.94 N m^{-1}

The force constants of a Z-H bond: k(Z-H) = k(C-H) · $\dfrac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$

$$= 491.94\ \text{N m}^{-1} {\cdot} 450.2\ \text{kJ mol}^{-1} {\cdot} [438.4\ \text{kJ mol}^{-1}]^{-1} = 505.18\ \text{N m}^{-1}$$

The atomic mass and symbol of Z:

$$\frac{3\,M(\text{Z}) \times M(\text{H})}{3\,M(\text{Z}) + 4\,M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi\, c\ \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) \ = \frac{4}{3}\left(\frac{[2\pi\, c\ \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})}\right)^{-1}$$

$$M(\text{Z}) \ = \frac{4}{3}\left(\frac{[2\pi \times 3 \cdot 10^{10} \times 2938.45]^2}{505180 \times 6.022 \cdot 10^{23}} - \frac{1}{1.01}\right)^{-1} \text{g mol}^{-1}$$

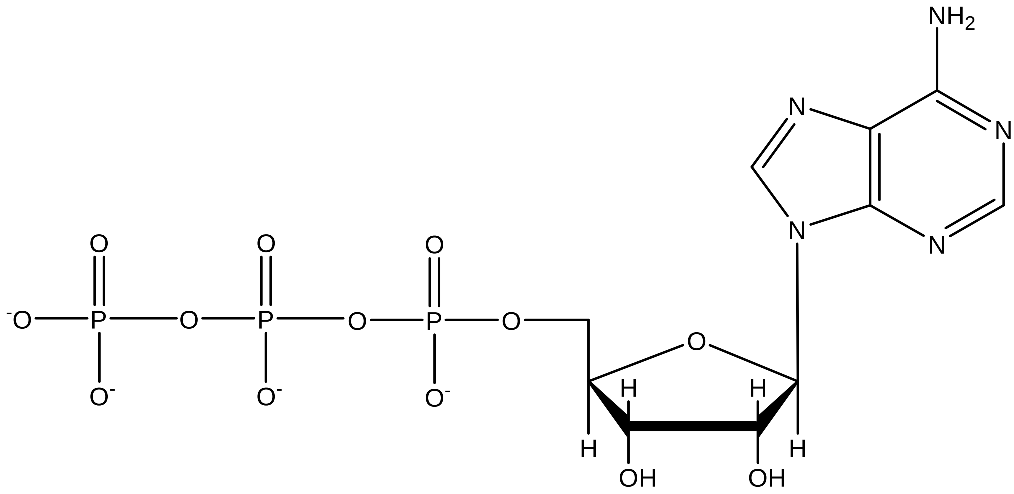
Atomic mass of Z: M(Z) = 72.68 g mol^{-1}

Chemical symbol of Z: Ge

PROBLEM 5

Biochemistry with Thermodynamics

Structure of ATP^{4-}



Shifting chemical equilibria with ATP:

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$c(\text{ATP}^{4-}) = 2.25\ \text{mmol dm}^{-3}$

$c(\text{ADP}^{3-}) = 0.25\ \text{mmol dm}^{-3}$

$c(\text{HPO}_4^{2-}) = 1.65\ \text{mmol dm}^{-3}$

Free energy stored in ATP can be released according to the following reaction:

$$\text{ATP}^{4-} + \text{H}_2\text{O} \rightleftharpoons \text{ADP}^{3-} + \text{HPO}_4^{2-} + \text{H}^+ \qquad \Delta G^o = -30.5\ \text{kJ mol}^{-1} \qquad (1)$$

As the pH is close to 7 in most living cells, biochemists use ΔG^o instead of ΔG°. The standard state of ΔG^o is defined as having a constant pH of 7. In equations with ΔG^o and K' for reactions at $pH = 7$ the concentration of H$^+$ is therefore omitted. Standard concentration is 1 mol dm^{-3}.

5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 °C and *pH* = 7.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive ΔG. The phosphorylation of glucose is an example:

glucose + HPO_4^{2-} $\rightleftarrows$ glucose 6-phosphate^{2-} + H_2O $\Delta G°' = +13.8$ kJ mol^{-1} (2)

5.2 Calculate first the equilibrium constant *K*' of reaction (2) and then the ratio *c*(glucose 6-phosphate) / *c*(glucose) in the red blood cell in chemical equilibrium at 25 °C and *pH* = 7.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:

$$\text{glucose} + \text{ATP}^{4-} \overset{\text{hexokinase}}{\rightleftarrows} \text{glucose 6-phosphate}^{2-} + \text{ADP}^{3-} + \text{H}^+ \qquad (3)$$

5.3 Calculate $\Delta G°$ and *K*’ of reaction (3).

What is now the ratio c(glucose 6-phosphate) / c(glucose) in the red blood cell in chemical equilibrium at 25 °C and *pH* = 7?

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of –52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.

b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?

c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

5.5 a) How many protons (H^+) are in a spherical mitochondrium with a diameter of 1 μm at $pH = 7$?

b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\Delta G' = \Delta G^{o\prime} + R\,T\,\ln\frac{[ADP^{3-}]\,[HPO_4^{2-}]}{[ATP^{4-}]}$$

$$= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1}\,\text{K}^{-1} \times 298.15 \text{ K} \times \ln\frac{0.00025\times 0.00165}{0.00225}$$

$$= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}$$

5.2 Equilibrium constant K' of reaction (2), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime} = -R\,T\,\ln K'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 0.0038$$

$$K' = \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]\,[HPO_4^{2-}]}$$

$$\frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} = K' \cdot [HPO_4^{2-}]$$

$$= 0.0038 \cdot 0.00165$$

$$= 6.3 \cdot 10^{-6}$$

5.3 ΔG^{o} and K' of reaction (3), ratio c(glucose 6-phosphate) / c(glucose):

$$\Delta G^{o\prime}(3) = \Delta G^{o\prime}(1) + \Delta G^{o\prime}(2) = -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1}$$

$$\Delta G^{o\prime} = -R\,T\,\ln K'$$

$$K' = e^{-\Delta G^{o\prime}/RT} = e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 843$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \times c(\text{ADP}^{3-})}{c(\text{glucose}) \times c(\text{ATP}^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K'\,\frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})}$$

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

Energy available for ATP synthesis: $8000 \text{ kJ day}^{-1} \times 0.5 = 4000 \text{ kJ day}^{-1}$

Energy required for synthesis of ATP: 52 kJ mol^{-1}

Amount of ATP produced: $4000 \text{ kJ day}^{-1} / 52 \text{ kJ mol}^{-1} = 76.9 \text{ mol day}^{-1}$

Mass of ATP produced: $76.9 \text{ mol day}^{-1} \times 503 \text{ g mol}^{-1} = 38700 \text{ g day}^{-1}$

$\underline{m_{\textbf{day-1}} = 38.7 \text{ kg day}^{-1}}$

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

Mass of ATP in the body: $38.7 \text{ kg day}^{-1} / (1440 \text{ min day}^{-1}) \cdot 1 \text{ min} = 26.9 \text{ g}$

$m_{\text{body}} = 26.9 \text{ g}$

c) What happens to the rest of the free energy? Mark one correct answer:

- It is used to reduce the entropy of the body. ☐
- It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐
- It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐
- It heats the body of the person. ☒

5.5 a) How many protons are in a spherical mitochondrium with a diameter of 1 m at $pH = 7$?

$V = 4/3\,\pi\,r^3 = 4/3\,\pi\,(0.5\times10^{-6} \text{ m})^3 = 5.2\times10^{-19} \text{ m}^3 = 5.2\times10^{-16} \text{ dm}^3$

$c = 1\times10^{-7} \text{ mol dm}^{-3}$

$n = V\,c\cdot N_A = 5.2\times10^{-16} \text{ dm}^3 \times 1\times10^{-7} \text{ mol dm}^{-3} \times 6.022\times10^{23} \text{ mol}^{-1} = 31$

b) How many protons have to enter a mitochondrium?

Number of ATP molecules:

$$n(ATP) \quad = \quad \frac{m(\text{ATP})\, N_A}{M(\text{ATP})} \quad = \quad \frac{0.2\times10^{-15} g \times 6.022\times10^{23}\,\text{mol}^{-1}}{503\ \text{g mol}^{-1}} \quad = \quad 239400$$

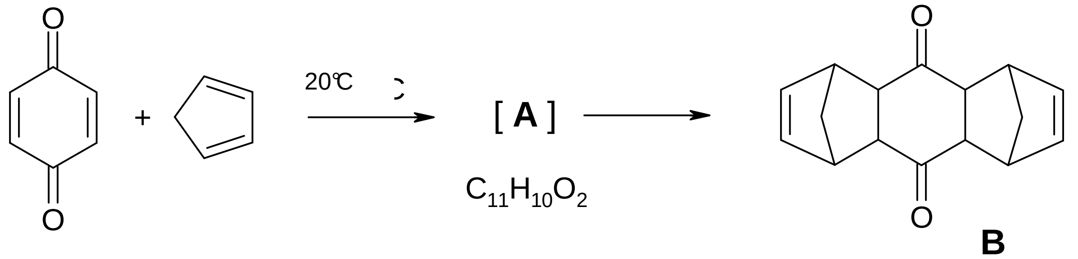
Number of H^+ per cell: $n(H^+_{\text{per cell}})$ $= n(\text{ATP}) \times 3 = 718300$

Number of H^+ per mitochondrium: $n(H^+_{\text{mit}}) = n(H^+_{\text{per cell}}) / 1000 = 718$

PROBLEM 6

Diels-Alder Reactions

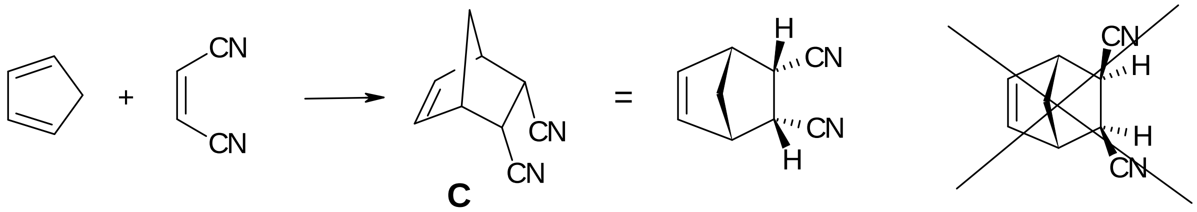
The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



B

6.1 Draw the structure of **A** (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



C

Not formed

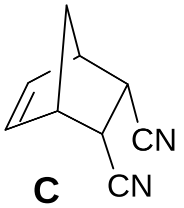
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

6.2 Give the structures of **D1** and **D2**.

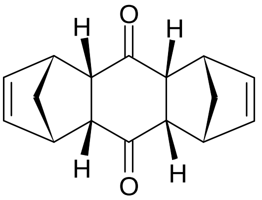
Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

Hints:

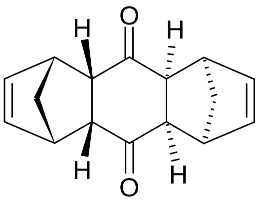
- keep the stereospecific formation of **C** in mind and
- the sterically less hindered isomer forms.



C



1



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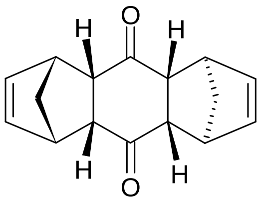

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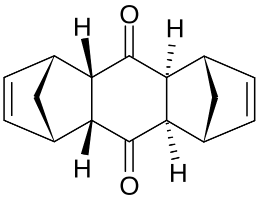

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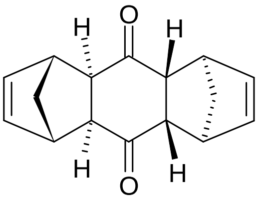

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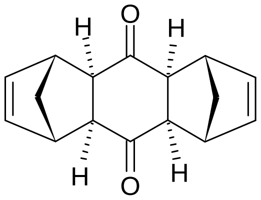


6

6.3 Which single isomer of the six stereoisomers 1-6 of B shown above did they isolate?

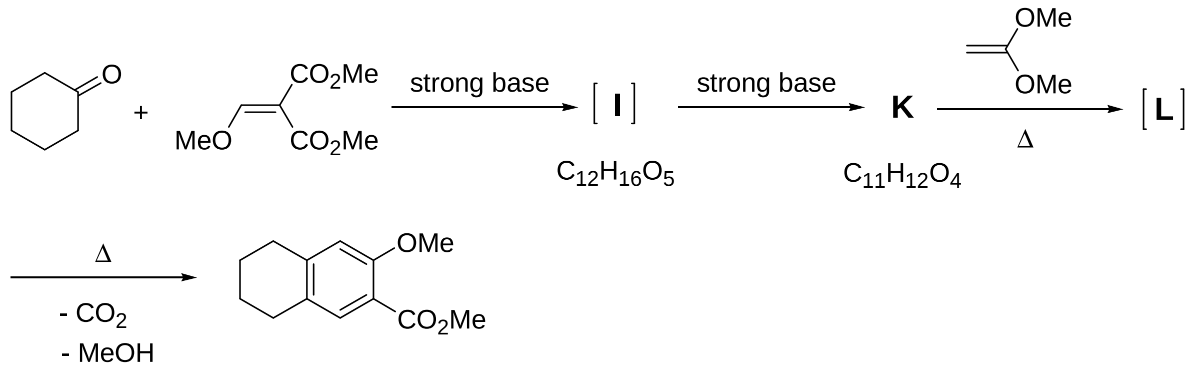
After prolonged heating (15h, 120 °C) of the originally isolated stereoisomer **B** (melting point mp: 157 °C), Diels and Alder obtained two new stereoisomers **E** (mp: 153 °C) and **F** (mp: 163 °C). Equilibration of **B** with a catalytic amount of a strong base at 25 °C gave a further stereoisomer **G** (mp: 184 °C).

B	⇌	**E**	+	**F**
10%		20%		70%

B	⇌	**G**
60%		40%

6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.
Hint: You do not need to know, which of the six stereoisomers 1 – 6 (shown above) corresponds to either **E**, **F** or **G** in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



6.5 Draw the structures for **I**, **K** and **L**.

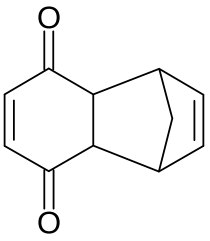
Hints: - **K** has only one methyl group.

- **L** is the Diels-Alder adduct of K and the alkene shown.

SOLUTION

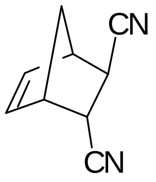
6.1 Structure of **A** only:

[**A**] :

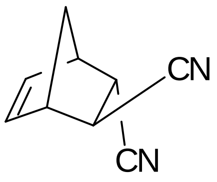


6.2 Structures of **D1, D2 only:**

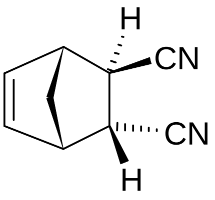
D1:

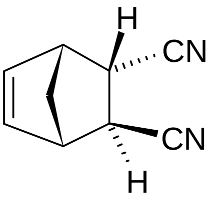


D2:



alternatively, the following structures are also correct:





Note: The two compounds are enantiomers

6.3 Correct structure of **B** (circle only one):

1 [✓ **2**] **3** **4** **5** **6**

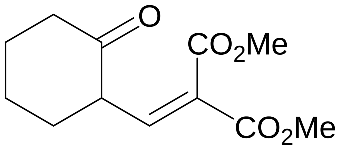
*Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure **C**. As shown in structure **C** this endo- configuration is characterized by the two H atoms and the CH_2-bridge of the bicyclic system being on the same side of the ring. Only structures **1** and **2** of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure **1** the three rings form a U-shaped molecule which is sterically more hindered than structure **2** which has a zig-zag structure.*

6.4 Decide the questions concerning the Diels-Alder reaction.

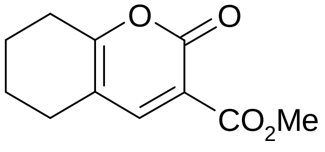
	true	false	no decision possible
• The Diels-Alder reaction is reversible	☒	☐	☐
• The formation of **B** in the original reaction is thermodynamically controlled	☐	☒	☐
• **B** is thermodynamically more stable than **E**	☐	☒	☐
• **E** is thermodynamically less stable than **F**	☒	☐	☐
• **G** is an enantiomer of **B**	☐	☒	☐
• **G** is thermodynamically more stable than **F**	☐	☐	☒

6.5 Structures of **I**, **K**, **L** only:

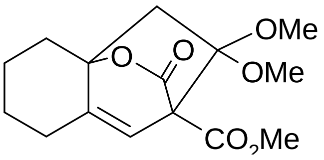
I



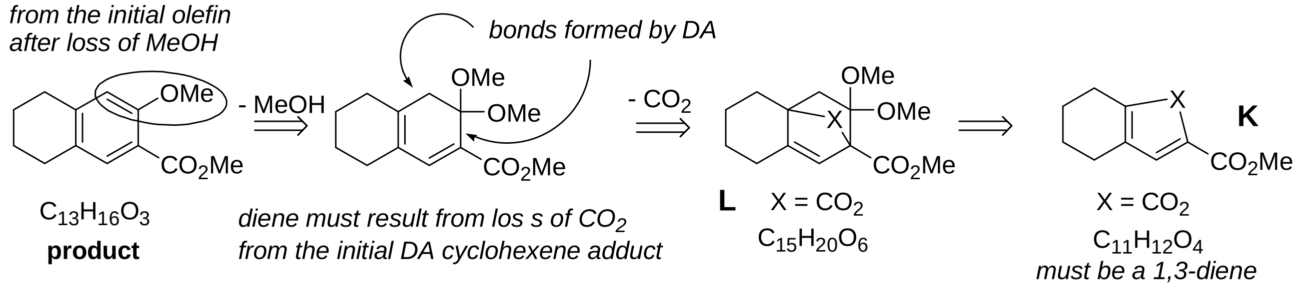
K

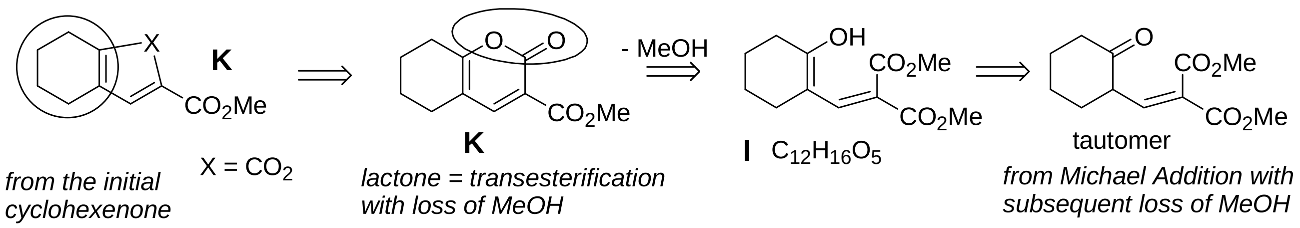


L



Notes:


from the initial olefin
after loss of MeOH
bonds formed by DA
OMe
- MeOH
OMe
OMe
- CO2
OMe
X
OMe
X
K
CO2Me
CO2Me
CO2Me
CO2Me
C13H16O3
product
diene must result from los s of CO2
from the initial DA cyclohexene adduct
L
X = CO2
C15H20O6
X = CO2
C11H12O4
must be a 1,3-diene


X
K
CO2Me
X = CO2
from the initial
cyclohexenone
O
O
CO2Me
K
lactone = transesterification
with loss of MeOH
- MeOH
OH
CO2Me
CO2Me
I
C12H16O5
O
CO2Me
CO2Me
tautomer
from Michael Addition with
subsequent loss of MeOH

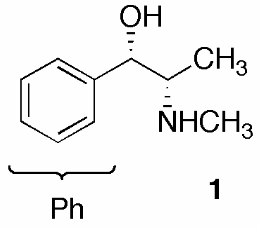
PROBLEM 7

Stereochemistry in Drugs

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine (**1**) is a constituent in many common drugs against colds, e.g. in nasal sprays.



1

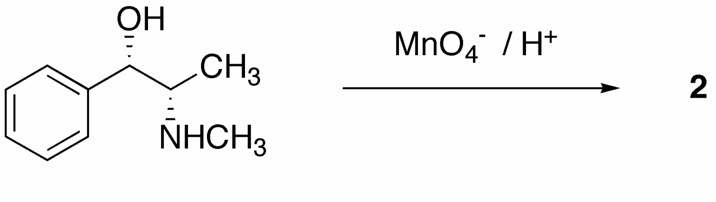
7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

Order the substituents on each stereocenter in **1** according to their priority and determine their absolute configuration (*R* or *S*).

7.3 Draw a Newman or a sawhorse representation of **1**.

Draw a Fischer representation of **1**.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



1

7.4 Draw the stereochemically correct structure of compound **2** and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on <u>all</u> atoms which undergo a change in their formal oxidation numbers.

The treatment of **2** with $LiAlH_4$ results exclusively in compound **3**, which differs from **1** in its melting point.

$$\mathbf{2} \xrightarrow{LiAlH_4} \mathbf{3}$$

7.5 a) Draw the stereochemically correct structure of **3**.

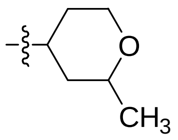
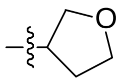
b) Decide the statements on the answer sheet concerning isomers.

c) Draw a structural model to rationalize the exclusive formation of **3** from **2**.

SOLUTION

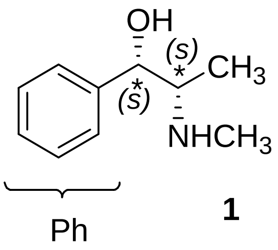
7.1 Fill in < or > (A < B means A has a priority lower than B) :

$-SCH_3$ $\boxed{>}$ $-P(CH_3)_2$

 $\boxed{<}$ 

$-CCl_3$ $\boxed{<}$ $-CH_2Br$

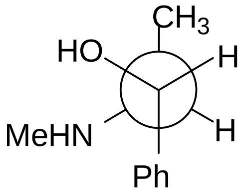
7.2



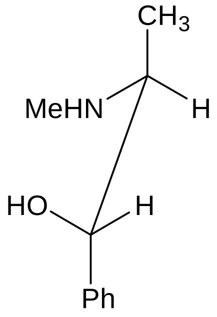
1

highest priority	→	→	lowest priority
OH	$CH(NHCH_3)CH_3$	Ph	H
$NHCH_3$	$CH(OH)Ph$	CH_3	H

7.3 Newman projection or sawhorse projection of **1**:

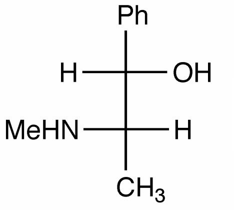


or

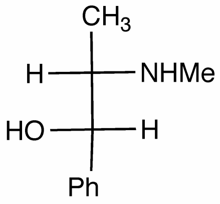


(Me = CH_3)

Fischer projection of **1**:

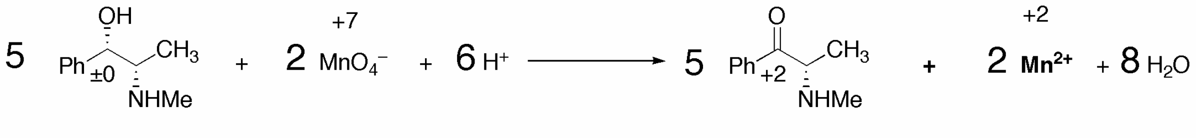


or



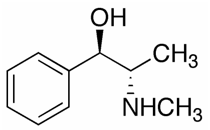
(Me = CH_3)

7.4 Equation with oxidation numbers and stereochemically correct structure of **2**:



1 **2**

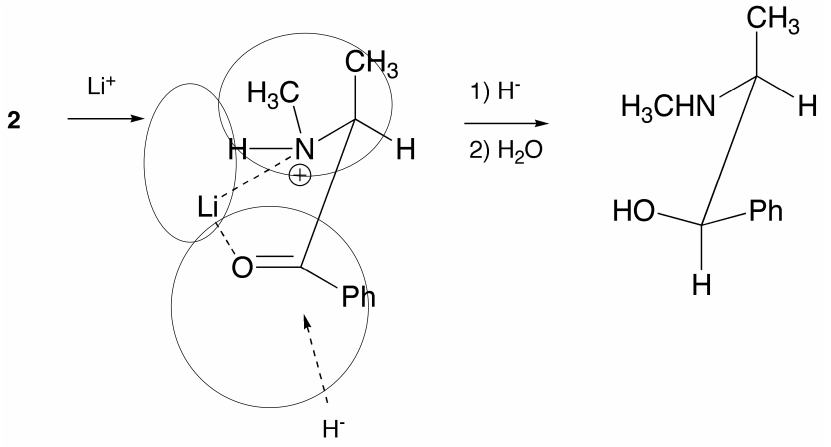
7.5 a) Structure of **3** (correct stereochemistry)**:**



b) Statements concerning isomers:

	true	false
1 and **3** are stereo-isomers	☒	☐
1 and **3** are enantiomers	☐	☒
1 and **3** are diastereomers	☒	☐
1 and **3** are conformational isomers	☐	☒

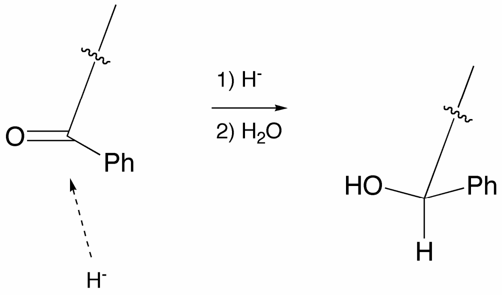
c) Draw a structural model to rationalize the exclusive formation of **3** from **2**



Notes: Attack of hydride occurs from the sterically least hindered side.

Full points will also be given for an explanation using the formation of a hydrogen bond.

1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.



PROBLEM 8

Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

(T = 298.15 K throughout whole problem)

Solution **A** is an aqueous solution of $CaCl_2$ with a concentration of 1.780 g dm^{-3}. Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3}.

$pK_{a1}(H_2CO_3) = 6.37$ $\quad\quad$ $pK_{a2}(HCO_3^-) = 10.33$

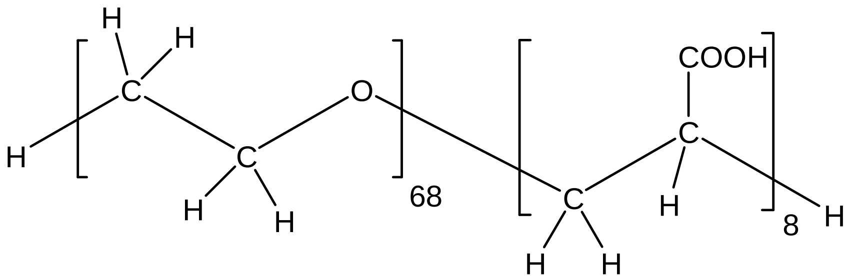
8.1 Calculate the *pH* of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to *pH* 10. A precipitate forms.

$K_{sp}(Ca(OH)_2) = 6.46\times10^{-6}$ $\quad\quad$ $K_{sp}(CaCO_3) = 3.31\times10^{-9}$

8.2 Show by calculation for each of the compounds $Ca(OH)_2$ and $CaCO_3$ whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A**+**B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm^3 of an aqueous NaOH solution (c(NaOH) = 0.19 mol dm^{-3}). The solution is diluted by the addition of 200 cm^3 of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a *pH* of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8$ g mol^{-1}
- The charge of the particles is found to be Z = –800 (number of unit charges).
  (pK_a(COOH, copolymer) = 4.88)

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm^{-3}
Vaterite	2.54 g cm^{-3}
Aragonite	2.95 g cm^{-3}

SOLUTION

8.1 pH of solution **B**:

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1\ \text{mol dm}^{-3}) \times c(\text{OH}^-)/(1\ \text{mol dm}^{-3})}{c(\text{CO}_3^{2-})/(1\ \text{mol dm}^{-3})} \qquad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14\times10^{-4}$$

$K_{b1} = 2.34\times10^{-8}$

Since $K_{b2} >> K_{b1}$, only one protonation step of the CO_3^{2-} *has to be considered*.

$c(HCO_3^-) = c(OH^-) = x$ and $c(CO_3^{2-}) = c_0(CO_3^{2-}) - x$

$$c_0(Na_2CO_3) = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}}$$

$c_0(Na_2CO_3) = c_0(CO_3^{2-}) = 0.016 \text{ mol dm}^{-3}$

$$K_{b2} = \frac{x^2/(1 \text{ mol dm}^{-3})}{(c_0(CO_3^{2-}) - x)} \qquad x = c(OH^-) = 1.75\times10^{-3} \text{ mol dm}^{-3}$$

$pH = 11.2$

8.2 $Ca(OH)_2$, $CaCO_3$ in the precipitate?

$M(CaCl_2) = 110.98 \text{ g mol}^{-1}$ $pH = 10$, $c(OH^-) = 1\times10^{-4} \text{ mol dm}^{-3}$

$$c_0(Na_2CO_3) = \frac{1.700 \text{ g cm}^{-3}}{105.99 \text{ g mol}^{-1}\times 2} \qquad c(CaCl_2) = \frac{1.780 \text{ g dm}^{-3}}{110.98 \text{ g mol}^{-1}\times 2}$$

$c_0(Na_2CO_3) = 8.0\times10^{-3} \text{ mol dm}^{-3}$ $c(CaCl_2) = c_0(Ca^{2+}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

Calculations for $Ca(OH)_2$:

$c(OH^-)^2 \times c_0(Ca^{2+}) = 8\times10^{-11} < 6.46\times10^{-6} = K_{sp}(Ca(OH)_2)$ no precipitate

Calculations for $CaCO_3$:

$$K_{b2} = \frac{c(HCO_3^-)\times c(OH^-)}{c(CO_3^{2-})}, \qquad c(HCO_3^-) = \frac{K_{b2}}{c(OH^-)} \times c(CO_3^{2-})$$

$c(HCO_3^-) = 2.14 \times c(CO_3^{2-})$ and $c(HCO_3^-) + c(CO_3^{2-}) = c_0(Na_2CO_3)$

$2.14 \times c(CO_3^{2-}) + c(CO_3^{2-}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

Initial concentration of CO_3^{2-} in solution **C**: $c(CO_3^{2-}) = 2.55\times10^{-3} \text{ mol dm}^{-3}$

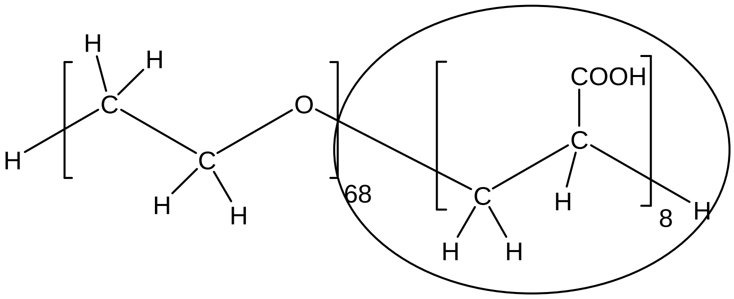
Initial concentration of Ca^{2+} in solution **C**: $c(Ca^{2+}) = 8.0\times10^{-3} \text{ mol dm}^{-3}$

hence $c(CO_3^{2-}) \times c(Ca^{2+}) = 2.04\times10^{-5} > 3.3\times10^{-9} = K_{sp}(CaCO_3)$ precipitate

$Ca(OH)_2$ will be found in the precipitate yes ☐ no ☒

$CaCO_3$ will be found in the precipitate yes ☒ no ☐

8.3 Circle the <u>block</u> that attaches to the $CaCO_3$ crystal:



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

$$RCOOH + OH^- \rightleftarrows RCOO^- + H_2O \qquad pK_b = 9.12$$

pH and *pK*$_a$ lead to the total concentration of COOH groups in the solution:

$c(COO^-) = x$ $\qquad c(COOH) = c_0(COOH) - x$ $\qquad x = c_0(OH^-) - c(OH^-)$

$c_0(OH^-) = \dfrac{50\ cm^3}{250\ cm^3}\ 0.19\ mol\ dm^{-3}$ $\qquad c_0(OH^-) = 0.038\ mol\ dm^{-3}$

$c(OH^-) = 10^{-1.7}\ mol\ dm^{-3} = 0.02\ mol\ dm^{-3}$ $\qquad x = 0.018\ mol\ dm^{-3}$

$$K_b = \frac{(c_0(COOH)\ \text{-x}) / (1\ mol\ dm^{-3}) \times c(OH^-) / (1\ mol\ dm^{-3})}{x / (1\ mol\ dm^{-3})}$$

$$c_0(\text{COOH}) = \frac{K_b\ \text{x} \times (1\ \text{mol dm}^{-3})}{c(\text{OH}^-)} + \text{x}$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018\right) \text{mol dm}^{-3}$$

$c_0(\text{COOH}) = 0.018\ \text{mol dm}^{-3}$

(Or as pH >> pK_a : $c_0(\text{COOH}) = c(\text{COOH}) + \ \text{x} \approx \text{x}$)

To*tal concentration of polymer chains* $c(\text{polymer}) = \dfrac{c_0(\text{COOH})}{8}$

$M(\text{polymer}) = M(C_{160}O_{84}H_{306}) = 3574.66\ \text{g mol}^{-1}$

$m(\text{polymer}) = c(\text{polymer}) \times V \times M(\text{polymer})$

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \times V \times M(\text{polymer})}{8} = \frac{0.018 \times 0.250 \times 3574.66}{8}\ \text{g} = 2.0\ \text{g}$$

8.5 Modification of $CaCO_3$:

The charge of the particles is caused by the number of protolized COOH groups per particle.

$c(\text{COO}^-) \approx c_0(\text{COOH})$, $\alpha \approx 1$

Number of COOH groups per particle: $N_{\text{COOH}} = \dfrac{|Z|}{\alpha}$ $N_{\text{COOH}} = 800$

Number of polymer chains per particle: $N_{\text{polymer}} = \dfrac{N_{\text{COOH}}}{8} = 100$

The number of polymers per particle indicates the mass of polymer per particle.

Thus, the mass of the calcium carbonate particle can be calculated:

$M(CaCO_3\ \text{particle}) = M(\text{total particle}) - N_{\text{polymer}}\ M(\text{polymer})$

$M(CaCO_3\ \text{particle}) = 8.01 \times 10^8\ \text{g mol}^{-1} - 100 \times 3574.66\ \text{g mol}^{-1}$

$M(CaCO_3\ \text{particle}) = 8.01 \times 10^8\ \text{g mol}^{-1}$

Mass of one $CaCO_3$ particle: $m(CaCO_3\ \text{particle}) = M(CaCO_3\ \text{particle}) \cdot N_A^{-1}$

and with the volume of the spherical particle ($V = \frac{4}{3}\pi r^3$) the density can be calculated:

$$\rho(\text{CaCO}_3) = \frac{m(\text{CaCO}_3 \text{ particle})}{V(\text{CaCO}_3 \text{ particle})} = \frac{3\, m(\text{CaCO}_3 \text{ particle})}{4\pi r^3}$$

$$= \frac{3\,(M \text{ (total particle) - } N_{\text{polymer}}\, M(\text{polymer})\,)}{N_a 4\pi\, r^3}$$

$$= \frac{3 \times 8.01 \times 10^8 \text{ g mol}^{-1}}{N_A \cdot 4\pi\, (5 \times 10^{-6} \text{cm})^3} = 2.54 \text{ g cm}^{-3}$$

The modification of calcium carbonate is Calcite ☐ Vaterite ☒ Aragonite ☐

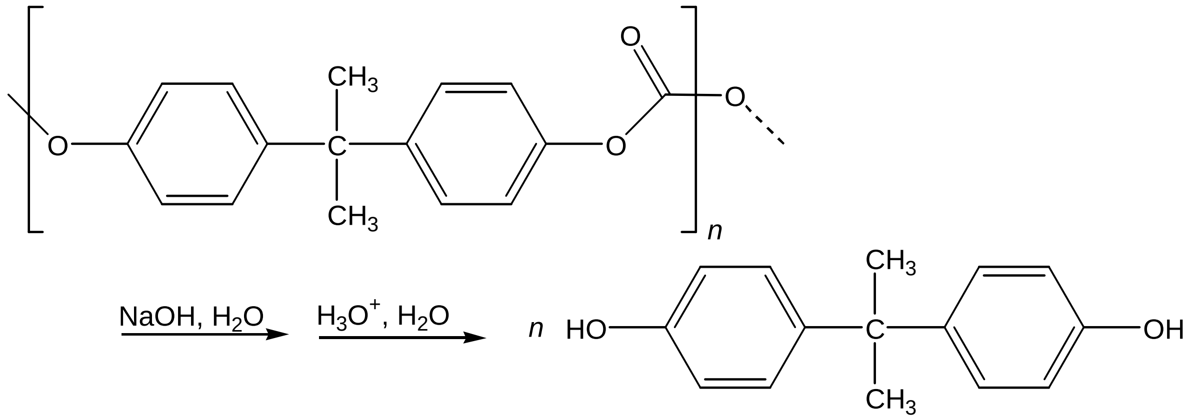
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

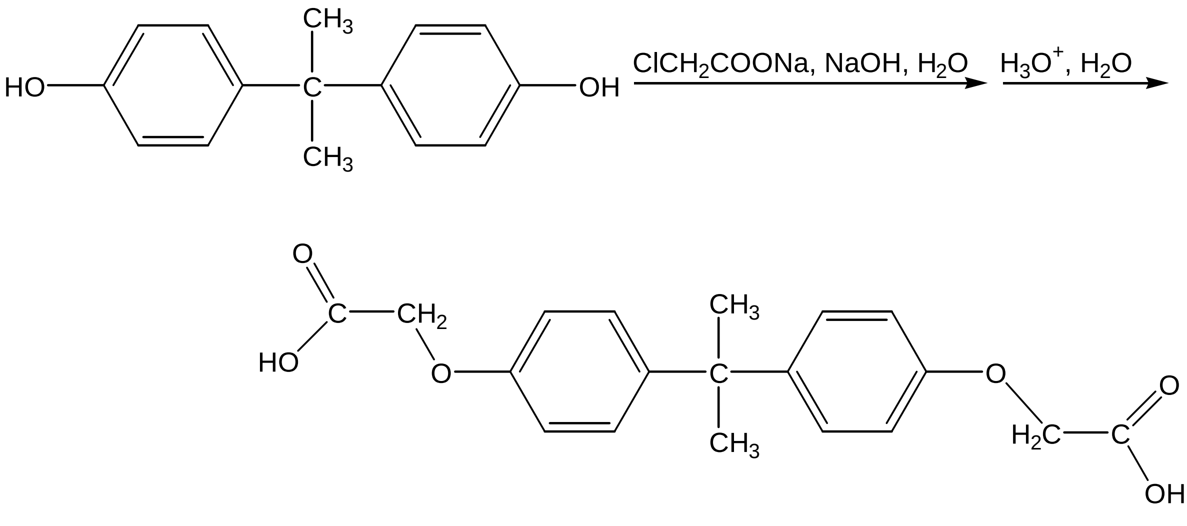
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyaceticacid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
  (Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
  (Filling of the melting point tubes in step 1 will be done by the organizer.)
  (The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. **1**), 4.0 g of sodium hydroxide (No. **5**) and 3 cm^3 of demineralized water into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm^3 of ethanol (No. **2**) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm^3 of demineralized water and transfer the reaction mixture into a 400 cm^3 beaker. Rinse the Erlenmeyer flask with 25 cm^3 of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm^3 with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm^3 of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. 28), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2: Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(p-phenyleneoxyacetic acid)propane

(Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm^3 Erlenmeyer flask with ground-glass joint.
- Add 10 cm^3 of an aqueous sodium-hydroxide solution (No. **6**), 1 cm^3 of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm^3 of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm^3 of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm^3 of ethanol (No. **2**). The precipitate is washed twice with 10 cm^3 portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm^3 of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm^3 of hydrochloric acid (No. **3**) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm^3 portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

SOLUTION

1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

$M_1(\text{polycarbonate}) = M_1(C_{16}H_{14}O_3)_nH_2 \approx M_1(C_{16}H_{14}O_3) = 254.30 \text{ g mol}^{-1}$

$m_1 = 2.54$ g

M_2 $(C_{15}H_{16}O_2) = 228.31$ g/mol

$m_2 = m_1 \times M_1^{-1} \times M_2$

Theoretical yield of bisphenol A: 2.28 g

1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

M_2 $(C_{15}H_{16}O_2) = 228.31$ g/mol

$m_2 = 2.00$ g

M_3 $(C_{19}H_{20}O_6) = 344.39$ g/mol

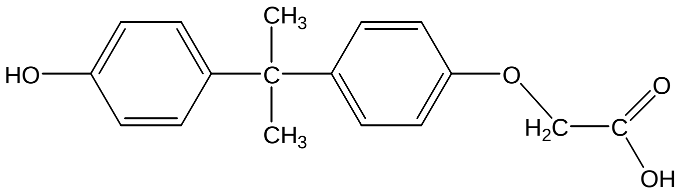
$m_3 = m_2 \times M_2^{-1} \times M_3$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

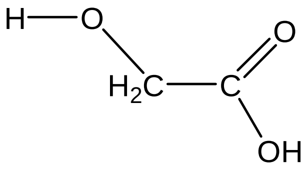
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 *Qualitative determination of the alkaline earth metal(s)*

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($La_xM_{(2-x)}CuO_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.
All steps must be carried out in the hood!
Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow $BaCrO_4$ precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is devided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

  1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

<u>Preparation of the superconductor parent solution</u>

There is a superconductor solution ($La_xM_{(2-x)}CuO_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3. From now on this solution is called "parent solution".

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of about 75 cm^3. The *pH*-value has to be about ***pH* 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na_2-EDTA solution (No. **7**). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 *Quantitative determination of the copper content*

Transfer 25.00 cm^3 of your parent solution (No. **13**) into the 100 cm^3 volumetric flask and fill up with demineralized water to a volume of 100.0 cm^3. For each titration, transfer 25.00 cm^3 of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. **6**), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. **12**) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm^3 of sodium-iodide solution (No. **9**), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. **10**). Add some starch solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

Ca ☐ Sr ☐ Ba ☒

Ca and Sr ☐ Ca and Ba ☐ Sr and Ba ☐

Ca and Sr and Ba ☐

Complete the following reaction equations:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$$

$$Sr^{2+} + CO_3^{2-} \rightleftharpoons SrCO_3$$

$2\ Ba^{2+} + Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ BaCrO_4 + 2\ H^+$

2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm^{-3} EDTA solution: V = 11.60 cm^3

(accoding to 100 cm^3 of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution: V = 10.50 cm^3

(according to 100 cm^3 of superconductor solution)

Complete the following reaction equations:

$2\ Cu^{2+} + 4\ I^- \rightleftharpoons I_2 + 2\ CuI$

$I_2 + 2\ S_2O_3^{2-} \rightleftharpoons 2\ I^- + S_4O_6^{2-}$

2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

[M(Cu) = 63.55 g mol^{-1}; M(La) = 138.91 g mol^{-1}]

Amount of copper:

10,50 cm^3 × 0.01 mol dm^{-3} × 4 × 10 × 63.55 g mol^{-1} = 266.9 mg

Amount of lanthanum:

[11.60 – (10.50 / 10 × 4)] cm^3 × 0.1 mol dm^{-3} × 10 × 138.91 g mol^{-1} = 1028 mg

Mass Cu: m(Cu) = 266.9 mg
Mass La: m(La) = 1028 mg

2.5 Assume a fictive consumption of 39.90 cm^3 of 0.1000 mol dm^{-3} EDTA solution and 35.00 cm^3 of 0.01000 mol dm^{-3} $Na_2S_2O_3$ solution. Calculate the coefficient x in the formula $La_xM_{(2-x)}CuO_4$ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = [39.90 – (35.00/10 × 4)] cm^3 = 25.90 cm^3

Consumption for copper = (39.90 – 25.90) cm^3 = 14.00 cm^3

n(La) : n(Cu) = 25.90 : 14.00 = 1.85 : 1

coefficient x: 1.85 formula: $La_{1.85}Ba_{0.15}CuO_4$

37th

8 theoretical problems
2 practical problems

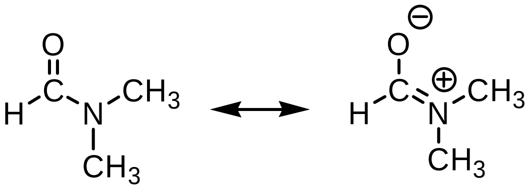
THE THIRTY-SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
16–25 JULY 2005, TAIPEI, TAIWAN

THEORETICAL PROBLEMS

PROBLEM 1

Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ($CH_3CONHCH_3$, compound **B**), and propionamide (compound **C**, $CH_3CH_2CONH_2$,). Express your answer from high to low melting point as follows:

____ > ____ > ____ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

(a) 1660 cm^{-1} because of the shorter carbonyl bond length.

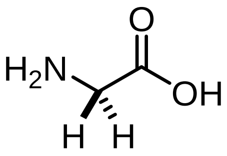
(b) 1660 cm^{-1} because of the longer carbonyl bond length.

(c) 1740 cm^{-1} because of the shorter carbonyl bond length.

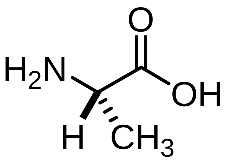
(d) 1740 cm^{-1} because of the longer carbonyl bond length.

1.3 Glycine (H_2N-CH_2-COOH) is an α-amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

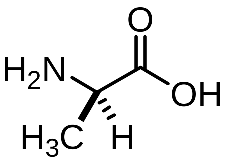
1.4 When an α-amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



D-Alanine (D-Ala)

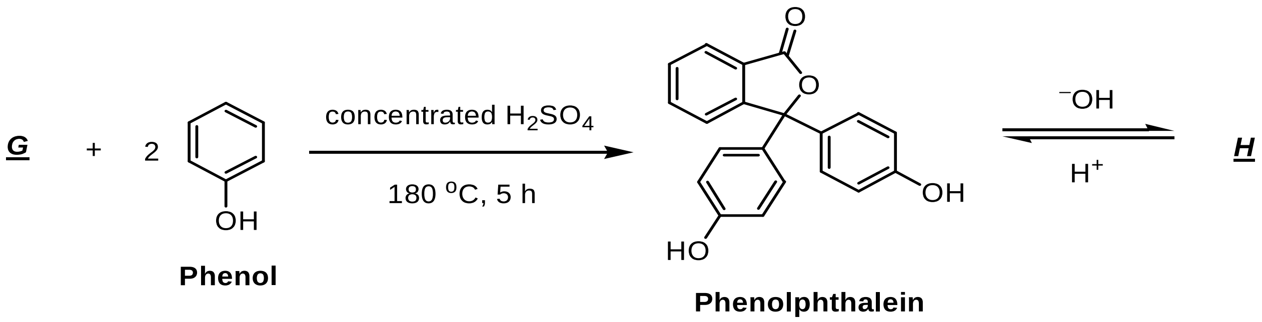
1.5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

1.6 Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

______>______>_ (Insert compound codes **D**, **E**, and **F**)

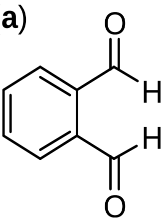
The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions (*pH* 8.3 – 10.0).



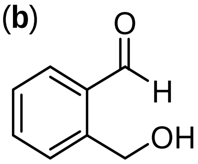
1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.

1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.

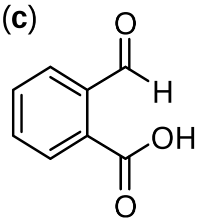
(**a**)



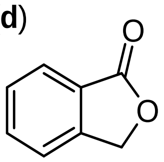
(**b**)



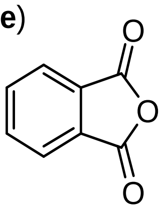
(**c**)



(**d**)



(**e**)



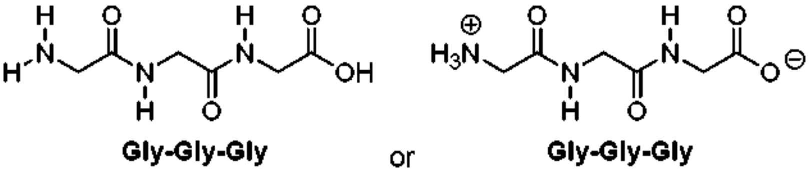
SOLUTION

1.1 The order of the melting points is: **C** > **B** > **A**

The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bonding, but not tertiary amide.
Propionamide, m.p. = 79 °C; *N*-methylacetamide, m.p. = 28 °C;
N,*N*-dimethylformamide, m.p. = -61 °C.

1.2 Correct: (b), 1660 cm^{-1} due to a longer carbonyl bond length.

1.3



1.4 There are 27 possible tripeptides.

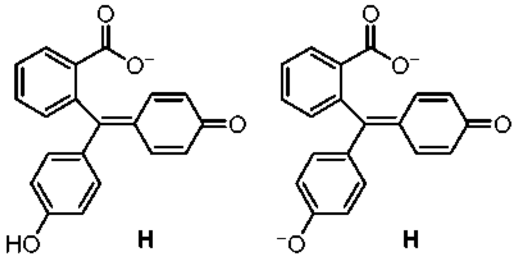
1.5 Among them, 26 tripeptides are optically active.

Optically inactive tripeptide: H_2N-GGG-OH

Optically active tripeptides: H_2N-GG^{L}A-OH, H_2N-GG^{D}A-OH, H_2N-G^{L}AG-OH, H_2N-^{L}AG^{D}A-OH, H_2N-^{L}A^{L}A^{D}A-OH, and so on.

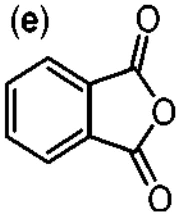
1.6 The relative binding strength with polyamide gel for phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) is: **F** > **D** > **E**

1.7



The range *pH* 8.3 – 10.0 for colour change of phenolphthalein.

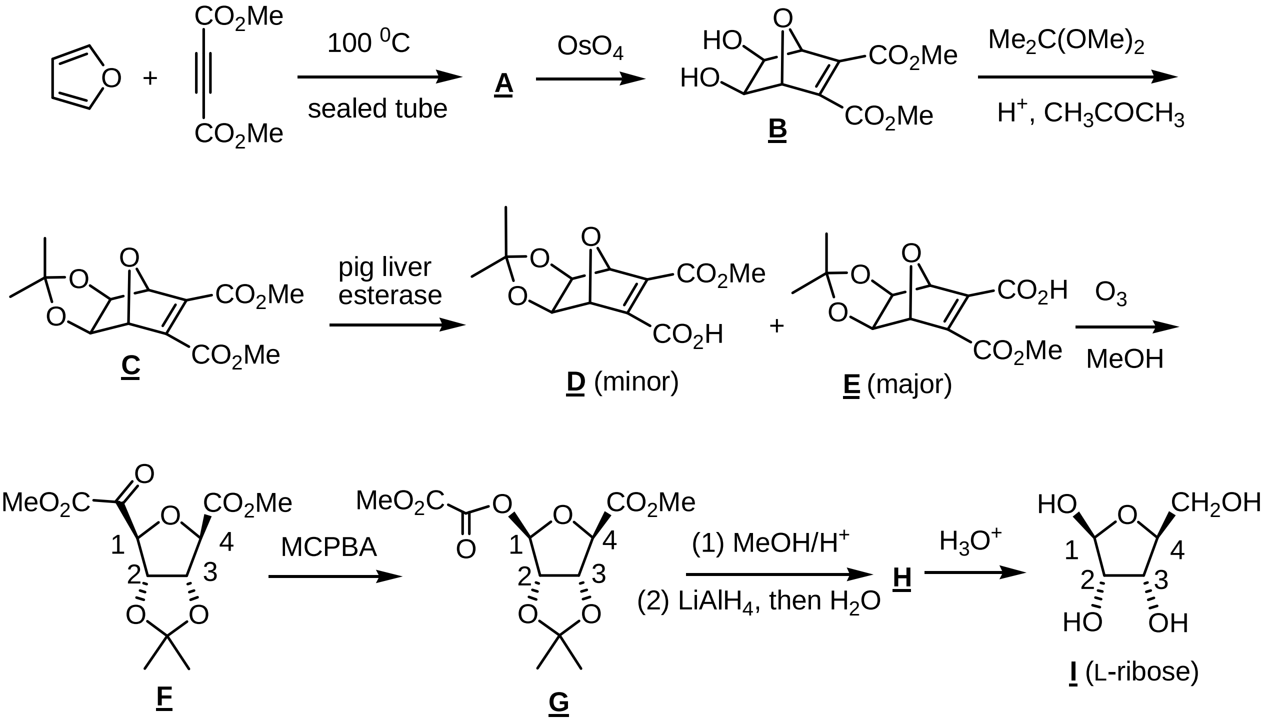
1.8



PROBLEM 2

Organic Synthesis and Stereochemistry

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound I).



2.1 Compound **A** has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of **A**.

2.2 Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

___ (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.

___ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.

___ (c) Protons act as the catalyst in the transformation of **B** to **C**.

___ (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^{o}$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^{o}$.

2.3 What is the molar ratio of **D**/**E** in the product mixture before the recrystallization? Show your work.

2.4 Reaction of **F** with meta-chloroperbenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

____ (a) The reaction was to oxidize compound **F**.

_____ (b) The oxygen atom inserted originated from MCPBA.

____ (c) The *R*/*S* notation of C-1 remained unchanged before and after the reaction.

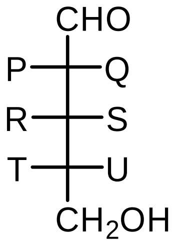
The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows: ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, J = 6 Hz, 1H), 4.74 (d, J = 6 Hz, 1H), 4.89 (s, 1H).

2.5 Draw the configurational formula of **H**.

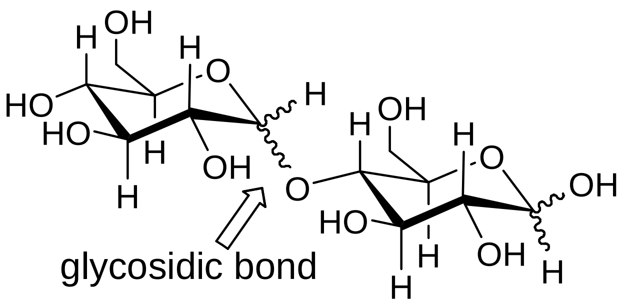
2.6 Assign R/S notations for compound I at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: ____; C-2: ____; C-3: ____; C-4: ____.

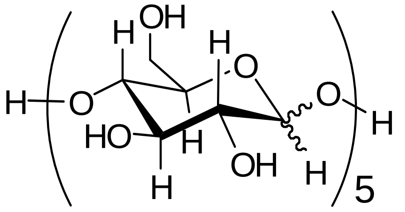
2.7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound I (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



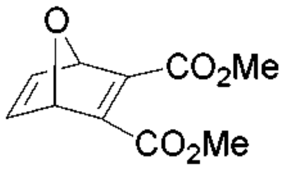
2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

SOLUTION

2.1



2.2 T or F

T (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.

T (b) MeOH is generated as a by-product in the reaction of **B** to **C**.

T (c) Protons act as the catalyst in the transformation of **B** to **C**.

T (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$

2.3 12.1 : 87.9 or 12.2 : 87.8

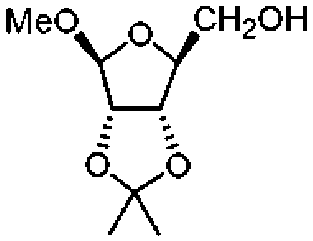
2.4 T or F

T (a) The reaction was to oxidize compound **F**.

T (b) The oxygen atom inserted originated from MCPBA.

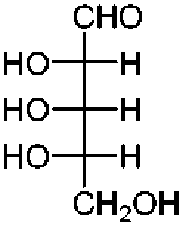
F (c) The *R*/*S* notation of C-1 remained unchanged before and after the reaction

2.5



2.6 C-1: *S*; C-2: *S*; C-3: *R*; C-4: *S*.

2.7



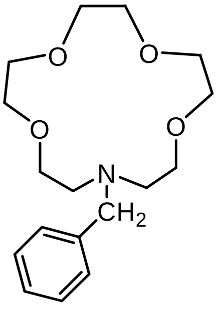
OH group for P, R, and T and H atom for Q, S, and U.

2.8 The number of stereoisomers = 2^5

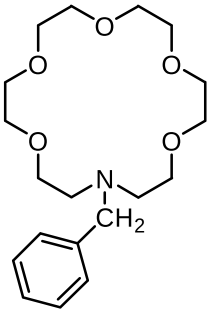
PROBLEM 3

Organic Photochemistry and Photophysics

Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns A and B exhibit different binding constants for Na^+, K^+, and Cs^+.



A

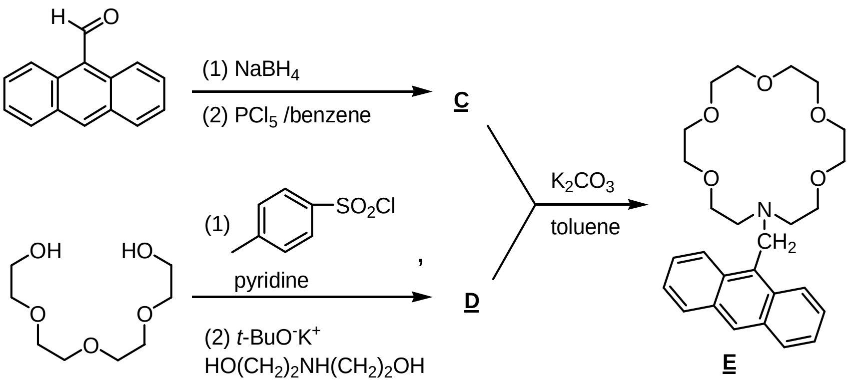


B

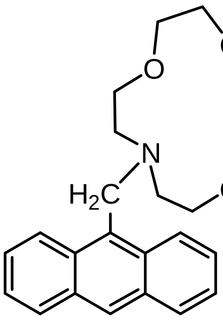
Metal ion	Radius (pm)	Binding constant ($\log_{10}$ K) Compound **A**	Binding constant ($\log_{10}$ K) Compound **B**
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

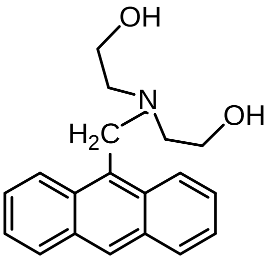
3.1 Provide the structural formula of **C** and **D** in the following synthesis.



For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



F



G

3.2 Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.

(a) none of them (b) **E** and **F** only (c) **G** only (d) all of them

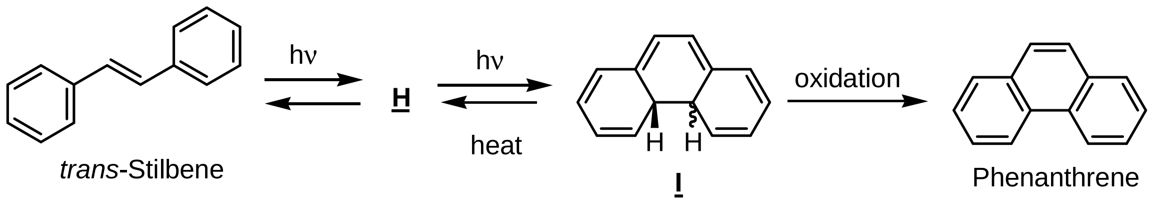
3.3 By adding one equivalent of potassium acetate into a dilute solution (1×10^{-5} M) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.

(a) **E** (b) **F** (c) **G**

3.4 Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.

(a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

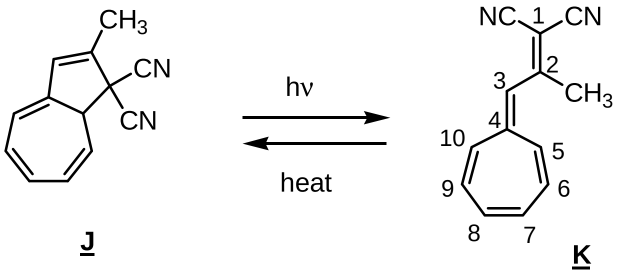
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of I gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound I?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

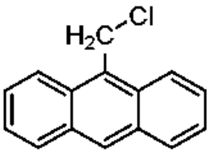
3.8 Compound **K** can react with one equivalent of CF_3CO_2H to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

(a) C-2 (b) C-3 (c) C-4 (d) C-5

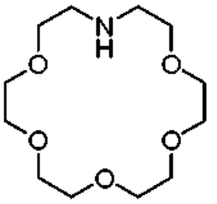
SOLUTION

3.1

C:



D:



3.2 Correct is (d): All of them

3.3 Correct is (a): **E**

3.4 Correct is (a): sodium acetate

3.5

H:

3.6 Trans

3.7 Correct is (b): **K**

3.8 Correct is (b): C-3

PROBLEM 4

A

Gold Capital of Asia

Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines In Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $Au(CN)_2^-$, which is stable in aqueous solution.

$$4\ Au(s) + 8\ CN^- (aq) + O_2(g) + 2\ H_2O\ (l) \rightleftharpoons 4\ Au(CN)_2^- (aq) + 4\ OH^- (aq)$$

4.A-1 Draw a structure for $Au(CN)_2^-$ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:

$$Au(s) + NO_3^- (aq) + Cl^- (aq) \rightleftharpoons AuCl_4^- (aq) + NO_2(g)$$

4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion $AuCl_4^-$ forms. Consider the following half-reactions:

$Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $E^0 = + 1.50\ V$

$AuCl_4^- (aq) + 3\ e^- \rightarrow Au(s) + 4\ Cl^-$ $E^0 = + 1.00\ V$

An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for $AuCl_4^-$ at 25 °C:

$$K = \frac{[AuCl_4^-]}{[Au^{3+}][Cl^-]^4}$$

4.A-6 The function of HCl is to provide $Cl^–$. What is the purpose of the $Cl^–$ for the above reaction. Select your answer from the following choices.

(a) $Cl^–$ is an oxidizing agent
(b) $Cl^–$ is a reducing agent
(c) $Cl^–$ is a complexing agent
(d) $Cl^–$ is a catalyst

____

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of $HAuCl_4$ is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of $NaBH_4$. Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

(a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
(b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry $AlCl_4^–$ from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

(a) one side of the molecule is electropositive, the other side is electronegative.

(b) one side of the molecule is hydrophilic, the other side is hydrophobic.

(c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of $NaBH_4$ in this preparation? Select your answer from the following choices.

(a) reducing agent

(b) oxidizing agent

(c) neutralization agent

(d) complexing agent

4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

(a) 10^2

(b) 10^3

(c) 10^4

(d) 10^5

4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

(a) 20 – 30 %

(b) 40 – 50 %

(c) 60 – 70 %

(d) 80 – 90 %

SOLUTION

4.A-1 $|N\equiv C-Au-C\equiv N|^{(-)}$

The structure of $Au(CN)_2^-$ is linear.

4.A-2 $4\ Au + 8\ KCN + O_2 + 2\ H_2O \rightleftharpoons 4\ KAu(CN)_2 + 4\ KOH$

$20\ g \div 197\ g\ mol^{-1} \approx 0.10\ mol\ (Au)$

$0.10\ mol \times (8/4) \times 65.12\ g\ mol^{-1} = 13.024\ g\ KCN$

4.A-3 Oxidation: $Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$

Reduction: $3\ NO_3^-(aq) + 6\ H^+(aq) + 3\ e^- \rightarrow 3\ NO_2(g) + 3\ H_2O(l)$

$Au(s) + 3\ NO_3^-(aq) + 6\ H^+(aq) + 4\ Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + 3\ NO_2(g) + 3\ H_2O(l)$

4.A-4 Oxidizing agent: HNO_3 or nitric acid

Reducing agent: Au

4.A-5 $Au^{3+}(aq) + 3\ e^- \rightarrow Au(s)$ $E° = 1.50\ V$

$Au(s) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + 3\ e^-$ $E° = 1.00\ V$

$- 3\ e^-$

$Au(s) + Au^{3+}(aq) + 4\ Cl^-(aq) \rightarrow AuCl_4^-(aq) + Au(s)$ $E° = +0.50\ V$

$+ 3\ e^-$

$E = E° - (0.059 / n) \log Q$

At equilibrium, $Q = K$, $E = 0$, $K = [AuCl_4] / [Au^{3+}]\ [Cl^-]^4$

$E = (0.059 / n) \log K$, $0.50 = (0.059 / 3) \log K$, $K = 10^{25.42} = 2.6\times10^{25}$

$\Delta G^0_1 + \Delta G^0_2 = \Delta G^0_3$

$(-n F E^0_1) + (-n F E^0_2) = -RT \ln K$

$E° = (RT / nF) \ln K = (0.059 / n) \log K$,

$0.50 = (0.059 / 3) \log K$,

$K = 10^{2542} = 2.6\times10^{25}$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question**:** (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3}\pi\, r^3_{\text{AuNPs}}$$

$$V_{\text{Au}} = \frac{4}{3}\pi\, r^3_{\text{Au}}$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3}\pi\, r^3_{\text{AuNPs}}}{\frac{4}{3}\pi\, r^3_{\text{Au}}} = \left(\frac{r^3_{\text{AuNPs}}}{r^3_{\text{Au}}}\right)^3 = \left(\frac{15\ \text{A}}{1{,}44\ \text{A}}\right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$4/\,3 \times \pi \times r_{\text{AuNPs}}{}^3 \; = \; 4/\,3 \times \pi \times r_{\text{Au}}{}^3 \times N_{\text{Au}}$

$r_{\text{AuNPs}}{}^3 \; = \; \text{r}_{\text{Au}}{}^3 \times N_{\text{Au}}$

Surface area of a gold nanoparticle: $\text{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{AuNPs}}{}^2$

$\text{S}_{\text{AuNPs}} = 4\,\pi\, r_{\text{Au}}{}^2\ \text{N}_{\text{Au}}{}^{2/3}$

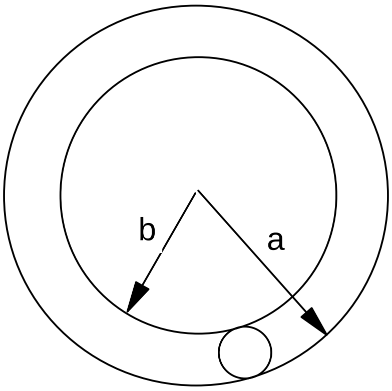
$N_{\text{S}} \approx \text{S}_{\text{AuNPs}} /\, \pi\, r_{\text{Au}}{}^2 = 4\ N_{\text{Au}}{}^{2/3}$

$\text{P} \approx N_{\text{S}} / N_{\text{Au}} = 4/\,N_{\text{Au}}{}^{1/3}$

$\text{N}_{\text{Au}} \approx 1000$

$\text{P} \approx 40\ \%$

or Method 2:



$a = r_{AuNPs}$

$b = r'_{AuNPs} = r_{AuNPs} - 2\, r_{Au}$

$$P\ \% = \frac{\dfrac{V_{AuNPs}}{V_{Au}} - \dfrac{V'_{AuNPs}}{V_{Au}}}{\dfrac{V_{AuNPs}}{V_{Au}}} \times 100\ \% = \frac{\left(\dfrac{r_{AuNPs}}{r_{Au}}\right)^3 - \left(\dfrac{r'_{AuNPs}}{r_{Au}}\right)^3}{\left(\dfrac{r'_{AuNPs}}{r_{Au}}\right)^3} \times 100\ \% =$$

$$= \frac{(15\ \text{A})^3 - (12.12\ \text{A})^3}{(15\ \text{A})^3} \times 100\ \% = 47\ \%$$

PROBLEM 5

Lewis Structure

5.1 Draw one Lewis structure for each of the following molecules.

a) N_2

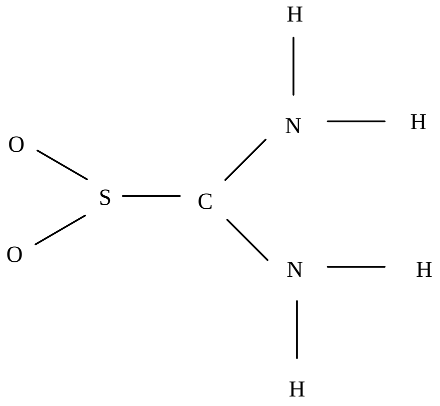
b) NH_3

c) O_3

d) SO_3

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

a) trigonal pyramidal

b) triangular planar

c) T-shape

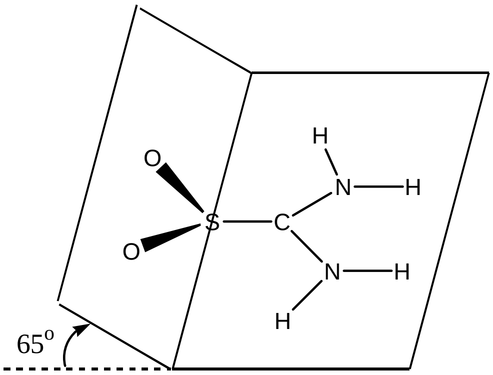
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

a) trigonal pyramidal
b) triangular planar
c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



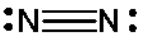
All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

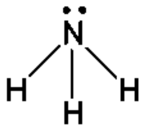
SOLUTION

5.1

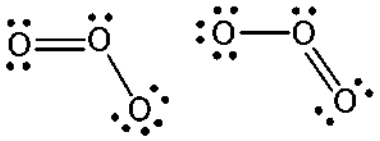
(a)



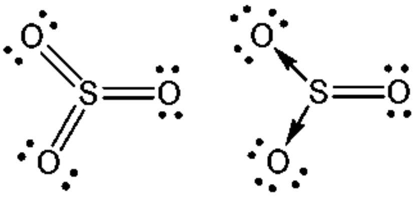
(b)

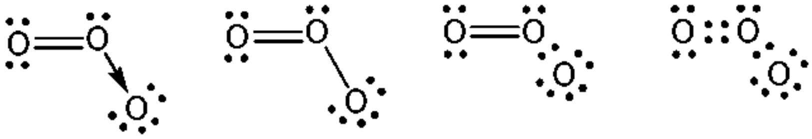


(c)



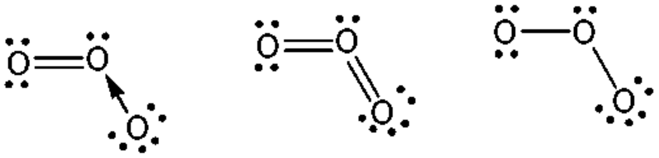
(d)



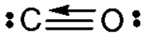


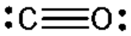
are all correct answers

But



are incorrect answers





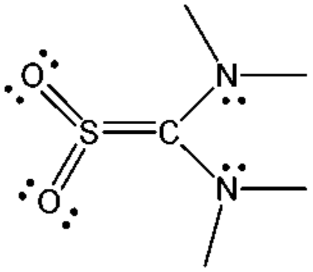
acceptable

5.2

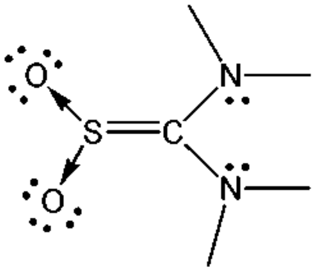
Formal charge C^{-1} ; O^{+1}

Oxidation state C^{2+} ; O^{2-}

5.3



The structure is correct.



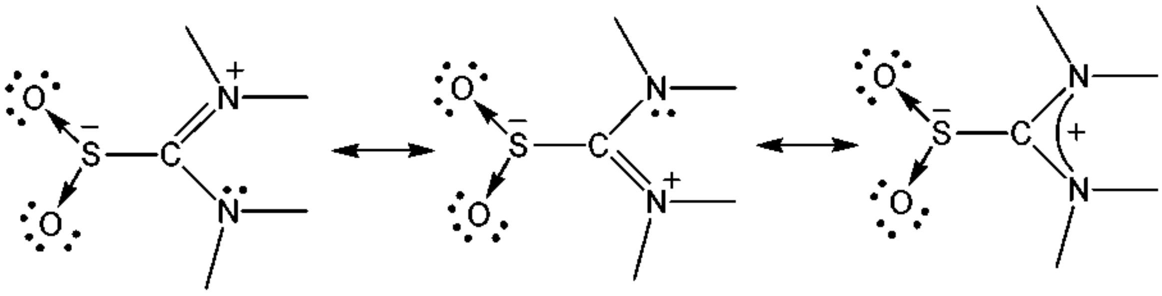
The structure would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

5.5



PROBLEM 6

Alkalinity of Water and Solubility of CO_2

The capacity of water to accept H^+ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO_3^-, CO_3^{2-}, and OH^-. At *pH* values below 7, H^+ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO_3^-, CO_3^{2-}, and OH^- are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$$

The contributions made by different species to alkalinity depend upon pH. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \qquad K_{CO_2} = 3.44\times10^{-2}$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad K_{H_2CO_3} = 2.00\times10^{-3}$$

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad K_{a1} = 2.23\times10^{-4}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \qquad K_{a2} = 4.69\times10^{-11}$$

$$CaCO_{3(s)} \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K_{sp} = 4.50\times10^{-9}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = 1.00\times10^{-14}$$

Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO_2. The ratio of $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}]$ in a water at $[H^+] = 1.00\times10^{-7}$ M will be:

_(a)_ : 1.00 : _(b)_. Calculate (a) and (b).

6.2 Gaseous CO_2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of $CO_{2\,(aq)}$ (mol dm^{-3}) in pure water that is in equilibrium with the unpolluted air at 1.01×10^5 Pa and 298 K containing 0.0360 % (molar ratio) CO_2. (assuming standard pressure = 1.01×10^5 Pa).

If you are unable to solve this problem, assume that concentration of $CO_{2\ (aq)}$ is equal to 1.11×10^{-5} M for further calculations.

The solubility (S) of CO_2 in water can be defined as

$$S = [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}].$$

The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01×10^5 Pa will vary with alkalinity.

6-3 Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.

6.4 Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a 1.00×10^{-3} mol dm^{-3} NaOH solution.

At 298 K, 1.01×10^5 Pa unpolluted air is in equilibrium with natural water saturated with $CaCO_3$. The following main equilibrium may exist:

$$CaCO_{3(s)} + CO_{2\ (aq)} + H_2O \rightleftharpoons Ca^{2+} + 2\ HCO_3^-$$

6.5 Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{eq} = 5.00\times10^{-5}$ for further calculations.

6.6 Calculate the concentration of Ca^{2+} (mg dm^{-3}) in $CaCO_3$-saturated natural water that is in equilibrium with atmospheric CO_2.

If you are unable to solve this problem, assume that concentration of $Ca^{2+}_{(aq)}$ = 40.1 mg dm^{-3} for further calculations.

6.7 Find the alkalinity (mol/L) of the above solution.

6.8 In an underground lake saturated with $CaCO_3$, the water has a high content of CO_2. The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3}. Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

SOLUTION

6.1 $[H^+] = 1.00\times10^{-7}$

$K_{a1} = [HCO_3^-]\,[H^+] / [H_2CO_3] = 2.23\times10^{-4}$,

$[HCO_3^-] / [H_2CO_3] = 2.23\times10^{3}$

$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69\times10^{-11}$,

$[CO_3^{2-}] / [HCO_3^-] = 4.69\times10^{-4}$

$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] =$ **4.48×10^{-4}** $: 1.00 :$ **4.69×10^{-4}**

6.2 $p(CO_2(aq)) = 1.01\times10^{5}\ Pa \times 3.60\times10^{-4} = 36.36\ Pa$

$[CO_2(aq)] = K_{CO_2} \times p(CO_2) = 0.0344 \times (36.36\ Pa / 1.01\times10^{5}\ Pa) =$ **1.24×10^{-5}**

(If you are unable to solve this problem, for further calculations assume that $[CO_2(aq)] = 1.11\times10^{-5}$.)

6.3

(a) Solubility $= [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

($[H_2CO_3] = [CO_2(aq)] \times K_{H_2CO_3} = 2.48\times10^{-8}$

and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$

both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6-2: $[CO_2(aq)] = 1.24\times10^{-5}$,

$[H^+] =$ **$[HCO_3^-] = 2.35\times10^{-6}$**

Solubility $= [CO_2(aq)] + [HCO_3^-] = 1.24\times10^{-5} + 2.35\times10^{-6} = 1.48\times10^{-5}\ mol\ dm^{-3}$

(b) (Using $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Solubility $= [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-]$

($[H_2CO_3] = [CO_2(aq)] \times \boldsymbol{K_{H_2CO_3}} = 2.22\times10^{-8}$ and $[CO_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$ both can be neglected.)

$[H^+][HCO_3^-] / [CO_2(aq)] = K_{a1}\ K_{H_2CO_3} = (2.23\times10^{-4})\ (2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6.2: $[CO_2(aq)] = 1.11 \times 10^{-5}$

$[H^+] = [\mathbf{HCO_3^-}] = 2.225 \times 10^{-6}$

Solubility = $[CO_2(aq)] + [HCO_3^-] = 1.11 \times 10^{-5} + 2.225 \times 10^{-6} = 1.34 \times 10^{-5}$

6.4 (Using $[CO_{2(}aq)] = 1.24 \times 10^{-5}$ for calculation)

In 1.00×10^{-3} mol dm^{-3} NaOH solution the solubility of CO_2 will be much higher because of the following reactions:

(1) $CO_2(aq) + 2\,OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad K = K_{H_2CO_3} \times K_{a1} \times K_{a2} / (1.00 \times 10^{-14})^2 = 2.09 \times 10^{11}$

(2) $CO_2(aq) + CO_3^{2-} + H_2O \rightleftharpoons 2\,HCO_3^- \qquad K = K_{H_2CO_3} \times K_{a1} / K_{a2} = 9.37 \times 10^3$

Combining (1) and (2): $CO_2(aq) + OH^- \rightleftharpoons HCO_3^- \quad K = 4.43 \times 10^7$

With such a large *K* value all OH^- will finally be converted to HCO_3^-.

$$[HCO_3^-] = 1.00 \times 10^{-3}$$

$[OH^-] = 1.82 \times 10^{-6}$

$[H^+] = 5.49 \times 10^{-9} \quad [CO_3^{2-}] = 8.54 \times 10^{-6}$

Solubility = $[CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \approx [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}] =$

$= 1.24 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = 1.02 \times 10^{-3}$ mol dm^{-3}

6.5 $K_{eq} = K_{sp} \times K_{H_2CO_3} \times K_{a1} / K_{a2} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4}) / (4.69 \times 10^{-11}) =$

$= 4.28 \times 10^{-5}$

(If you are unable to solve this problem, assume that $K_{eq} = 5.00 \times 10^{-5}$ for further calculations.)

6.6

(a) (Using $K_{eq} = 4.28 \times 10^{-5}$ and $[CO_2(aq)] = 1.24 \times 10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28 \times 10^{-5} = [Ca^{2+}][HCO_3^-] / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24 \times 10^{-5}$

$[Ca^{2+}] = 0.510 \times 10^{-3} = 20.5$ mg dm^{-3}

(b) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] = 0.5177\times10^{-3}$ = 20.75 mg dm^{-3}

(c) (Using $K_{eq} = 5.00\times10^{-5}$ and $[CO_2(aq)] = 1.24\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.24\times10^{-5}$

$[Ca^{2+}] = 0.5372\times10^{-3}$ = 21.53 mg dm^{-3}

(d) (Using $K_{eq} = 4.28\times10^{-5}$ and $[CO_2(aq)] = 1.11\times10^{-5}$ for calculation)

Mass balance **:** $[HCO_3^-] = 2\,[Ca^{2+}]$

From **6.5:** $K = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = [Ca^{2+}]\,(2\,[Ca^{2+}])^2 / [CO_2(aq)]$

From **6.2:** $[CO_2(aq)] = 1.11\times10^{-5}$

$[Ca^{2+}] = 0.4916\times10^{-3}$ = 19.70 mg dm^{-3}

(If you are unable to solve this problem, assume that $[Ca^{2+}]_{(aq)}$ = 40.1 for further calculations.)

6.7 HCO_3^- is the major species in solution.

The pH of the solution can be estimated as $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 =$
$= 6.99 \approx 7.00$,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3.

At pH 7.00, both $[OH^-]$ and $[H^+]$ can be neglected. Besides, $[CO_3^{2-}] << [HCO_3^-]$ (from **6.1**)

Alkalinity = $[HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+] \approx [HCO_3^-]$

From 6-6, mass balance, $[HCO_3^-] = 2\ [Ca^{2+}]$

(a) 1.02×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6.6 (a))

(b) 1.035×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6.6 (b))

(c) 1.0744×10^{-3} (using $[Ca^{2+}]_{(aq)}$ from 6-6 (c))

(d) 0.9831×10^{-3} (using $[Ca^{2+}]_{(aq)}$) from 6-6 (d))

(e) 2.00×10^{-3} (assuming $[Ca^{2+}]_{(aq)} = 40.1$)

Alkalinity = (a) or (b) or (c) or (d) or (e)

6.8

(a) (Using $K_{eq} = 4.28\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\ [Ca^{2+}]$

$[Ca^{2+}] = 100\ \text{mg dm}^{-3} = 2.50\times10^{-3}\ \text{mol dm}^{-3}$

Inserting into $K_{eq} = 4.28\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\ [Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.46\times10$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\ \text{Pa} = 4.28\times10^3\ \text{Pa}$

(b) (Using $K_{eq} = 5.00\times10^{-5}$ for calculation)

Mass balance : $[HCO_3^-] = 2\ [Ca^{2+}]$

$[Ca^{2+}] = 100\ \text{mg dm}^{-3} = 2.50\times10^{-3}\ \text{mol dm}^{-3}$

Inserting into $K_{eq} = 5.00\times10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_2(aq)] = 4\ [Ca^{2+}] / [CO_2(aq)]$

$[CO_2(aq)] = 1.25\times10^{-3}$

$p_{CO_2} = ([CO_2(aq)] / K_{CO_2}) \times 1.01\times10^5\ \text{Pa} = 3.67\times10^3\ \text{Pa}$

PROBLEM 7

Kinetic Behaviour of Ozone

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,

$$2\,O_3 \rightarrow 3\,O_2.$$

One of the proposed mechanisms is expressed as

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2 \qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2\,O_2 \qquad (2)$$

where k_1, k_{-1}, and k_2 are the rate constants.

7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3, O_2, and O at time t, assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is d[O]/dt = 0, show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:

$$CCl_2F_2 \xrightarrow{h\nu} CF_2Cl + Cl \qquad (3)$$

7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad (4)$$

Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1}, while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1}. Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25 ^{o}C. Assume the frequency factor is the same for each reaction.

SOLUTION

7.1 $$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O][O_2] + k_2[O_3][O]$$

$$-\frac{d[O_2]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] - 2k_2[O_3][O]$$

$$-\frac{d[O]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O]$$

7.2 Equilibrium constant *K* is expressed as

$$K = \frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}}$$

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$-\frac{d[O_3]}{dt} = k_2[O_3][O] = \frac{k_1\,k_2\,[O_3]^2}{k_{-1}\,[O_2]}$$

7.3 $$-\frac{d[O]}{dt} = 0$$

$$-k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O] = 0$$

Thus $$-\frac{d[O_3]}{dt} = 2k_2[O_3][O] = \frac{2\,k_1\,k_2\,[O_3]^2}{k_{-1}\,[O_2] + k_2\,[O_3]}$$

7.4 $ClO(g) + O_3(g) \rightarrow Cl(g) + 2\,O_2(g)$

7.5 According to equation $k = A\exp(-E_a / RT)$,

the ratio of rate constants yields

Ratio = $\exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122$.

PROBLEM 8

Protein Folding

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:

$$\mathbf{N} \xrightleftharpoons{K(T)} \mathbf{U}$$

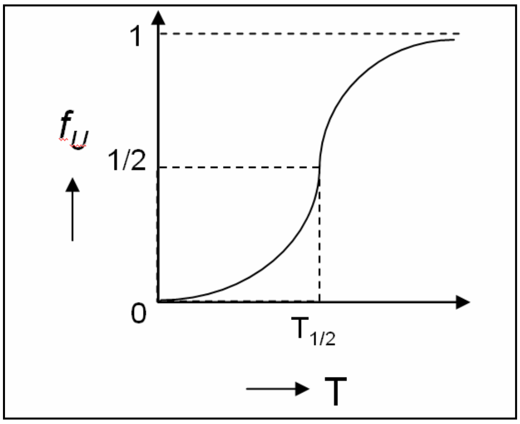
where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. K(*T*) is the equilibrium constant for the process at absolute temperature *T*.

8.1 What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?

8.2 What is the standard free energy change of the process ($\Delta G°(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.

8.3 If $(C_N)_{eq}$ and $(C_U)_{eq}$ denote the equilibrium concentrations of *N* and *U* in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{eq}/C$. Deduce an expression for f_U in terms of the equilibrium constant *K*. Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by f_U = ½ and $T = T_{½}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{½}$, f_U increases above ½, but at temperatures lower than $T_{½}$, f_U decreases below ½.

8.4 What is the sign of $\Delta G°(T)$ at temperatures below and above $T_{½}$? Select your answer from the following choices.

a) Negative both below and above $T_{½}$.

b) Positive both below and above $T_{½}$.

c) Positive below $T_{½}$, but negative above $T_{½}$.

d) Negative below $T_{½}$, but positive above $T_{½}$..

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{½}$ and (ii) decreases below $T_{½}$? Select your answer from the following choices.

a) Decrease in both cases.

b) Increase in both cases.

c) Increases above $T_{½}$, but decreases below $T_{½}$.

d) Decreases above $T_{½}$, but increases below $T_{½}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:

$$\mathbf{N} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{U}$$

where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b?

8.7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{eq}$.

SOLUTION

8.1 Answer: 1

8.2 Answer: 0 kJ mol^{-1}

8.3 $f_U = \dfrac{C_U^{eq}}{C_N^{eq} + C_U^{eq}} = \dfrac{\dfrac{C_U^{eq}}{C_N^{eq}}}{1 + \dfrac{C_U^{eq}}{C_N^{eq}}} = \dfrac{K}{1+K}$

8.4 Correct answer is (c). Positive below $T_{1/2}$, but negatíve above $T_{1/2}$

8.5 Correct answer is (d). Decreases above $T_{1/2}$, but increases below $T_{1/2}$.

8.6 Answer: $K = k_f / k_b$

8.7 $dC_U/dt = k_f C_N - k_b C_U$

$= k_f(C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b)\, C_U$ (1)

$K = k_f / k_b = (C_U)_{eq} / (C_N)_{eq}$

$1 / K = k_b / k_f = (C_N)_{eq} / (C_U)_{eq}$

$\Rightarrow \quad k_b / k_f + 1 = (C_N)_{eq} / (C_U)_{eq} + 1$

$\Rightarrow \quad (k_b + k_f) / k_f = [(C_N)_{eq} + (C_U)_{eq}] / (C_U)_{eq}$

$\Rightarrow \quad (k_b + k_f) / k_f = C/(C_U)_{eq}$

$C = [(k_b + k_f)\, (C_U)_{eq}\,] / k_f$ (2)

Now substitute C obtained from eq (2) to eq (1).

We get $k_f\{\, [(k_b + k_f)\, (C_U)_{eq}] / k_f\} - (k_f + k_b)\, C_U$

$\Rightarrow \quad [(k_b + k_f)\, (C_U)_{eq}] - (k_f + k_b)\, C_U$

$\Rightarrow \quad - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

So we get

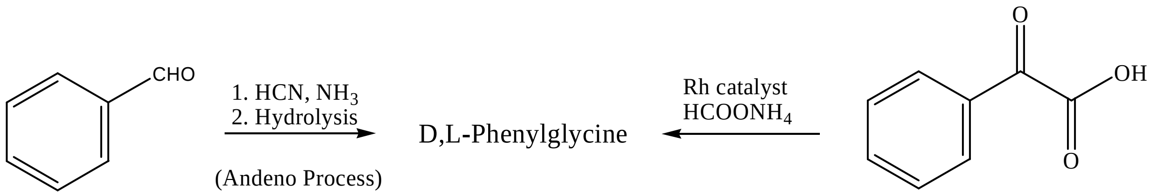
$dC_U/dt = - (k_f + k_b)\, [C_U - (C_U)_{eq}]$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β-lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH_3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



Benzaldehyde D,L-phenylglycine Benzoylformic acid

In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H_2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H_2O at 25 ℃. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 cm^3 of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 ℃ by adjusting the thermostat of the hot plate/stirrer.
3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
4. Add 15 cm^3 of deionized water to the resulting mixture and stir for 10 minutes.
5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 cm^3 each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
6. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 ℃ for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

7. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^1H NMR spectrum

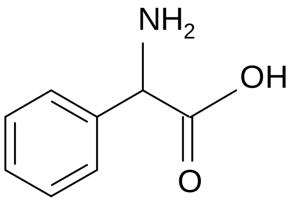
analysis. Turn in the product in a vial (**blue label** with ^{1}H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

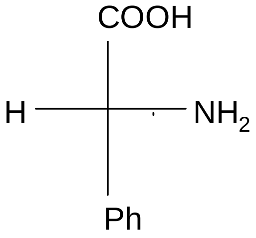
Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]

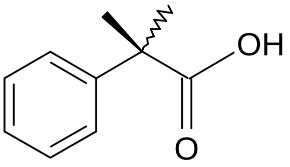
1. To a 25 cm^3 round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm^3) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm^3 each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

SOLUTION

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine: (Task appeared in the answer sheet only.)







A

B

PROBLEM 2 (Practical)

Identification of Unknown Inorganic Samples

Note

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in the equipment and reagent list.

(3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.

(4) The volume of each unknown solution is about 1.5 cm^3 (about 30 drops). No more reagents or samples will be provided.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag: 9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 cm^3 solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol dm^{-3}).

The unknown samples are as follows:

HCl H_2O_2 H_2SO_4 $ZnCl_2$ NH_4SCN

$NaOH$ Na_2CO_3 Na_2SO_3 $BaCl_2$ $K_4Fe(CN)_6$

Note

1) Two unknown samples are duplicates.

2) The crystal water (. H_2O) is omitted in the formulas listed above.

2.1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

2.2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is $ZnCl_2$.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).

SOLUTION

2.2A $Zn^{2+}(aq) + 2\ Cl^{-}(aq) \rightarrow Cl_2(g)$ (anode) + $Zn(s)$ (deposit on cathode)

2.2B $Zn(s) + 2\ H^{+}(aq) \rightarrow H_2(g) + Zn^{2+}(aq)$

or

$Zn(s) + 2\ OH^{-}(aq) + 2\ H_2O(l) \rightarrow H_2(g) + [Zn(OH)_4]^{2-}(aq)$

38th

11 theoretical problems
3 practical problems

THE THIRTY-EIGHTH
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 2006, GYEONGSAN, KOREA

THEORETICAL PROBLEMS

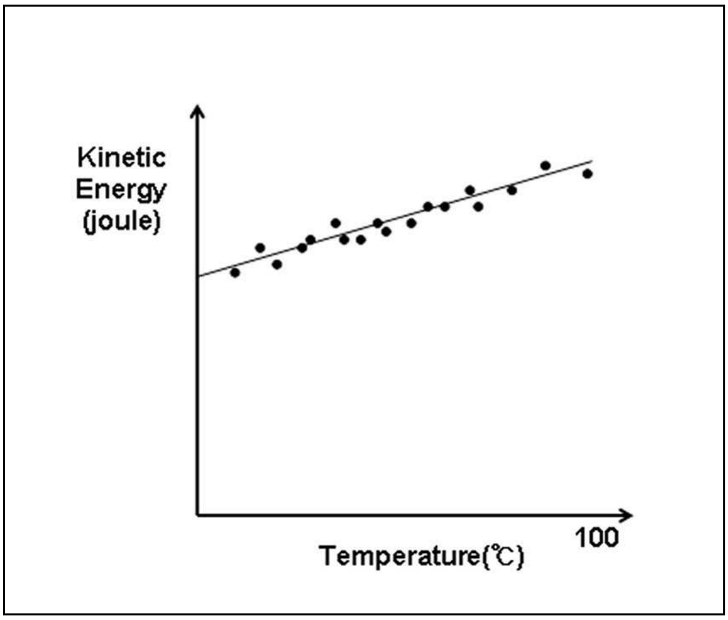
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 °C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s^{-1} at 27 °C. The density of a water droplet is 1.0 g cm^{-3}.

1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 °C. The volume of a sphere is given by $(4/3)\ \pi\ r^3$ where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 °C and 100 °C as a function of temperature is found to be linear. Assume that it remains linear below 0 °C.



At thermal equlibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is 0.31 J g^{-1} K^{-1}.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$m = V\rho = [(4/3)\ \pi\ r^3]\ \rho = (4/3)\ \pi\ (0.5\times10^{-6}\ \text{m})^3\ (1.0\ \text{g cm}^{-3}) = 5.2\times10^{-16}\ \text{kg}$

Average kinetic energy at 27°C:

$$E_k = \frac{m\,v^2}{2} = \frac{(5.2\times10^{-16}\ \text{kg})\times(0.51\times10^{-2}\ \text{m/s})^2}{2} = 6.9\times10^{-21}\ \text{kg m}^2/\text{s}^2 = \underline{6.9\times10^{-21}\ \text{J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet. E_k becomes zero at –273 °C.

From the linear relationship in the figure, $E_k = a\,T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9\times10^{-21}\ \text{J}}{(27+273)\ \text{K}} = 2.3\times10^{-23}\ \text{J K}^{-1}$$

S: specific heat of argon N: number of atoms in 1g of argon

$S = 0.31\ \text{J g}^{-1}\ \text{K}^{-1} = a\times N$

$$N = \frac{S}{a} = \frac{0.31\ \text{J g}^{-1}\ \text{K}^{-1}}{2.3\times10^{-23}\ \text{J K}^{-1}} = 1.4\times10^{22}\ \text{g}^{-1}$$

Avogadro's number (N_A) : Number of argon atoms in 40 g of argon

$N_A = 40\ \text{g mol}^{-1}\times1.4\times10^{22}\ \text{g}^{-1} = \underline{5.6\times10^{23}\ \text{mol}^{-1}}$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

2.1 There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3}; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

2.2 The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f)$ = = – $C(1/n_f^2 - 1/n_i^2)$, where *n* is principle quantum number, and C is a constant. For detection of the $\Delta E(3\rightarrow 2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the $n = 2$ state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1\rightarrow 2)$ transition.

2.3 According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature *T* is given by $\lambda T = 2.9\times10^{-3}$ m K. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

2.4 Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.

2.5 Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the "proton". Fill in the blank.

____

SOLUTION

2.1 Mass of a typical star = $(4/3) \times (3.1) \times (7\times10^8\ \text{m})^3 \times (1.4\times10^6\ \text{g m}^{-3}) = 2\times10^{33}$ g

Mass of protons of a typical star = $(2\times10^{33}\ \text{g}) \times (3/4 + 1/8) = 1.8\times10^{33}$ g

Number of protons of a typical star = $(1.8\times10^{33}\ \text{g}) \times (6\times10^{23}\ \text{g}^{-1}) = 1\times10^{57}$

Number of stellar protons in the universe = $(1\times10^{57}) \times (10^{23}) = \underline{1\times10^{80}}$

2.2 $\Delta E(2\rightarrow3) = C(1/4 - 1/9) = 0.1389\ C$ $\lambda(2\rightarrow3) = 656.3$ nm

$\Delta E(1\rightarrow2) = C(1/1 - 1/4) = 0.75\ C$

$\lambda(1\rightarrow2) = (656.3) \times (0.1389 / 0.75) = 121.5$ nm

2.3 $T = 2.9\times10^{-3}$ m K / 1.215×10^{-7} m = 2.4×10^4 K

2.4 $\lambda = 3\times10^8$ m / 1.42×10^9 = 0.21 m

$T = 2.9\times10^{-3}$ m K / 0.21 m = 0.014 K

2.5 $^{14}N + ^{4}He \rightarrow ^{17}O + ^{1}H$

PROBLEM 3

Interstellar chemistry

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH_2, CH_3, etc.

Depending on how energetically a molecule "jumps" from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A\ \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

3.1 Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1\times10^{12}$ s^{-1} and E_{des} = 12 kJ mol^{-1}.

3.2 Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1}, and the IIG is a sphere with a 0.1 μm radius. Each migratory jump laterally advances the molecule by 0.3 nm. Show work and choose your answer from (a) – (e) below.

(a) $t \le 1$ day (b) 10 days $\le t \le 10^2$ yr c) 10^3 yr $\le t \le 10^6$ yr

(d) 10^7 yr $\le t \le 10^{10}$ yr (e) $t \ge 10^{11}$ yr

3.3 Consider the reaction of CO with H_2 to form H_2CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K. Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K.

3.4 Which is a set of all true statements? Circle one.

(a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

(b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.

(c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

☐ (a) ☐ (b) ☐ (c) ☐ (a, b) ☐ (a, c) ☐ (b, c) ☐ (a, b, c)

SOLUTION

3.1 $k_{des} = A \exp(–E_{des}/RT) = (1\times10^{12}\ s^{-1}) \times (5\times10^{-32}) = 5\times10^{-20}\ s^{-1}$ at $T = 20$ K

surface residence time, $T_{residence} = 1 / k_{des} = 2\times10^{19}$ s = <u>6×10^{11} yr</u>

(full credit for $T_{half-life} = \ln 2 / k_{des} = 1\times10^{19}$ s $= 4\times10^{11}$ yr)

residence time = 2×10^{19} s

3.2 The distance to be traveled by a molecule: $x = \pi r = 300$ nm.

$k_{mig} = A \exp(–E_{mig} / RT) = (1\times10^{12}\ s^{-1}) \times (2\times10^{-16}) = 2\times10^{-4}\ s^{-1}$ at $T = 20$ K

Average time between migratory jumps, $T = 1 / k_{mig} = 5\times10^{3}$ s

Time needed to move 300 nm = (300 nm / 0.3 nm) jumps × (5×10^{3} s/jump) =

= 5×10^{6} s = <u>50 days</u>

<u>The correct answer is (b).</u>

(Full credit for the calculation using a random-walk model. In this case:

$t = T\,(x/d)^{2} = 5\times10^{9}$ s = 160 yr. The answer is still (b).)

3.3 $k(20\ K) / k(300\ K) = \exp[(E/R)\,(1/T_1 – 1/T_2)] = e^{-112} = \sim 1\times10^{-49}$ for the given reaction

The rate of formaldehyde production at 20 K = = ~ 1×10^{-49} molecule/site/s =

= ~ 1×10^{-42} molecule/site/ yr

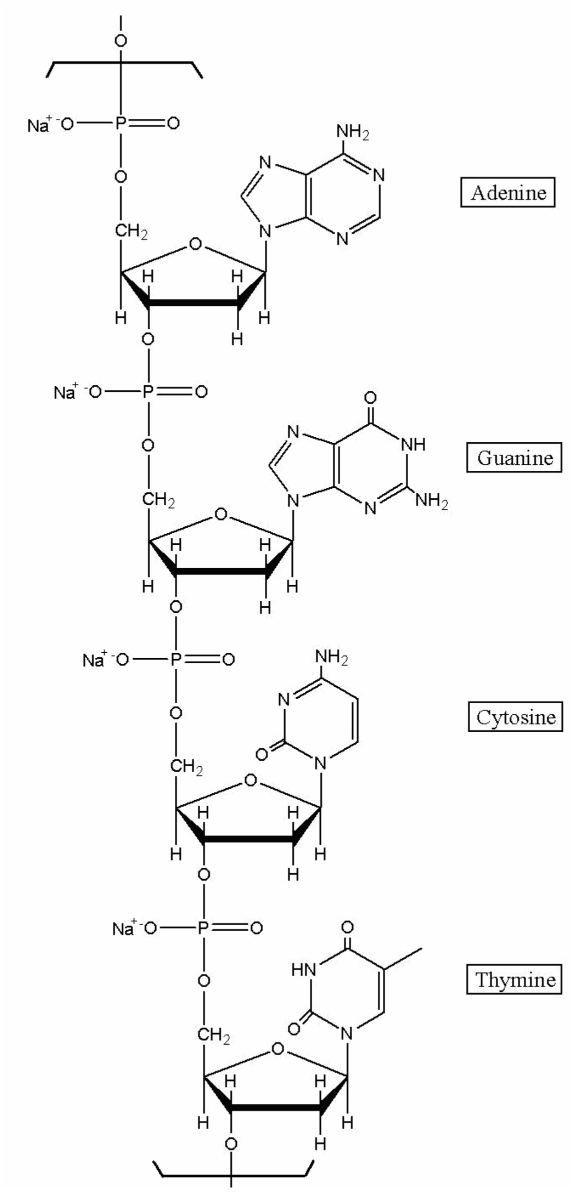
(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is <u>(b, c)</u>.

PROBLEM 4

The Chemistry of DNA

4.1 In 1944 Oswald Avery isolated a genetic material and showed by elemental analysis that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, write the number of H atoms per P atom. Calculate (to 3 significant figures) the theoretical weight percentage of H expected upon elemental analysis of DNA.

4.2 Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

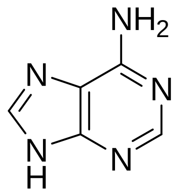
adenine to guanine = 1.43	thymine to cytosine = 1.43
adenine to thymine = 1.02	guanine to cytosine = 1.02

Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

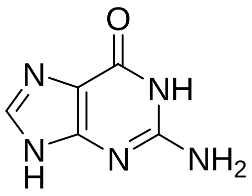
Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4.3 Mutation can occur through base pairings different from the above. Draw structures of any three alternative base pairs.

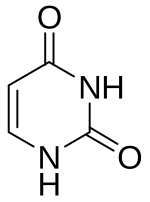
4.4 The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH_3, and H_2O has been demonstrated in the laboratory. Write the minimum number of HCN and H_2O molecules required for formation of the following compounds.



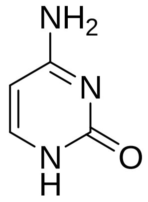
adenine



guanine



Uracil



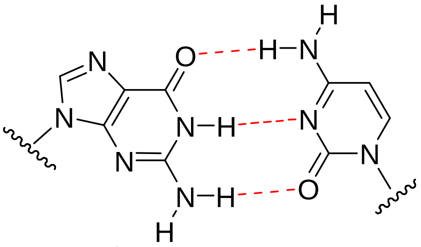
cytosine

SOLUTION

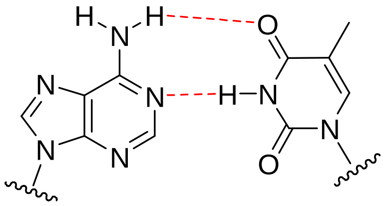
4.1

	H	P
Number of atoms:	11.3	1
theoretical wt %:	3.43	

4.2

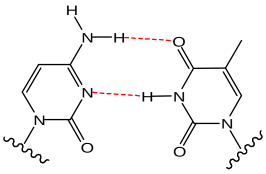


guanine cytosine

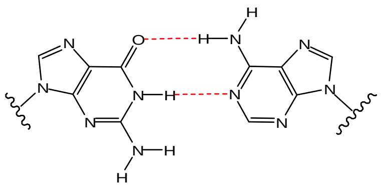


adenine thymine

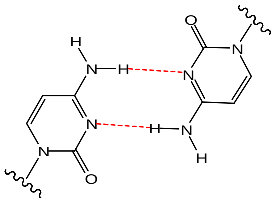
4.3



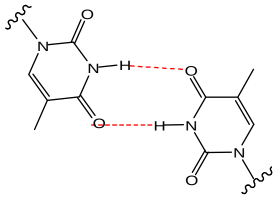
cytosine thymine



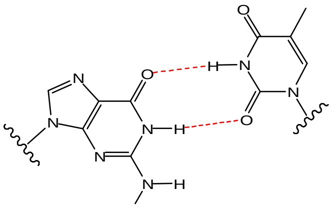
guanine adenine



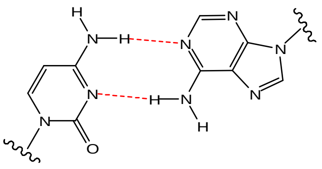
cytosine cytosine



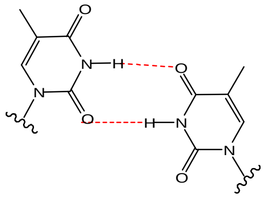
thymine thymine



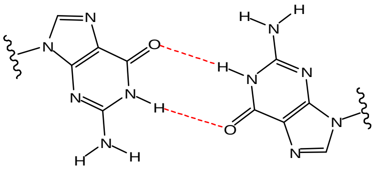
guanine thymine



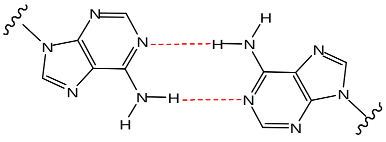
cytosine adenine



thymine thymine

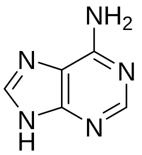


guanine guanine

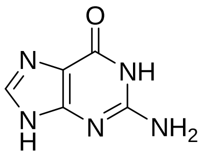


adenine adenine

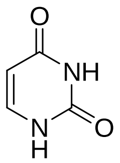
4.4



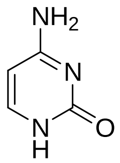
adenine



guanine



Uracil



cytosine

HCN	(5)	(5)	(4)	(4)
H_2O	(0)	(1)	(2)	(1)

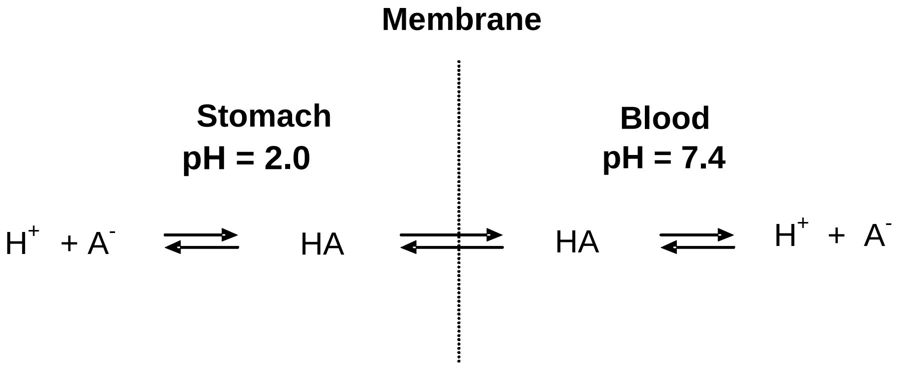
PROBLEM 5

Acid-Base Chemistry

5.1 Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0 \times 10^{-14}$, $K_2 = 1.2 \times 10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.

5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm^3 aqueous solution containing 3.48 cm^3 of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm^3, M_r = 98.00) (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.44).

5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ([HA] + [A^-]) of aspirin (acetylsalicylic acid, pK = 3.52) in the blood to that in the stomach.

SOLUTION

5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$[H_2SO_4] = 0$

2nd ionization: $[H^+][SO_4^{2-}] / [HSO_4^-] = K_2 = 1.2\times10^{-2}$ (1)

Mass balance: $[H_2SO_4] + [HSO_4^-] + [SO_4^{2-}] = 1.0\times10^{-7}$ (2)

Charge balance: $[H^+] = [HSO_4^-] + 2\,[SO_4^{2-}] + [OH^-]$ (3)

Degree of ionization is increased upon dilution.

$[H_2SO_4] = 0$

Assume $[H^+]_{H_2SO_4} = 2\times10^{-7}$

From (1): $[SO_4^{2-}] / [HSO_4^-] = 6\times10^4$ (2nd ionization is almost complete)

$[HSO_4^-] = 0$

From (2): $[SO_4^{2-}] = 1.0\times10^{-7}$

From (3): $[H^+] = (2\times10^{-7}) + 10^{-14} / [H^+]$

$[H^+] = 2.4\times10^{-7}$ (pH = 6.6)

$[OH^-] = 1\times10^{-14} / (2.4\times10^{-7}) = 4.1\times10^{-8}$

From (1):

$[HSO_4^-] = [H^+]\,[SO_4^{2-}] / K_2 = (2.4\times10^{-7}) \times (1.0\times10^{-7}) / (1.2\times10^{-2}) = 2.0\times10^{-12}$

Check charge balance:

$2.4\times10^{-7} \approx (2.0\times10^{-12}) + 2\,(1.0\times10^{-7}) + (4.1\times10^{-8})$

Check mass balance:

$0 + 2.0\times10^{-12} + 1.0\times10^{-7} \approx 1.0\times10^{-7}$

5.2 $n(H_3PO_4) = 0.85 \times 3.48\ cm^3 \times 1.69\ g\ cm^{-3} \times 1\ mol / 98.00\ g \times 1000 = 51.0\ mmol$

The desired pH is above pK_2.

A 1:1 mixture of $H_2PO_4^-$ and HPO_4^{2-} would have $pH = pK_2 = 7.20$.

If the *pH* is to be 7.40, there must be more HPO_4^{2-} than $H_2PO_4^-$.

We need to add NaOH to convert H_3PO_4 to $H_2PO_4^-$ and to convert to the right amount of $H_2PO_4^-$ to HPO_4^{2-}.

$$H_3PO_4 + OH^- \rightarrow H_2PO_4^- + H_2O$$

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O$$

The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to $H_2PO_4^-$ is:

51.0 mmol / 0.80 mol dm^{-3} = 63.75 cm^3

To get *pH* of 7.40 we need:

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-}$$

	$H_2PO_4^-$	OH^-	HPO_4^{2-}
Initial mmol	51.0	x	0
Final mmol	51.0 – x	0	x

$pH = pK_2 + \log [HPO_4^{2-}] / [H_2PO_4^-]$

7.40 = 7.20 + log {x / (51.0 – x)}; x = 31.27 mmol

The volume of NaOH needed to convert 31.27 mmol is:

31.27 mmol / 0.80 mol dm^{-3} = 39.09 cm^3

The total volume of NaOH = 63.75 + 39.09 = 102.84 cm^3 ≈ 103 cm^3

5.3 $pK = 3.52$

$pH = pK_a + \log ([A^-] / [HA])$

$[A^-] / [HA] = 10^{(pH-pKa)}$

In blood, $pH = 7.40$, $[A^-] / [HA] = 10^{(7.40-3.52)} = 7586$

Total ASA = 7586 + 1 = 7587

In stomach, $pH = 2.00$, $[A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02\times10^{-2}$

Total ASA = $1 + 3.02\times10^{-2} = 1.03$

Ratio of total aspirin in blood to that in stomach = 7587 / 1.03 = 7400

PROBLEM 6

Electrochemistry

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

6.1 Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.

6.2 Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.

6.3 When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

6.4 Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^{+})	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $Cu(OH)_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00\times10^{-14}$ at 25 °C.

6.5 Precipitation of $Cu(OH)_2$ begins at pH = 4.84. Determine the solubility product of $Cu(OH)_2$.

6.6 Calculate the standard reduction potential for $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu(s) + 2\ OH^-$.

6.7 Calculate the electrode potential at *pH* = 1.00.

Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge recharge cycles, the following reversible half-reactions occur.

$LiCoO_2 \rightleftarrows Li_{1-x}\,CoO_2 + x\ Li^+ + x\ e^-$

$C + x\ Li^+ + x\ e^- \rightleftarrows CLi_x$

The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION

6.1 $4\ H_2O + 4\ e^- \rightarrow 2\ H_2(g) + 4\ OH^-$ (or $2\ H_2O + 2\ e^- \rightarrow H_2(g) + 2\ OH^-$)

6.2 $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ (or $H_2O \rightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$)

6.3 $Cu \rightarrow Cu^{2+} + 2e^-$

6.4 Reduction of sodium ion seldom takes place.
It has a highly negative reduction potential of –2.710 V.

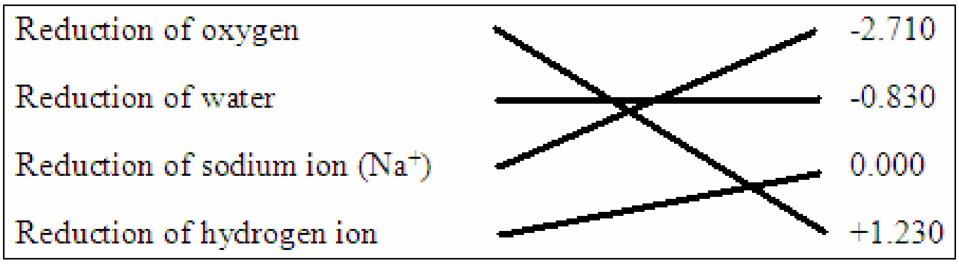
Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is –0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V.



6.5 pOH = 14.00 – 4.84 = 9.16

$[OH^-] = 6.92\times10^{-10}$

$K_{sp} = [Cu^{2+}]\,[OH^-]^2 = 0.100 \times (6.92\times10^{-10}) = 4.79\times10^{-20}$

6.6 $E = E^o(Cu^{2+}/ Cu) + (0.0592 / 2) \log [Cu^{2+}] = +0.340 + (0.0592/2) \log [Cu^{2+}] =$

$= +0.340 + (0.0592 / 2) \log (K_{sp} / [OH^-]^2)$

$= +0.340 + (0.0592 / 2) \log K_{sp} - (0.0592 / 2) \log [OH^-]^2$

$= +0.340 + (0.0592 / 2) \log K_{sp} - 0.0592 \log [OH^-]$,

By definition, the standard potential for

$Cu(OH)_2(s) + 2\,e^- \rightarrow Cu(s) + 2\,OH^-$

is the potential where $[OH^-] = 1.00$.

$E = E^o\left(Cu(OH)_2 / Cu\right) = + 0.340 + (0.0592/2) \log K_{sp}$

$= + 0.340 + (0.0592 / 2) \log (4.79\times10^{-20})$

$= + 0.340 – 0.572$

$= – 0.232$ V

One may solve this problem as follows.

Eqn 1: $Cu(OH)_2(s) + 2\ e^- \rightarrow Cu + 2\ OH^-$

$E_+^o = E^o\big(Cu(OH)_2 / Cu\big) = ?$

Eqn 2: $Cu(OH)_2(s) \rightarrow Cu^{2+} + 2\ OH^-$

$E^o = (0.05916 / n) \log K_{sp} = (0.05916 / 2) \log(4.79\times10^{-20}) = -\ 0.5715$ V

Eqn 1 – Eqn 2 : $Cu^{2+} + 2\ e^- \rightarrow Cu$

$E_-^o = E_+^o - E^o = E^o\,(Cu^{2+} / Cu) = 0.34$ V

Therefore, $E_+^o = E_-^o + E^o = +\ 0.34 + (-0.5715)\ =\ = -0.232$ V

6.7 Below *pH* = 4.84, there is no effect of $Cu(OH)_2$ because of no precipitation. Therefore,

$E = E\,(Cu^{2+} / Cu)\ =\ +0.340 + (0.0592 / 2) \log [Cu^{2+}]\ =$

$=\ +0.340 + (0.0592 / 2) \log 0.100\ =\ +0.340 - 0.0296 = +0.310$ V

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge 96487 × 0.0139 = 1340 coulombs.

1340 coulombs / g = 1340 A sec / g = 1340 × 1000 mA × (1 / 3600) h =

= 372 mAh / g

PROBLEM 7

Hydrogen Economy

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m^{-3}.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. ΔH_f^o [H_2O(l)] = -286 kJ/mol, ΔH_f^o [CO_2(g)] = -394 kJ/mol.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by [$1 - T_{cold}/T_{hot}$].

$S^o_{298}[H_2(g)] = 131$ J mol^{-1} K^{-1}

$S^o_{298}[O_2(g)] = 205$ J mol^{-1} K^{-1}

$S^o_{298}[H_2O(l)] = 70$ J mol^{-1} K^{-1}

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

SOLUTION

7.1
$$\frac{n}{V} = \frac{p}{RT} = \frac{80\times10^6 \text{ Pa}}{8{,}314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 32 \text{ kmol m}^{-3}$$

$$\rho = \frac{m}{V} = 32 \text{ kmol m}^{-3} \times 2 \text{ kg kmol}^{-1} = 64 \text{ kg m}^{-3}$$

7-2. $Hg_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$; $\Delta H_{\text{rexn-1}} = \Delta H_f\,[H_2O(l)] = -286\ \text{kJ mol}^{-1} = -143\ \text{kJ g}^{-1}$

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_{\text{rexn-2}} = \Delta H_f\,[CO_2(g)] = -394\ \text{kJ mol}^{-1} = -33\ \text{kJ g}^{-1}$

$$\frac{(-\Delta H_{\text{rexn}-1})}{(-\Delta H_{\text{rexn}-2})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{\text{rexn}-2})}{(-\Delta H_{\text{rexn}-1})} = 0.23$$

7.3 $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\Delta H_c = -286\ \text{kJ mol}^{-1} = -143\ \text{kJ g}^{-1} = -143\times10^3\ \text{kJ kg}^{-1}$

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

$\Delta S_c = 70 - 131 - 205/2 = -163.5\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta G_c = -286\ \text{kJ mol}^{-1} + 298\ \text{K} \times 163.5\ \text{J mol}^{-1}\ \text{K}^{-1} = -237\ \text{kJ mol}^{-1} = -1.2\times10^5\ \text{kJ kg}^{-1}$

(a) electric motor: $W_{\max} = \Delta G_c \times 1\ \text{kg} = -1.2\times10^5\ \text{kJ}$

(b) heat engine: $W_{\max} = \text{efficiency} \times \Delta H_c$

$= (1 - 298 / 573) \times (-143\times10^3\ \text{kJ}) = -6.9\times10^4\ \text{kJ}$

$119\times10^3\ \text{kJ} = 1\ \text{W} \times \text{t(sec)}$

$t = 1.2\times10^8\ \text{s} = 3.3\times10^4\ \text{h} = 1.4\times10^3$ days = 46 month = 3.8 yr

$\Delta G = -n\,F\,E$ n = number of electrons involved in the reaction

$F = 96.5\ \text{kC mol}^{-1}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ n = 2

$$E = \frac{-\Delta G}{n\,F} = \frac{237\ \text{kJ mol}^{-1}}{2\times 96.5\ \text{kC mol}^{-1}} = 123\ \text{V}$$

$$I = \frac{W}{E} = 0.81\ \text{A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

$C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH^0 = –393.51 kJ(/mol) (1)

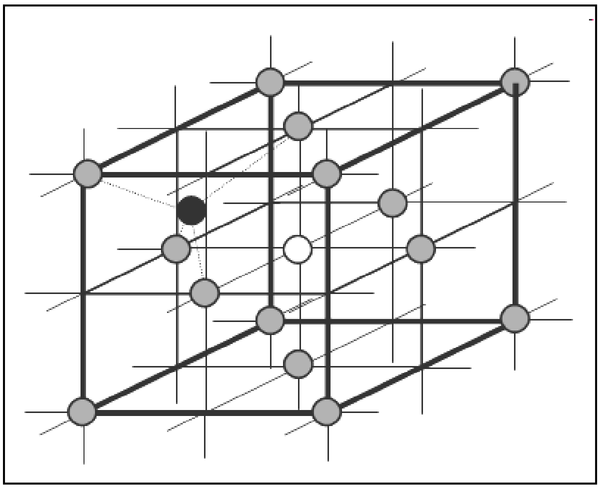
$CO_2(g) + C(s) \rightarrow 2\ CO(g)$ ΔH^0 = 172.46 kJ(/mol) (2)

$Fe_2O_3(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$ ΔH^0 = ? (3)

8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(Fe_2O_3(s)$ = –824.2 kJ mol^{-1}, S°(J mol^{-1} K^{-1}): Fe(s) = 27.28, Fe_2O_3(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO_2(g) = 213.74

In the manufacture of celadon pottery, Fe_2O_3 is partially reduced in a charcoal kiln to mixed oxides of Fe_3O_4 and FeO. The amount of the different oxides seems to be related to the "mystic" color of celadon ceramics. Fe_3O_4 (magnetite) itself is a mixed oxide containing Fe^{2+} and Fe^{3+} ions and belongs to a group of compounds with a general formula of AB_2O_4. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.



8.3 How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

8.4 What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4?

8.5 Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

8.1 (1): C (2): C (3): CO

8.2 Balanced equation (3): $Fe_2O_3(s) + 3\ CO(g) \rightarrow 2\ Fe(s) + 3\ CO_2(g)$

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0_{(1)} = -393.51$ kJ $= \Delta H_f^0\ (CO_2(g))$

(2) $CO_2(g) + C(s) \rightarrow 2\ CO(g)$ $\Delta H^0_{(2)} = 172.46$ kJ

From (1) and (2):

$\Delta H_f^0(CO(g)) = (1/2)\ \{172.46 + (-393.51)\} = -110.525$ kJ

$\Delta H_f^0(Fe_2O_3) = –824.2$ kJ

$\Delta H^0_{(3)} = 3 \times \Delta H_f^0(CO_2(g)) – \Delta H_f^0(Fe_2O_3) – 3 \times \Delta H_f^0(CO(g))$

$= [3 \times (–393.51)] – (–824.2) – [3 \times (–110.525)] = –24.8$ kJ

$\Delta S°_{(3)} = (2 \times 27.28) + (3 \times 213.74) – 87.4 – (3 \times 197.674) = 15.36$ J K^{-1}

$\Delta G^0_{(3)} = \Delta H^0 – T\Delta S^0 = –24.8$ kJ – (15.36 J K^{-1} × 1 kJ /1000 J x 1473.15 K) =

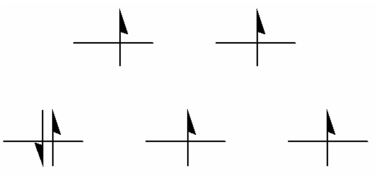
= – 47.43 kJ

$$K = e^{(-\Delta G°/RT)} = e^{(47430\,\text{J} \,/\, (8.314\,\text{J K}^{-1} \times 1473.15\,\text{K}))} = 48$$

8.3 One AB_2O_4 unit has available 4 (= 1 + (1/4 × 12) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives (1/8) x 100 % = 12.5 % occupancy in available tetrahedral sites.

8.5

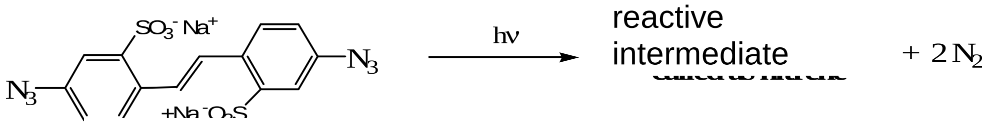


PROBLEM 9

Photolithographic process

Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.



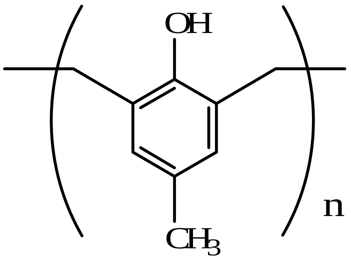
Bis(aryl azide)

9.1 Draw two possible Lewis structures of CH_3-N_3, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.

9.2 Draw the Lewis structure of nitrene expected from CH_3-N.

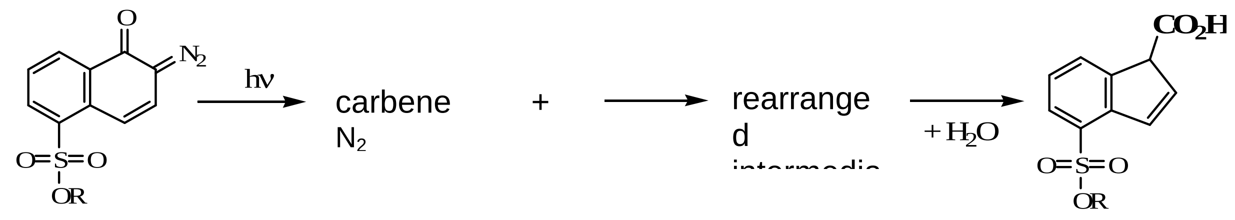
9.3 Draw the structures for two possible products, when this nitrene from CH_3-N_3 reacts with ethylene gas (CH_2CH_2).

Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, “Novolaks” have been the representative “positive” photoresists of the modern microelectronic revolution.



Novolak

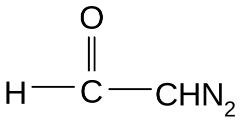
When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



Diazonahpthaquinone derivative

9.4 Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

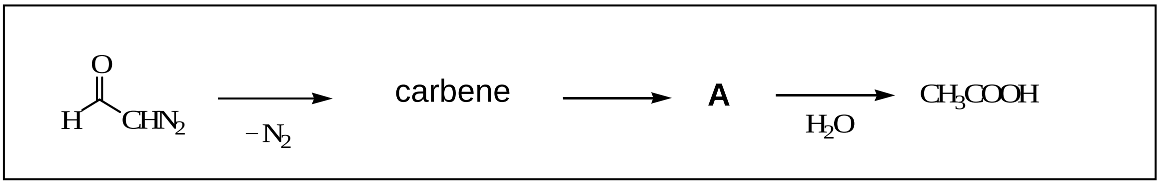
Diazonaphthaquinone
derivative



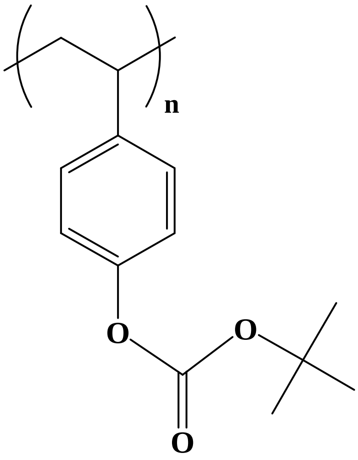
$$H-\overset{\overset{\large O}{\|}}{C}-CHN_2$$

diazoacetaldehyde

9.5 Draw a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N_2. A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH_3COOH.

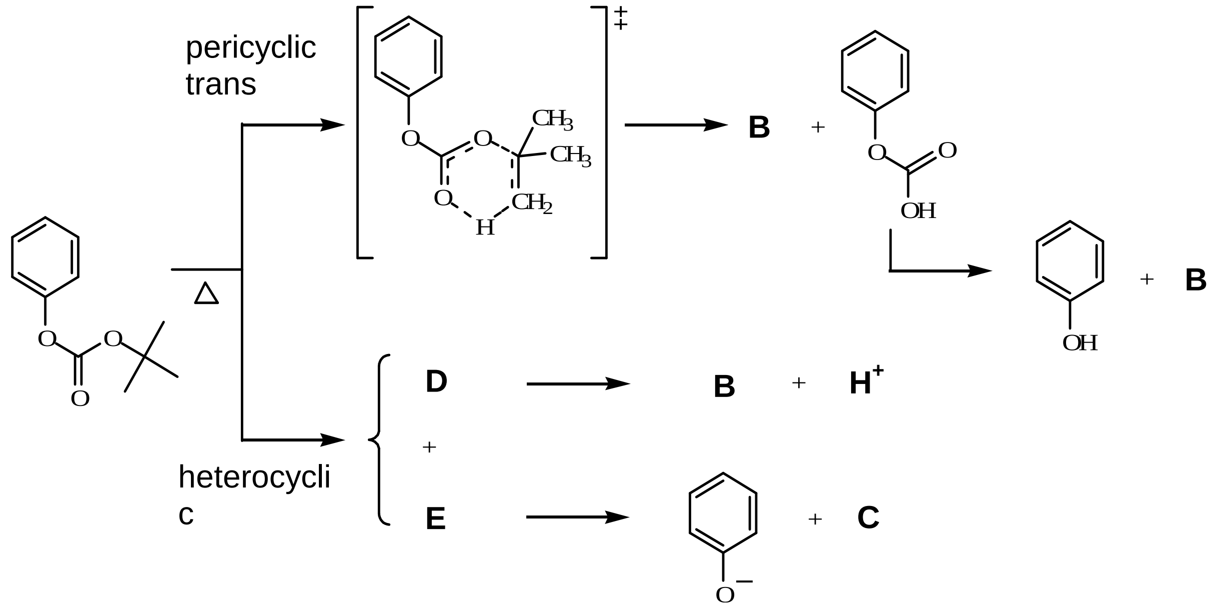


Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

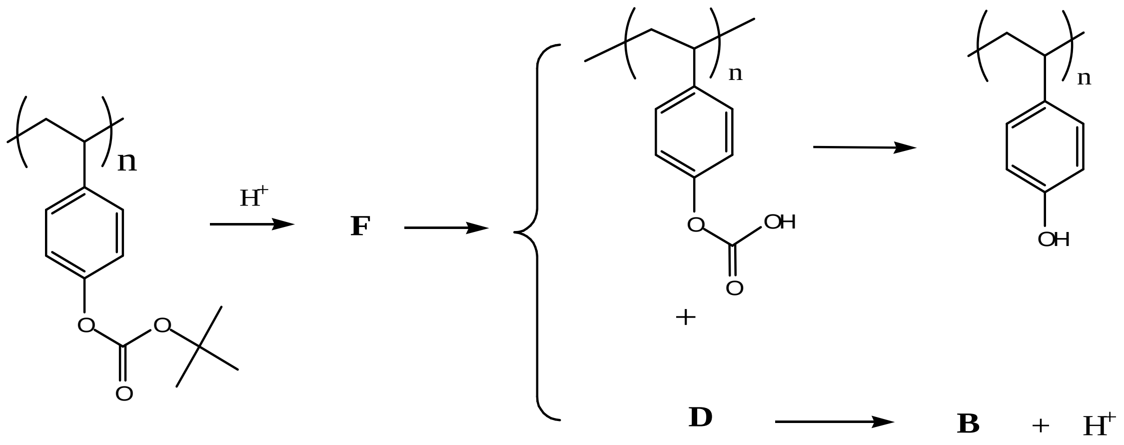


The thermal decomposition of carbonate ester itself normally occurs well above 150 °C.

9.6 Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.

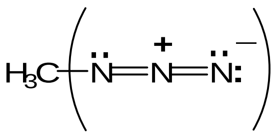


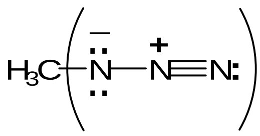
9.7 In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100 °C. Draw expected intermediate F from the following chemical amplification process based on using *t*-BOC.



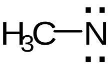
SOLUTION

9.1

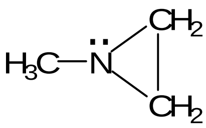


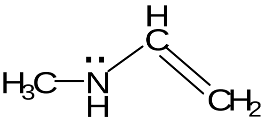


9.2

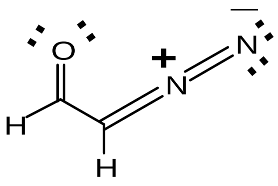


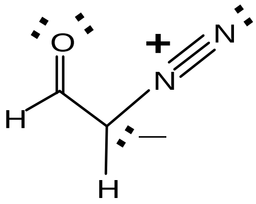
9.3

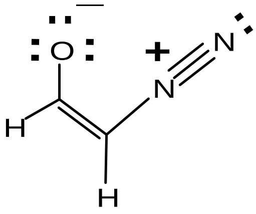




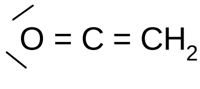
9.4





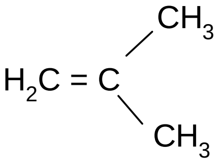


9.5



$O = C = CH_2$

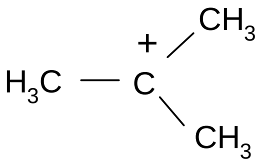
9.6



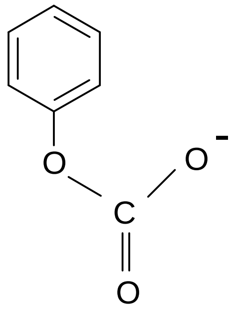
B

CO_2

C

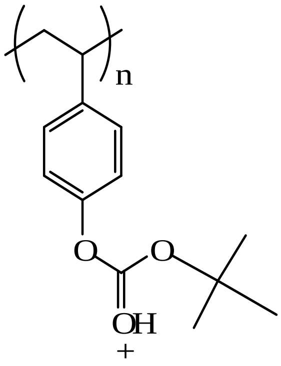


D



E

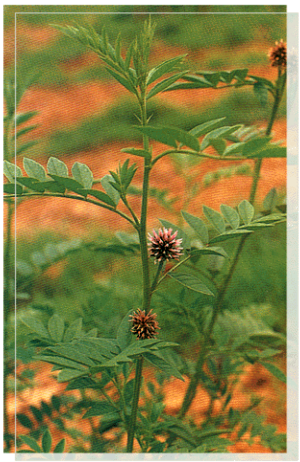
9.7



F

PROBLEM 10

Natural Products – Structural Analysis



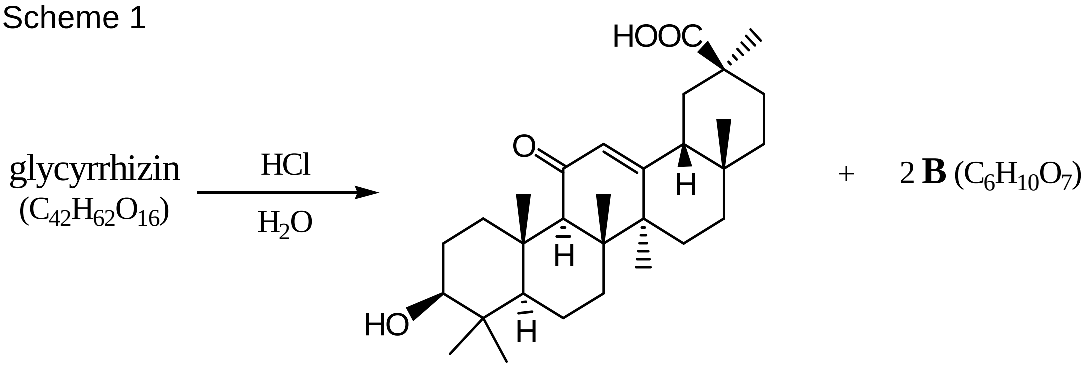
Licorice (Glycyrrhizia. Uralensis)

Licorice Root

The flavour extracted from the licorice root is 50 – 150 times sweeter than table sugar. The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

Glycyrrhizin requires three equivalents of NaOH to effect neutralization. When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_4$)) and **B** ($C_6H_{10}O_7$) were obtainned in a 1:2 molar ratio (Scheme 1).

Scheme 1



A (Glycyrrhizinic acid)

When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (Scheme 2). **B**, **C** and **D** exist as mixtures of anomers.

Scheme 2

$$\underset{(C_{42}H_{62}O_{16})}{\text{glycyrrhizin}} \xrightarrow[\text{ii) HCl / }H_2O]{\text{i) MeI, }Ag_2O} \mathbf{A'}\ (C_{31}H_{48}O_4) \quad + \quad \mathbf{C}\ (C_9H_{16}O_7) \quad + \quad \mathbf{D}\ (C_{10}H_{18}O_7)$$

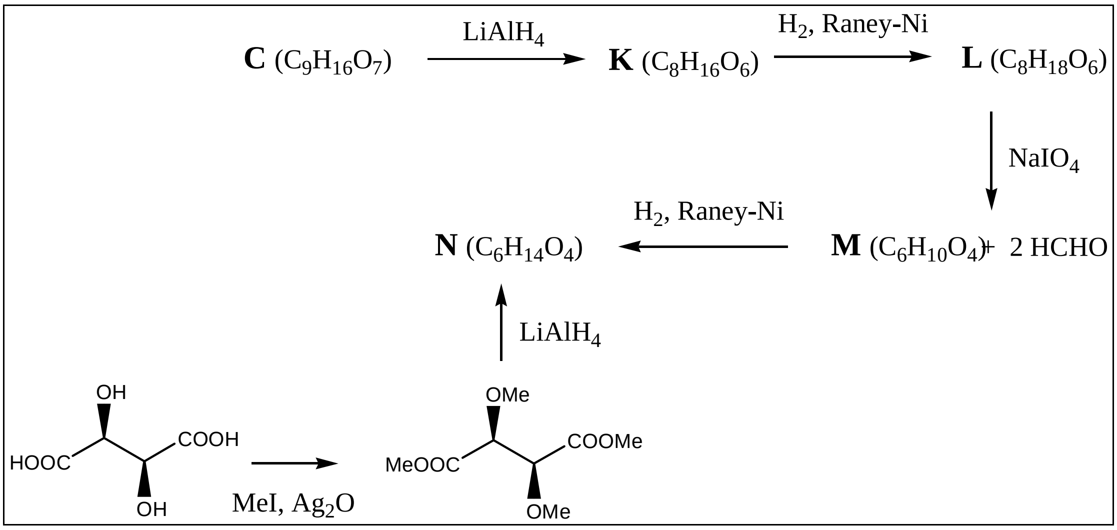
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (Scheme 3).

Scheme 3

$$\mathbf{C}\ (C_9H_{16}O_7) \xrightarrow{\text{MeI, }Ag_2O} \mathbf{J}\ (C_{11}H_{20}O_7) \xleftarrow{\text{MeI, }Ag_2O} \mathbf{D}\ (C_{10}H_{18}O_7)$$

C was reduced with LiAlH$_4$ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with NaIO$_4$ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (Scheme 4). A ^{1}H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in L)

Scheme 4

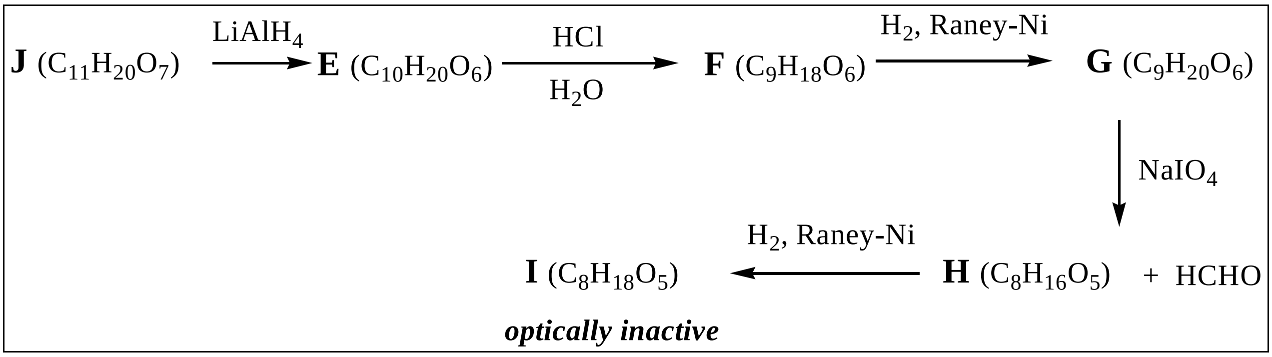


10.1 <u>Complete</u> structures for **L , M, and N** in the answer sheet.

10.2 How many structures for **C** are possible? <u>Complete</u> possible structures for **C**.

To determine the correct structure of **C**, following set of reactions were performed. **J** was reduced to **E,** and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G,** and **G** was oxidized with $NaIO_4$ to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (Scheme 5).

Scheme 5



10.3 Complete structures for **G** and **I**.

10.4 Which one is the correct structure for **C** among ones you have drawn in **10-2**?

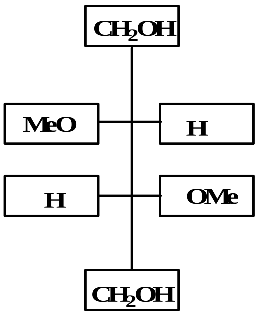
10.5 Complete structures for **B, D,** and **J**.

10.6 Complete the structure for Glycyrrhizin.

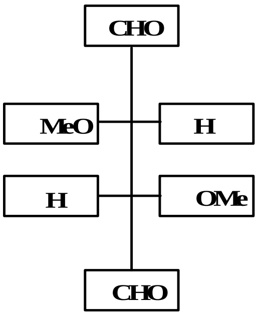
SOLUTION

10.1

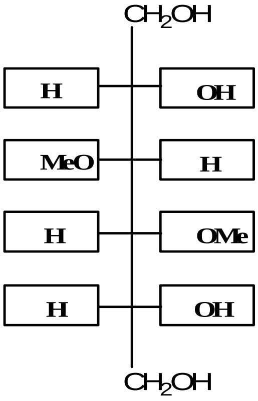
N



M

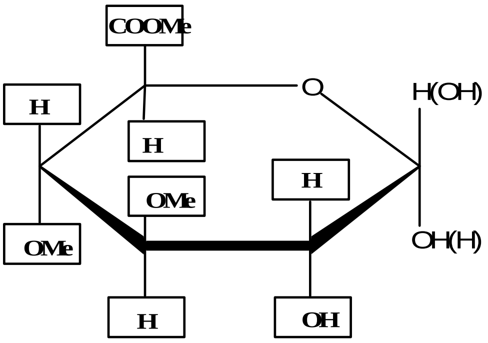


L

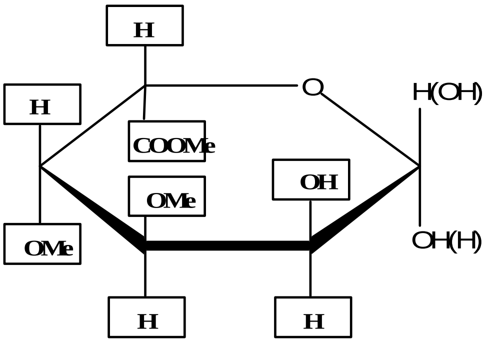


10.2 Number of possible structures **2**

1

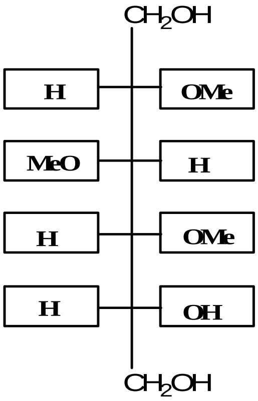


2

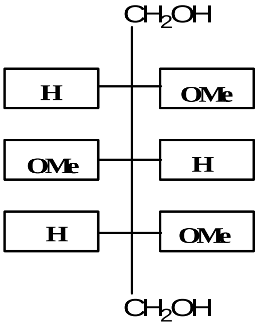


10.3

G



I

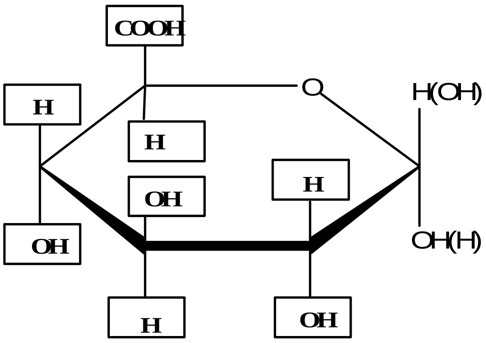


10.4

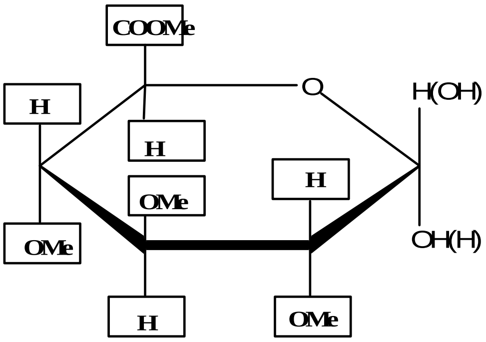
The correct structure for **C** from 10-2 is No. 1

10.5

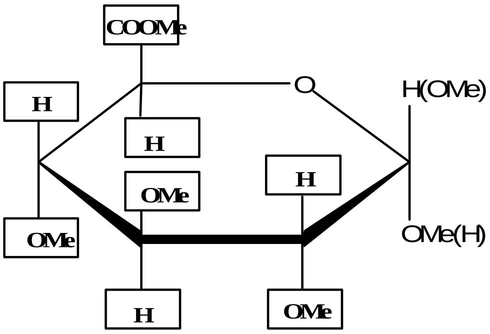
B



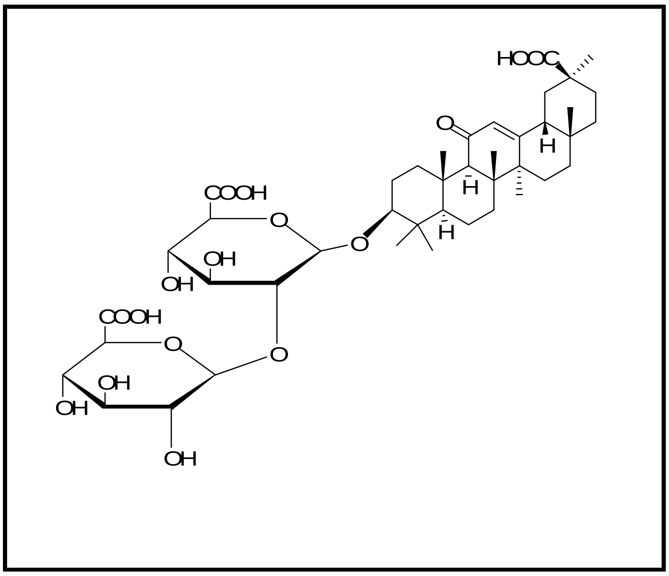
D


COOMe
H
H
OMe
H
OMe
H
OMe
O
H(OH)
OH(H)

J


COOMe
H
H
OMe
H
OMe
H
OMe
O
H(OMe)
OMe(H)

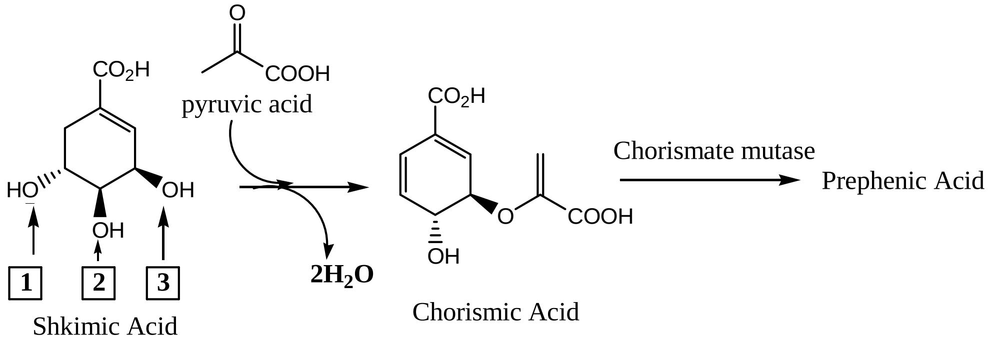
10.6


HOOC
O
H
H
H
COOH
O
OH
OH
O
COOH
O
O
OH
OH
OH

PROBLEM 11

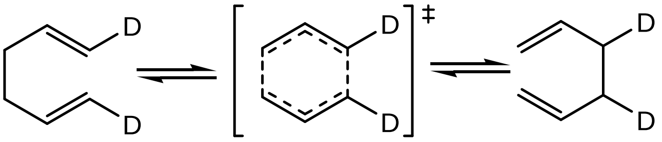
Enzyme Reaction

Shikimic acid biosynthesis is an important pathway for amino acids, alkaloids and heterocyclic natural product production. Nature converts shikimic acid to chorismic acid through a cascade of enzymatic reactions. Then chorismate mutase catalyzes the conversion of chorismic acid to prephenic acid at the branch point for the biosynthesis of aromatic amino acids such as tyrosine and phenylalanine.



11.1 During the transformation of shikimic acid to chorismic acid, dehydration is occurring. Choose the hydroxyl group in shikimic acid that is lost through above dehydration among all possible reactions.

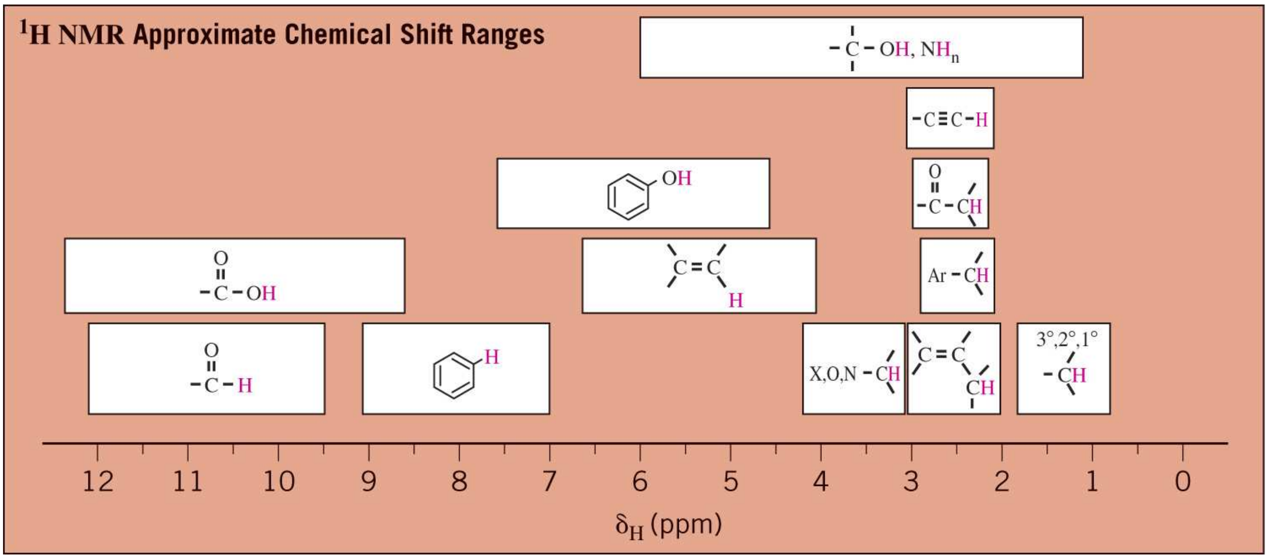
11.2 Chorismate mutase rearranges chorismic acid into prephenic acid without changing the molecular formula. Chorismic acid becomes prephenic acid through the Claisen rearrangement, a concerted pericyclic process like the Cope rearrangement as shown below:



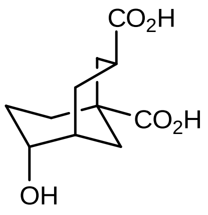
Based on the following spectral data, propose the structure of prephenic acid.

^{1}H-NMR (D_2O, 250 MHz): δ 6.01 (2H, d, J = 10.4 Hz), 5.92 (2H, dd J = 10.4, 3.1 Hz), 4.50 (1H, t, J = 3.1 Hz), 3.12 (2H, s). Note that there are three protons, which have been exchanged by D_2O very fast, and two protons at δ 3.12, which are exchanged slowly in prephenic acid. ^{13}C-NMR (D_2O, 75 MHz): δ 203, 178, 173, 132 (for two identical carbons), 127 (for two identical carbons), 65, 49, 48.

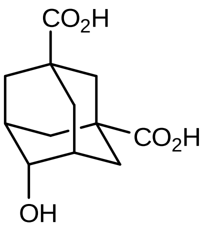
δ, chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet



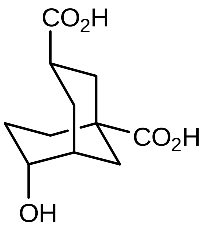
Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, *e.g.*, the species in brackets "[ ]" above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower is the IC$_{50}$ (inhibitor concentration of 50 % of the enzymatic activity) value, the better is the inhibitor.



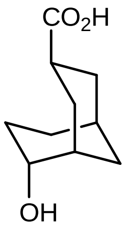
1
IC$_{50}$ = 2.5 mM



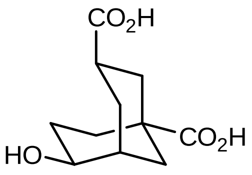
2
IC$_{50}$ = 1.3 mM



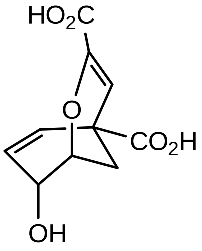
3
IC$_{50}$ = 0.78 mM



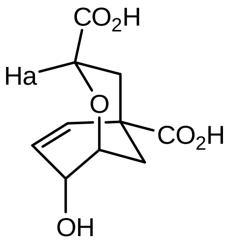
4
IC$_{50}$ = 1.1 mM



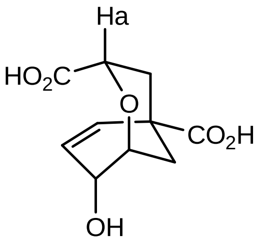
5
IC$_{50}$ = 5.3 mM



6
IC$_{50}$ = 0.017 mM



7
IC$_{50}$ =0.0059 mM



8
IC$_{50}$ = 0.00015 mM

11.3 Choose all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.

(a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.

(b) The presence of both carboxylic groups is important in the TS and inhibitor design.

(c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.

(d) **7** and **8** can be distinguished on the basis of the ^{1}H-NMR of H_a.

11.4 Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their IC_{50} values.

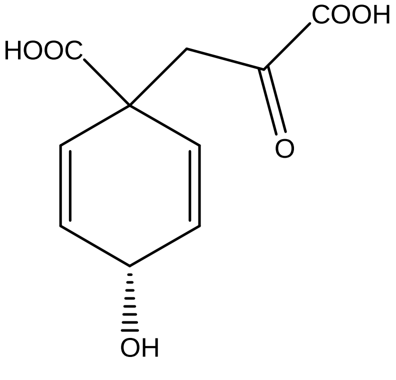
11.5 Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid 1.0×10^6 fold at 25 °C by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at 25 °C.

$\Delta H^{\neq}_{uncat}$ is 86,900 J mol^{-1} for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the *uncatalyzed* thermal conversion be the same as that of the *enzyme-catalyzed* conversion at 25 °C, assuming that $E_a = \Delta H^{\neq}$.

SOLUTION

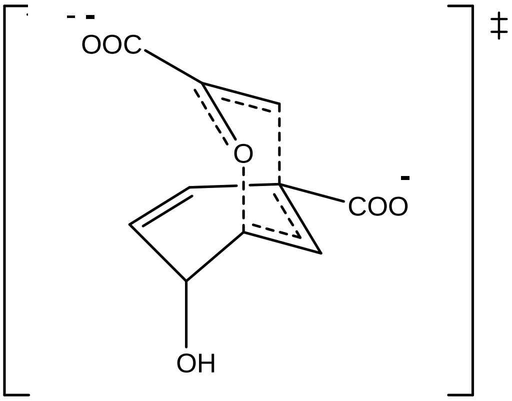
11.1 Hydroxyl group No. 3

11.2



11.3 Correct statements: (a), (c), (d).

11.4



Transition state

11.5 For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A\ \exp\ (-E_{a,\ \text{cat}}\ /\ \text{RT})}{A\ \exp\ (-E_{a,\ \text{uncat}}\ /\ \text{RT})} = \exp\ [-\Delta E_{a,\ \text{cat-uncat}}\ /\ RT] =$$

$$= \frac{\exp\ (-\Delta E_{a,\ \text{cat}-\text{uncat}}\ (\text{J mol}^{-1})}{2{,}480\ \text{J mol}^{-1}} = 1\times 10^{6}$$

Therefore, $-\Delta E_{a,\ \text{cat-uncat}} = 34{,}300\ \text{J mol}^{-1}$

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = \frac{A\ \exp\ (-\Delta H^{\neq}{}_{\text{uncat}}\ /\ RT)}{A\ \exp\ (-\Delta H^{\neq}{}_{\text{uncat}}\ /\ 298\ R)} = \exp\left[\left(\frac{-\Delta H^{\neq}{}_{\text{uncat}}}{R}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$\frac{k_{\text{uncat, T}}}{k_{\text{uncat, 298}}} = 13.8 = \exp\left[\left(\frac{-86900}{8.32}\right)\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

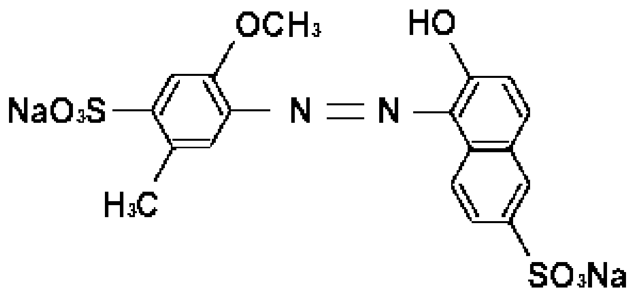
Therefore, T = 491 K, or 218 $^{\circ}$C

PRACTICAL PROBLEMS

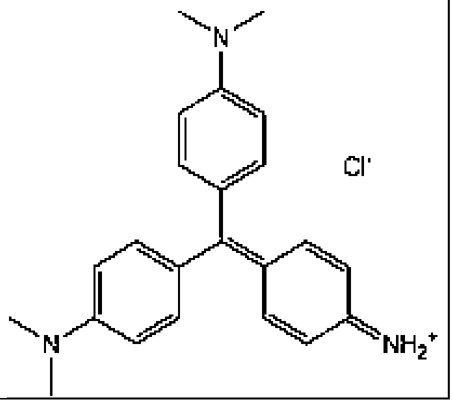
PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



Food Red No. 40



Methyl Violet 2B

1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).

b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

a) Elute the cartridge with about 10 cm^3 of Solution E using 10 cm^3 syringe (Fig. C).

b) Load 1.00 cm^3 of solution MD onto the cartridge (Fig. D).

c) Using 1 cm^3 syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm^3 volumetric flask. Repeat until the red compound is completely eluted and collected.

d) Fill the flask to the 10 cm^3 mark with Solution E and mix. Call this Solution F.

e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.

f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.

g) Report the concentration of R in the original Solution MD.

h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.

PROBLEM 2 (Practical)

Reverse-phase Chromatography:
Acid-Base Titration of Acetic Acid and Salicylic Acid

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

a) Titrate 10 cm^3 of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm^3 of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.

b) Standardize NaOH solution with 2.00 cm^3 of the standard KHP (potassium hydrogen phthalate) solution (1.00×10^{-2} M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.

c) Withdraw 1.00 cm^3 of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm^3 of Solution MA.

2-2. Reverse-phase Separation and Titration

a) Elute a new C-18 cartridge with about 10 cm^3 of distilled water using 10 cm^3 syringe.

b) Load 1.00 cm^3 of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).

c) Elute with 1 cm^3 of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm^3 liquid in each tube.

d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.

e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.

f) Calculate the mole percent of AA in solution MA.

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

a) The weight of a spatula tip-full of a solid is about 15~20 mg.

b) Wipe spatula cleanly with Kimwipe between uses.

c) After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.

d) To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm^3 of CH_3CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm^3 of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm^3 of the cerium(IV) ammonium nitrate solution in dilute HNO_3 (labelled as CAN) with 3 cm^3 of CH_3CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm^3 of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water first, and then add 1 cm^3 of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of CH_3CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm^3 of water.) To the solution, slowly add five drops of the 0.5 % $KMnO_4$ solution, drop by drop while shaking.

Test 5: *pH* test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm^3 of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm^3 of water). Measure the pH of the solution with pH paper.

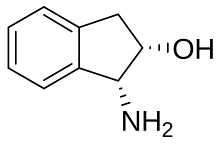
Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % $FeCl_3$ solution.

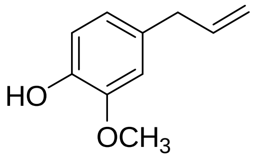
Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

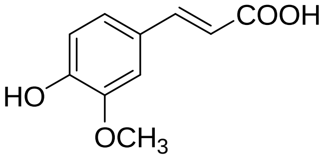
Possible Unknown Compounds (next page):



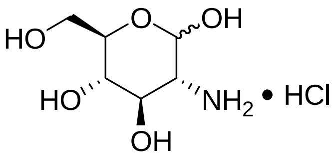
(A)



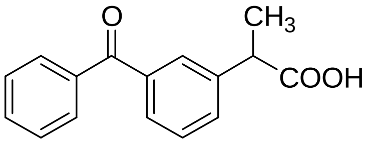
(E)



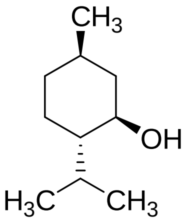
(F)



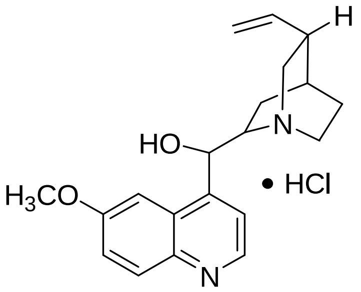
(G)



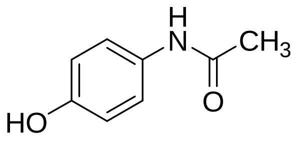
(K)



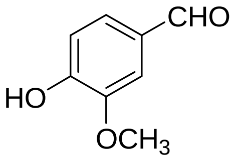
(M)



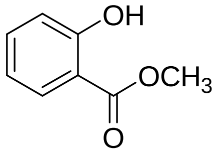
(Q)



(T)



(V)



(W)

39th

International Chemistry Olympiad

8 theoretical problems
2 practical problems

THE THIRTY-NINTH
INTERNATIONAL CHEMISTRY OLYMPIAD
15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

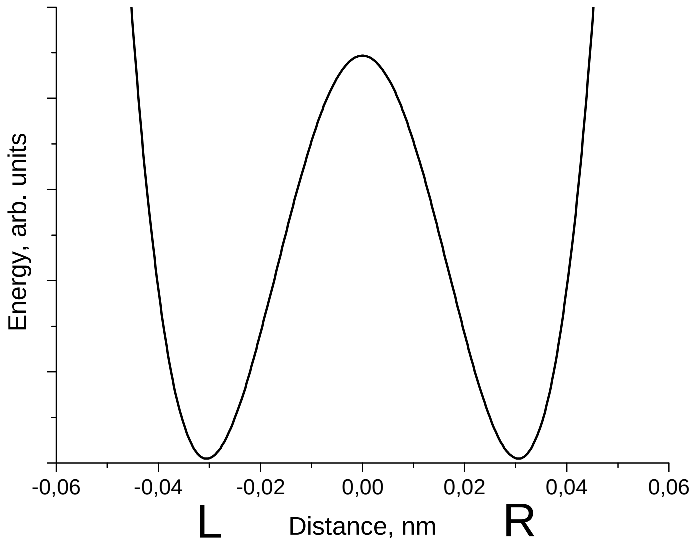
Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.

1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

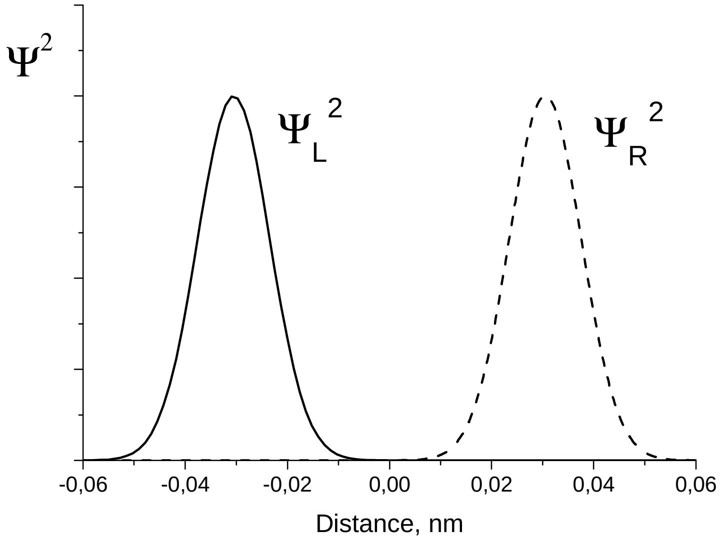


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48\times10^{11}$ s^{-1}. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) + \left(\Psi_L^2(x) - \Psi_R^2(x)\right)\cos\left(\omega t\right)\right],$$

wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.

1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$

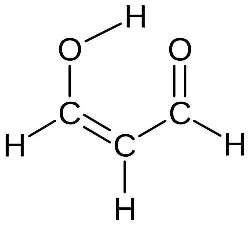
1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?

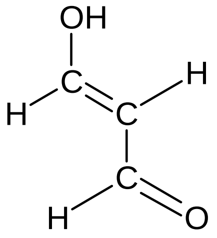
1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in **1.6** and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

1.1 The structures of propanedial and two of its isomers:

$O=CH–CH_2–CH=O$





1.2 Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH).

The stability of propanedial is caused by (one of the following answers had to be chosen):

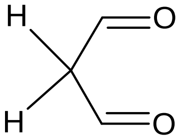
a) the stability of carbanion due to conjugation with two carbonyl groups,

b) weakness of C – H bond in a carbonyl group,

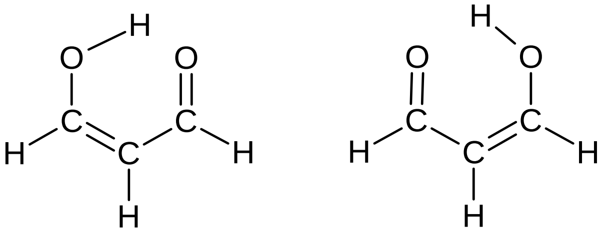
c) hydrogen bonds between two propanedial molecules.

The first answer is correct.

1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



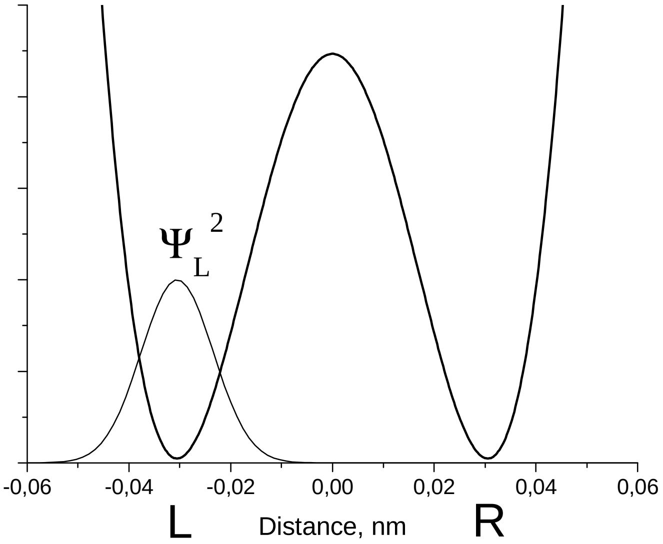
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

(a) $\Psi^2(x,0) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x) + \Psi_L^2(x) - \Psi_R^2(x)\right] = \Psi_L^2(x)$

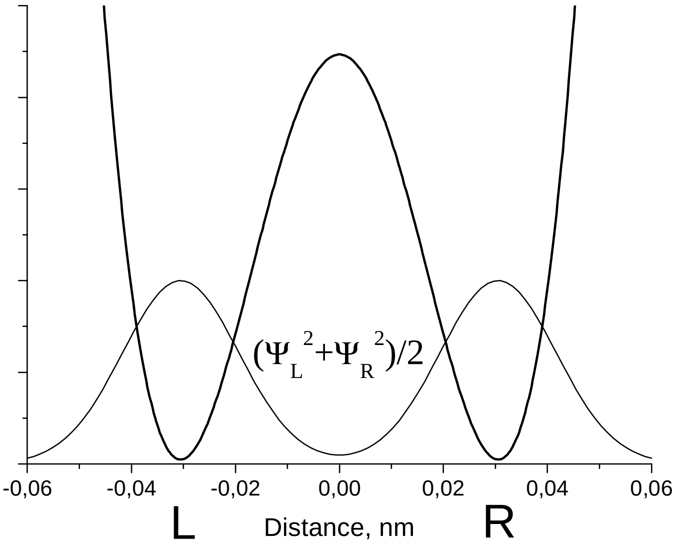
The probability density is concentrated in the left well:



(b) In the middle of the time interval

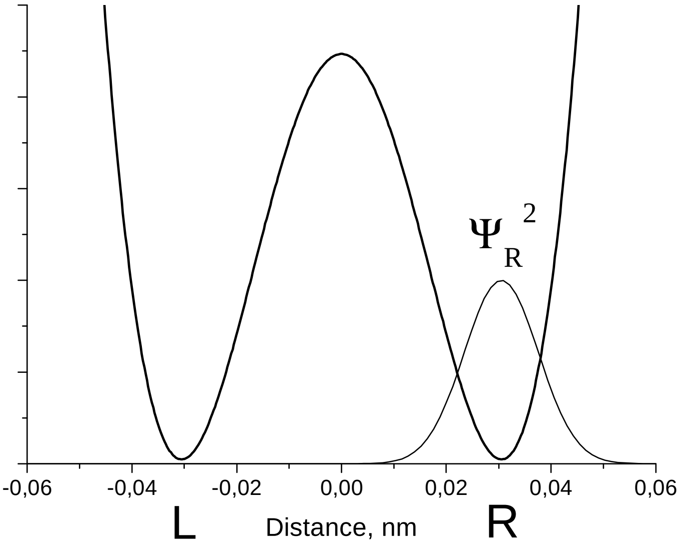
$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x) + \Psi_R^2(x)\right]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



(c) $$\Psi^2\left(x,\frac{\pi}{\omega}\right) = \frac{1}{2}\left[\Psi_L^2(x)+\Psi_R^2(x)-\Psi_L^2(x)+\Psi_R^2(x)\right] = \Psi_R^2(x)$$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is t = π / ω.

$$t = \frac{3.14}{6.48\times10^{11}} = 4.85\times10^{-12} \text{ s.}$$

The proton velocity:

$$v = \frac{0.06\times10^{-9}}{4.85\times10^{-12}} = 12 \text{ m s}^{-1}.$$

1.7 The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2\,m\,\Delta x} = \frac{1.055\times10^{-34}}{2\times\dfrac{0.001}{6.02\times10^{23}}\times0.03\times10^{-9}} \approx 1000 \text{ m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 2

Nanochemistry

Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)

$$CO + 3\ H_2 \xrightarrow{Fe,Co} CH_4 + H_2O$$

Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:

$$Co(s) + H_2O(g) \rightleftarrows CoO(s) + H_2(g) \qquad (1)$$

Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

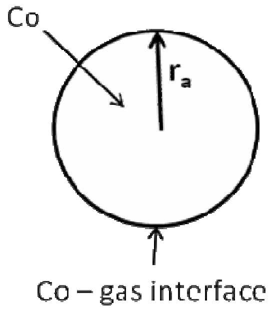


Fig. 1

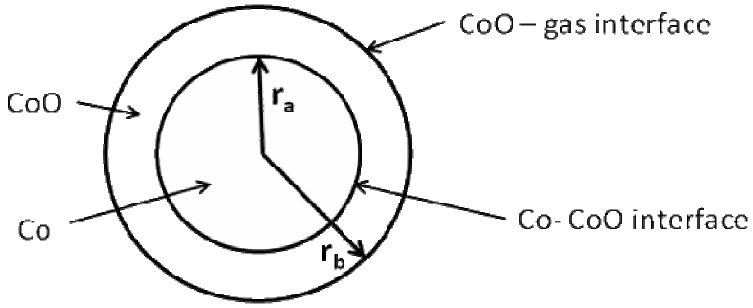


Fig. 2

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^0(r) = G^0(\text{bulk}) + \frac{2\sigma}{r}V$$

2.1 Calculate the standard Gibbs energy $\Delta_r G^0(1)$ and the equilibrium constant for the reaction (1) at T = 500 K.

2.2 Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

(a) 10^{-8} m,

(b) 10^{-9} m.

The surface tension at the Co-gas interface is 0.16 J m^{-2}. CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO, CH_4, H_2, H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is p = 1 bar, temperature is T = 500 K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

2.3 At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of

(a) a bulk phase

(b) spherical nanoparticles with r_a = 1 nm (Fig. 1).

2.4 What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

(a) to increase r_a;

(b) to decrease r_a;

(c) change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a, r_b, molar volumes as V(Co); V(CoO).

2.5 Write down the expression for the standard molar Gibbs function of CoO.

2.6 Write down the expression for the standard molar Gibbs function of Co.

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2\frac{\sigma_1}{r_1} + 2\frac{\sigma_2}{r_2}$$

r_i, σ_i are radius and surface tension at the spherical interface i, respectively.

2.7 Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a, r_b, V(Co); V(CoO) and $\Delta_r G^0(1)$.

2.8 When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, r_a = r_b = r_0, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1,r_0)$ on r_0?

2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(H_2O)/p(H_2)$ and a constant temperature:

a) increase r_0

b) decrease r_0

c) change of r_0 has no effect.

.

Reference data:

Substance	ρ, g cm^{-3}	$\Delta_f G^0_{500}$, kJ mol^{-1}
Co (s)	8.90	
CoO (s)	5.68	–198.4
H_2O (gas)		–219.1

SOLUTION

2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G^0_{500}(1) = \Delta G^0_{f,500}(\text{CoO,s}) - \Delta G^0_{f,500}(\text{H}_2\text{O,g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G^0_{500}(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88 \times 10^{-3}$$

2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\Delta_r G^0_{500}(1,r_a) = G^0_{\text{bulk},500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,g}) - G^0_{\text{sph}}(\text{Co}) =$$

$$= G^0_{500}(\text{CoO,s}) + G^0_{500}(\text{H}_2\text{,g}) - G^0_{500}(\text{H}_2\text{O,gas}) - \left(G^0_{500}(\text{Co,s}) + \frac{2\,\sigma_{\text{Co-gas}} \text{V(Co)}}{r_a} \right) =$$

$$= \Delta_r G^0_{500}(1) - \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a};$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1\times 10^{-6} \times 59.0}{8.90} = 6.6\times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\,\sigma_{\text{Co-gas}}\,V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G^o_{500}(1,r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1}, respectively.

The equilibrium constant is calculated from the equation

$$K(1,r_a) = \exp\left(-\frac{\Delta_r G^o_{500}(1,r_a)}{RT}\right)$$

$K(1,\text{r}_a) = 7.22\times10^{-3}$; $r_a = 10^{-8}$ m $\qquad K(1,r_a) = 11.4\times10^{-3}$; $r_a = 10^{-9}$ m

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G^o_{500}(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a}V(\text{Co})$$

$\Delta_r G^o_{500}(1)$ is 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm $\Delta_r G^o_{500}(1,r_a)$ is 18.6 kJ mol^{-1}.

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G^o_{500}(1) + RT\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G^o_{500}(1) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and for spherical cobalt nanoparticles with r_a = 1 nm:

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1,r_a) + \text{RT}\ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) =$$

$$= \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a}V(\text{Co}) - \text{RT}\ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

$\Delta_r G^o_{500}(1)$ is equal to 20.7 kJ mol^{-1}. For spherical cobalt particles with r_a = 1 nm equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1,r_a) = \Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \le 0$$

and

$$\Delta_r G^o_{500}(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \le RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right)$$

The left hand side of the last inequality becomes more positive with the increase of *r_a.* At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a. The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G^0_{\text{sph}}(\text{CoO}, r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^o(\text{CoO,s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$G^0_{\text{sph}}(\text{Co}, r_a, r_b) = G_{\text{bulk}}(\text{Co}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= G^o(\text{Co,s}) + V(\text{Co})\left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a}\right)$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\Delta_r G^0(1, r_a, r_b) = G^0_{\text{sph}}(\text{CoO}, \text{r}_b) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^0_{\text{sph}}(\text{Co}, r_a, r_b) =$$

$$= G^o(\text{CoO,s}) + G^o(\text{H}_2,\text{gas}) - G^o(\text{H}_2\text{O},\text{gas}) - G^o(\text{Co,s}) +$$

$$+ \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co})\left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a}\right) =$$

$$= \Delta_r G^o(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co})$$

2.8 Under the assumptions made

$$\Delta_r G^{o}(1, r_a, r_b) = \Delta_r G^{0}(1, r_0) =$$

$$= \Delta_r G^{o}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b}\left(V(\text{CoO}) - V(\text{Co})\right) - \frac{2\sigma_{\text{CoO-Co}}}{r_a}\text{V(Co)} =$$

$$= \Delta_r G^{o}(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right)$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) = 6.56\times10^{-6}\ \text{m}^3$$

$\Delta_r G^0(1, r_0)$ is directly proportional to $\left(\frac{1}{r_0}\right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1, r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0}\left(V(\text{CoO}) - \frac{3}{2}V(\text{Co})\right) \leq RT \ln\frac{p_{H_2O}}{p_{H_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0. At certain point the inequality will be violated and the spontaneous oxidation will not take place.

In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0.

The answer (b) is correct.

PROBLEM 3

Unstable chemical reactions

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:

$$B + 2\,X \xrightarrow{k_1} 3\,X$$

$$X + D \xrightarrow{k_2} P$$

(B and D are reagents, X is an intermediate and P is a product).

3.1 Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.

3.2 Deduce a rate equation using steady-state approximation. Find the orders:

(i) a partial reaction order with respect to B;

(ii) a partial reaction order with respect to D;

(iii) the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: [B] = [D] = const.

3.3 Without solving the kinetic equation draw the kinetic curve [X](t) for the cases:

1) $[X]_0 > \dfrac{k_2}{k_1}$; 2) $[X]_0 < \dfrac{k_2}{k_1}$.

3.4 Without solving the kinetic equation draw the kinetic curve [X](t) for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[B]_0 = [D]_0$, $[X]_0 > \dfrac{k_2}{k_1}$.

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:

$$C_2H_6 + X + ... \xrightarrow{k_1} 2\,X$$

$$X + Y \xrightarrow{k_2} 2\,Y + ...$$

$$C_2H_6 + Y + ... \xrightarrow{k_3} 2\,P$$

Under specific conditions this reaction displays oscillatory behavior: Intermediates are peroxide $C_2H_6O_2$ and aldehyde C_2H_4O, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, cm^3 mol^{-1}s^{-1}	E$_A$, kJ mol^{-1}
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation

B + D → P

The kinetic equation for X

$$\frac{d[X]}{dt} = k_1[B][X]^2 - k_2[D][X]$$

3.2 Under the steady-state conditions

$$\frac{d[P]}{dt} = k_2[D][X] = k_1[B][X]^2,$$

whence

$$[X] = \frac{k_2[D]}{k_1[B]}$$

$$\frac{d[P]}{dt} = \frac{k_2^2[D]^2}{k_1[B]}$$

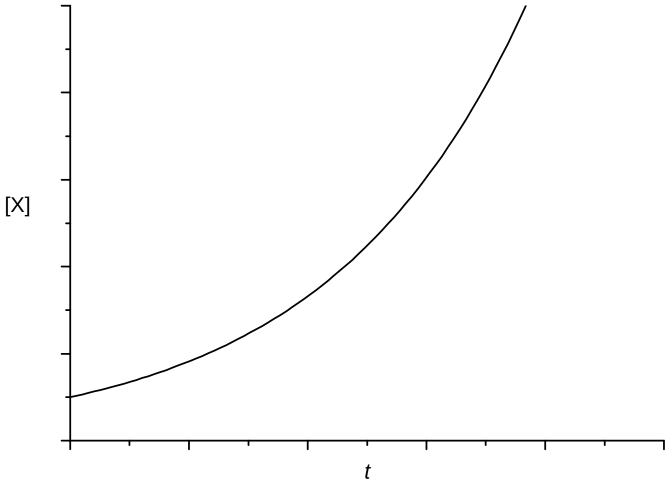
The reaction order is 2 with respect to D, and –1 with respect to B.

The overall order is 1.

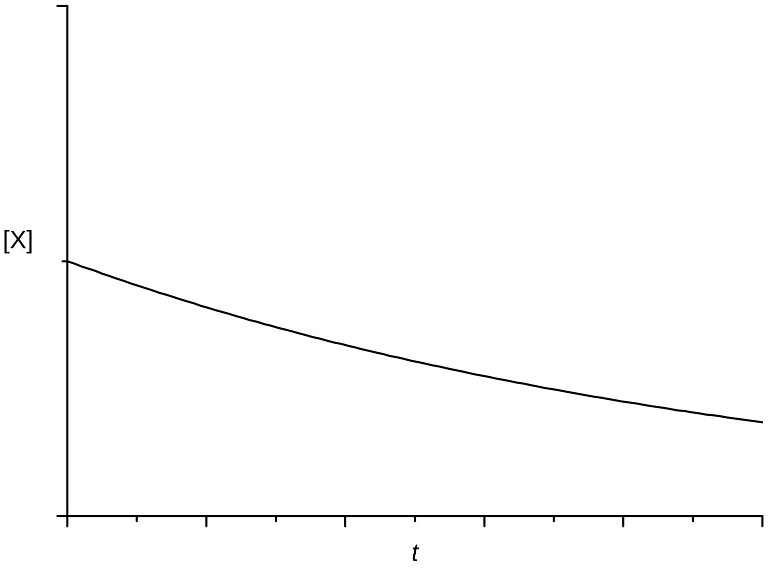
3.3 In an open system the initial reaction rate is:

$$\frac{d[X]}{dt} = [B][X](k_1[X] - k_2)$$

1) If $[X]_0 > k_2/k_1$, then d[X]/dt > 0 at any time, and the concentration of X monotonically increases:



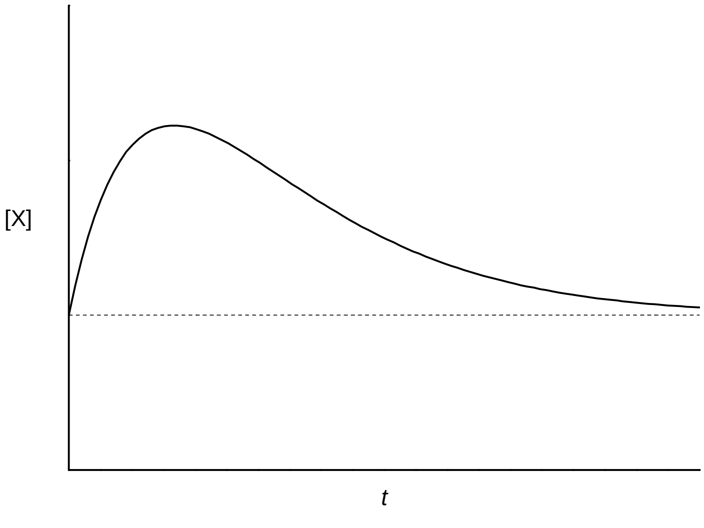
2) If $[X]_0 < \frac{k_2}{k_1}$1, then $\frac{d[X]}{dt} < 0$ at any time, and the concentration of X monotonically decreases:



3.4 In a closed system the initial reaction rate is:

$$\left.\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t}\right|_{t=0} = k_1[\mathrm{B}]_0[\mathrm{X}]_0^2 - k_2[\mathrm{D}]_0[\mathrm{X}]_0 = [\mathrm{B}]_0[\mathrm{X}]_0\left(k_1[\mathrm{X}]_0 - k_2\right) > 0$$

Hence, at the beginning of the reaction [X] increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – $C_2H_6O_2$, Y – C_2H_4O, P – C_2H_6O. Dots denote O_2 and H_2O.

$$C_2H_6 + C_2H_6O_2 + O_2 \rightarrow 2\,C_2H_6O_2$$

$$C_2H_6O_2 + C_2H_4O \rightarrow 2\,C_2H_4O + H_2O$$

$$C_2H_6 + C_2H_4O + H_2O \rightarrow 2\,C_2H_6O$$

3.6 At the highest possible temperature the rate constants are equal:

$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \dfrac{A_2}{A_1}} = 354\ \text{K}$$

PROBLEM 4

Determination of water by Fischer titraton

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO_2 and pyridine (C_5H_5N, Py) – Fischer reagent. The following reactions occur during the titration:

$$SO_2 + CH_3OH + H_2O + I_2 \rightarrow 2\ HI + CH_3OSO_3H$$

$$Py + HI \rightarrow PyH^+I^-$$

$$Py + CH_3OSO_3H \rightarrow PyH^+CH_3OSO_3^-$$

Iodine content is usually expressed in mg of water reacting with 1 cm^3 of the titrant solution (hereunder T, mg cm^{-3}), which equals the mass of water (mg) reacting with 1.00 cm^3 of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I_2 with SO_2 and H_2O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm^3 of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate $Na_2C_4H_4O_6 \cdot 2\ H_2O$.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm^3 volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm^3 of the obtained solution, 22.70 cm^3 of Fischer reagent solution were needed, whereas 2.20 cm^3 of iodine were used for titration of 25.00 cm^3 of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm^3 (solution **A**); 22.45 cm^3 of this solution were used for titration of 15.00 cm^3 of a Fischer reagent (solution **B**).

Then 25.00 cm^3 of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm^3 of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm^3 of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound $Fe_2(SO_4)_3 \cdot x\ H_2O$, 10.59 cm^3 of iodine solution (T = 15.46 mg/ cm^3) were consumed.

4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of $Fe_2(SO_4)_3 \cdot x\ H_2O$ with the Fischer reagent.

4.8 Calculate the composition of the hydrate $Fe_2(SO_4)_3 \cdot x\ H_2O$ (x = integer).

SOLUTION

4.1 Equation:

$I_2 + SO_2 + 2\ H_2O + 4\ Py \rightarrow 2\ PyHI + (PyH)_2SO_4$

4.2 T is equal to:

$M(Na_2C_4H_4O_6 \cdot 2\ H_2O)$ = 230.05 g mol^{-1} $2 \times M(H_2O)$ = 36.04 g mol^{-1}

$$m(H_2O) = \frac{13520 \times 36.04}{230.05} = 0.2118 \text{ g} = 211.8 \text{ mg}$$

$$T = \frac{2118}{12.20} = 17.36 \text{ mg cm}^{-3}$$

T = 17.36 mg cm^{-3}

4.3 T is equal to:

Volume of iodine consumed for 10 cm^3 of pure CH_3OH = $\frac{2.20 \times 10.00}{25.00}$ = 0.88 cm^3

$$T = \frac{21537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87 \text{ mg cm}^{-3}$$

More exactly

10.00 cm^3 of the solution contains $\frac{(1000 - 21.5) \times 10.00}{1000}$ = 9.785 cm^3 of methanol.

Volume of iodine consumed for 9,785 cm^3 of pure CH_3OH = $\frac{2.20 \times 9{,}785}{25.00}$ =

= 0.86 cm^3

$$T = \frac{21537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86 \text{ mg cm}^{-3}$$

T = 9.87 mg cm^{-3}

4.4 T is equal to:

Approach 1

Let 1 cm^3 of CH_3OH contains x mg H_2O, then 1 cm^3 of **A** contains

[(1.000 – 0.006) x + 5.624] mg H_2O.

15.00 T = 22.45 (0.994 x + 5.624) – 1st titration,

10.00 T = 25.00 x + 10.79 (0.994 x + 5.624) – 2nd titration.

Hence, x = 1.13 mg cm^{-3}, T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm^3 of **B** be consumed for the titration of water, contained in 1 cm^3 of CH_3OH.

Then $T = \frac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y}$ (1st titration) = $\frac{10.79 \times 5.624}{10.00 - 25.00\,y - 10.79\,y}$

(2nd titration).

Hence, y = 0.1116 and T = 10.10 mg cm^{-3}

T = 10.09 mg cm^{-3} (10.10 without taking into account 0.994 factor)

4.5 Equation(s):

$CaO + SO_2 \rightarrow CaSO_3$

$2\ CaO + 2\ I_2 \rightarrow CaI_2 + Ca(OI)_2$

$6\ CaO + 6\ I_2 \rightarrow 5\ CaI_2 + Ca(IO_3)_2$

(Instead of CaO, $Ca(OH)_2$ may be written.)

4.6 Equation(s):

$Fe_2(SO_4)_3 + 2\ HI \rightarrow 2\ FeSO_4 + \mathbf{I_2} + H_2SO_4$

$Fe_2(SO_4)_3$ + $\mathbf{H_2O}$ + SO_2 + $CH_3OH \rightarrow 2\ FeSO_4 + CH_3OHSO_3 + H_2SO_4$

(or in ionic form)

4.7 Equation:

$$Fe_2(SO_4)_3 \cdot x\ H_2O + (x - 1)\ I_2 + x\ SO_2 + x\ CH_3OH \rightarrow 2\ FeSO_4 + x\ CH_3OHSO_3 + H_2SO_4 + 2(x - 1)\ HI$$

4.8 The composition of the crystallohydrate is:

$M(Fe_2(SO_4)_3 \cdot x\ H_2O) = 399.9 + 18.02\ x$

$$m(H_2O) = \frac{0.6387 \times 18.02\ x}{(399.9 + 18.02\ x)}$$

$$m(H_2O) = 10.59\ cm^3 \times 15.46\ mg\ cm^{-3} \times 0.001\ g\ mg^{-1} \times \frac{x}{x - 1}$$

$0.1637 \times (399.9 + 18.02\ x) = 11.51\ x - 11.51$

$x = 8.994 \approx 9$

Formula: $Fe_2(SO_4)_3 \cdot 9\ H_2O$

PROBLEM 5

A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three coluorless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added o the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

^{1}H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

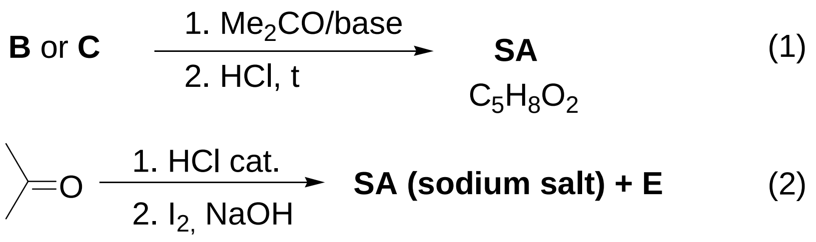
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm^3 (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).

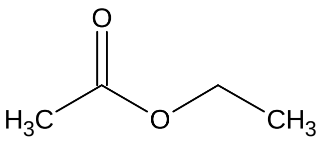


5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

SOLUTION

5.1 Structure of product **D**



Ethyl acetate, ethyl ethanoate

5.2 Which class of organic compounds does **D** belong to? Check the appropriate box.

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
☐	☐	☐	☑	☐	☐	☐

5.3 The expected yield of **D**

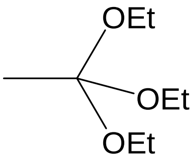
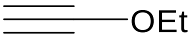
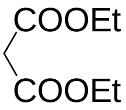
The reaction is an equilibrium without any further actions. Qualitative estimation: The yield is lower than 85 %.

Assuming that the reaction is at equilibrium and that the equilibrium constant is supposed not to vary with temperature and composition of the reaction mixture, we can calculate:

$$K = \frac{[\text{AcOEt}][\text{H}_2\text{O}]}{[\text{AcOH}][\text{EtOH}]} = \frac{(0.85)^2}{0.15 \times 1.15} = 4.2$$

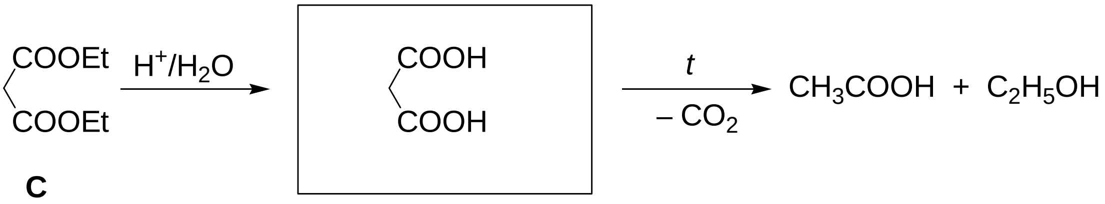
Using this constant calculation of yield in 1 : 1 mixture gives 67 %.

5.4 The structures of **A**, **B**, and **C**.

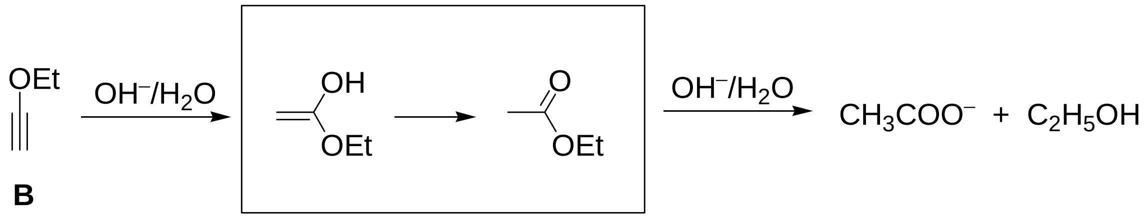
 $CH_3C(OEt)_3$ triethyl orthoacetate, 1,1,1-triethoxyethane	 HC≡COEt ethoxyacetylene, ethynylethyl ether	 $CH_2(COOEt)_2$ diethyl malonate
A	**B**	**C**

5.5 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate:

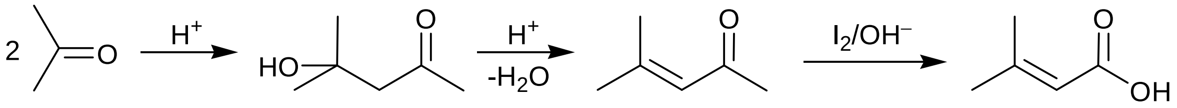


b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



5.6 The structure of senecioic acid:

From acetone alone the synthesis includes aldol condensation and dehydration with subsequent iodoform reaction:



5.7 The structure of **E**.

Iodoform, triiodomethane, CHI_3

PROBLEM 6

Silicates as the base of the Earth crust

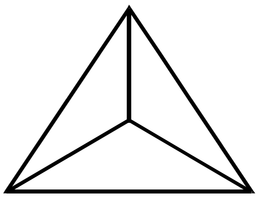
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of "liquid glass" (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the "Yes" box if it leads to changes of pH. Otherwise check the "No" box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-}, **1**):



(**1**)

For $[Si_3O_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

Charged monolayers with the composition $[Si_4O_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3 - 6.5**, depict a fragment of the layered structure joining 16 tetrahedra **(1)**. Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $CuSO_4 \cdot 5\ H_2O$ produce “trees” of blue colour, whereas those of $NiSO_4 \cdot 7\ H_2O$ form green “trees”.

6.7 Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[Cu(H_2O)_4]^{2+}$ $K_a^{I} = 1\times10^{-7}$.

6.8 Write down equation of a reaction between aqueous solutions of $CuSO_4$ and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

SOLUTION

6.1 $SiO_3^{2-} + 2\ CO_2 + 2\ H_2O \rightarrow$ “H_2SiO_3”↓ (Silica acid gel) + 2 HCO_3^- or

$SiO_2(OH)_2^{2-} + 2\ CO_2 + H_2O \rightarrow$ “H_2SiO_3”↓+ 2 HCO_3^- or

$SiO_3^{2-} + CO_2 + H_2O \rightarrow$ “H_2SiO_3”↓ + CO_3^{2-}

6.2 a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:

$SiO_4^{4-} + H_2O \rightarrow [SiO_3(OH)]^{3-} + OH^-$ or

$SiO_4^{4-} + H^+ \rightarrow [SiO_3(OH)]^{3-}$ or YES ☑

$[SiO_2(OH)_2]^{2-} + H^+ \rightarrow [SiO(OH)_3]^-$

b) formation of hydrated $[SiO_4(H_2O)_2]^{4-}$ anions NO ☑

$SiO_4^{4-} + 2\ H_2O \rightarrow [SiO_4(H_2O)_2]^{4-}$

c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds

$2\ SiO_4^{4-} + H_2O = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + 2\ OH^-$ or

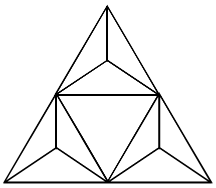
$2\ SiO_4^{4-} + 2\ H^+ = [O_3Si\text{-}O\text{-}SiO_3]^{6-} + H_2O$ or YES ☑

$2\ SiO_2(OH)_2^{2-} + H_2O = [O\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}O]^{2-} + 2\ OH^-$

6.3 n = 6 (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

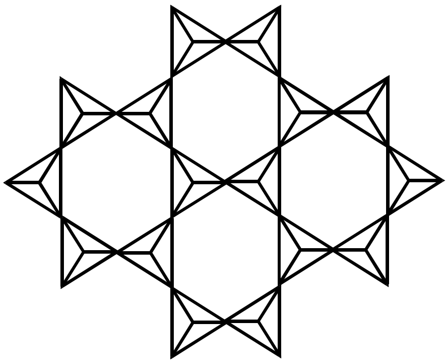
6.4 $Si_3O_9 \equiv 3\ [SiO_4] - 3\ O$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 m = 4 (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$Si_4O_{10} \equiv 4[SiO_4] - 6\ O$, i. e. the formula of the tetrahedron is now $SiO_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $Cu(H_2O)_4^{2+} + H_2O \rightleftharpoons Cu(OH)(H_2O)_3^{+} + H_3O^{+}$,

$[H^+] \approx (c\ K_a^{I})^{1/2} = 1\times10^{-4}$, $pH = -\log[H^+] = 4$

$pH = 4$

6.8 $CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu(OH)_2\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

or

$2\ CuSO_4 + Na_2SiO_3 + 2\ H_2O \rightarrow Cu_2(OH)_2SO_4\downarrow + \text{“}H_2SiO_3\text{”}\downarrow + Na_2SO_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

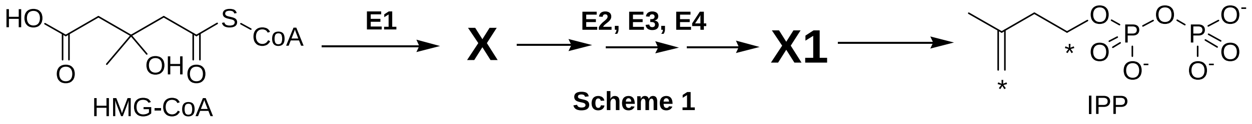
PROBLEM 7

Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

X is an optically active monocarbonic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:

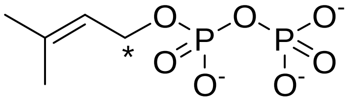


Scheme 1

7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

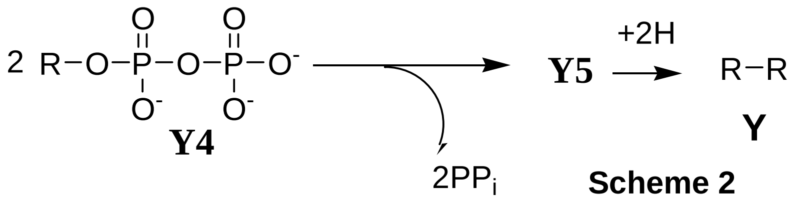
Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



DAP

7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



Scheme 2

At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

7.4 Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.

7.5 Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.

7.6 Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

7.7 Draw structures of **Y** and **Y4** with stereochemical details.

SOLUTION

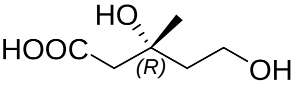
7.1 **E2** - **E4** catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β-oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

E1 4, 5

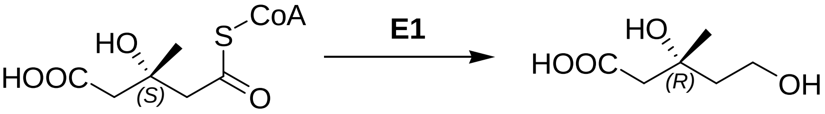
E3 6

7.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

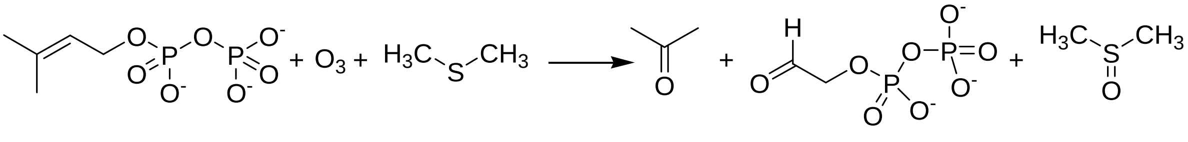


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.3 Reaction equation for reductive ozonolysis:



7.4 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in **7.2.1**). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(C) = 2*n_{Y1}(C) + 4* n_{Y2}(C) + n_{Y3}(C) = 2*3 + 4*5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(H) = 2*n_Y(C)+2 – 2*n_{c=c} = 30*2 + 2 – 6*2 = 50$$

Y (squalene) formula – $C_{30}H_{50}$.

Number of carbon atoms: <u>30</u>	Work: $n_Y(C) = 2*n_{Y1}(C)+4*n_{Y2}(C)+ n_{Y3}(C) = 2*3 + 4*5 + 4 = 30$
Number of hydrogen atoms: <u>50</u>	Work: $n(H) = 2*n_Y(C)+2–2*n_{c=c} = 30*2 + 2 - 6*2 = 50$

Gross formula of **Y** $\underline{C_{30}H_{50}}$

7.5 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

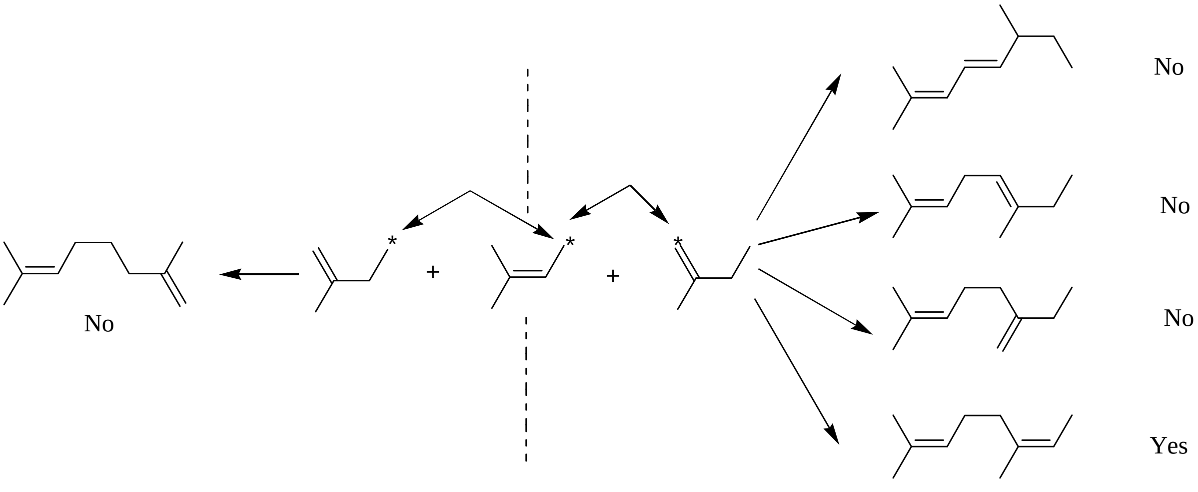
$$n(IPP\&DAP) = n_Y(C)/5 = 30/5 = 6$$

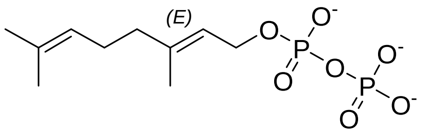
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

$n(IPP\&DAP) = n_Y(C)/5 = 30/5 = 6$

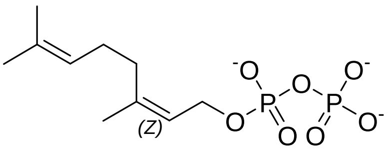
Number of DAP molecules: 2 Number of IPP molecules: 4

7.6 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details



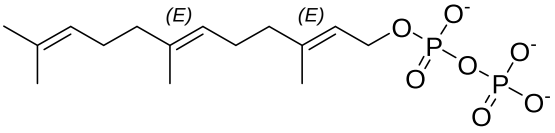


or



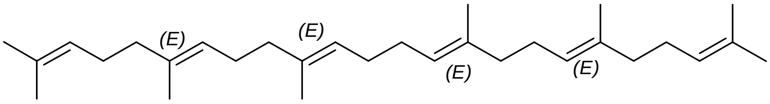
The upper isomer is geranyl pyrophosphate

7.7 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4,** since **Y3** is formed as a result of ozonolysis in a molar ratio of 1 : 1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



Y4, farnesyl pyrophosphate

Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:

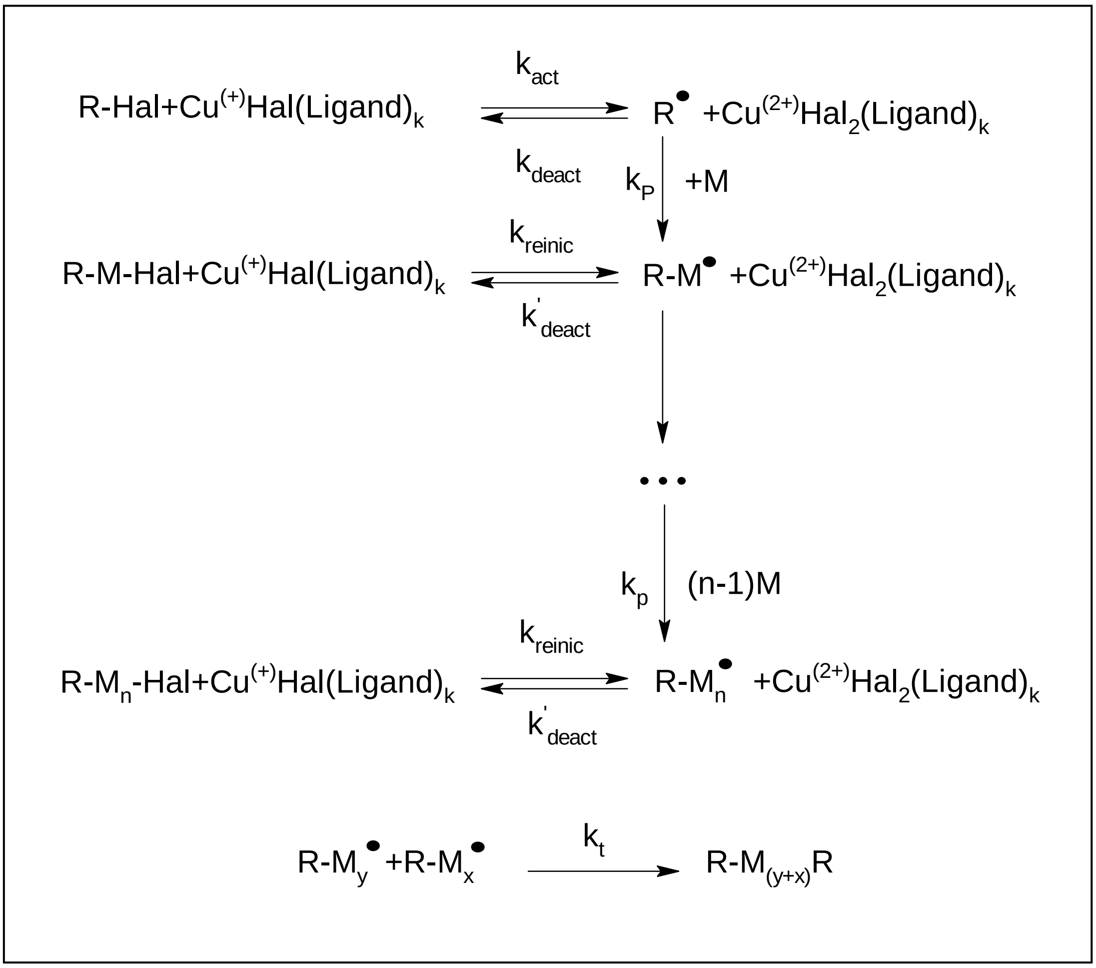


Y, squalene

PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

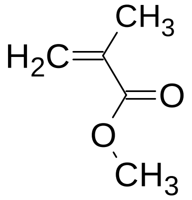
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ([M]) on reaction time (t) for ATRP is:

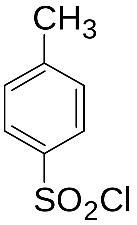
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p\,[R\bullet]\,t\,,$$

$[M]_0$ - initial monomer concentration, k_p – rate constant of propagation, $[R\bullet]$ – concentration of active radicals.

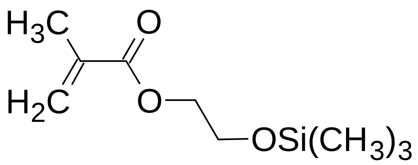
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is 1616 L $\text{mol}^{-1}\text{s}^{-1}$, and the steady state concentration of radicals is 1.76×10^{-7} mol dm^{-3}.



MMA



TsCl



HEMA-TMS

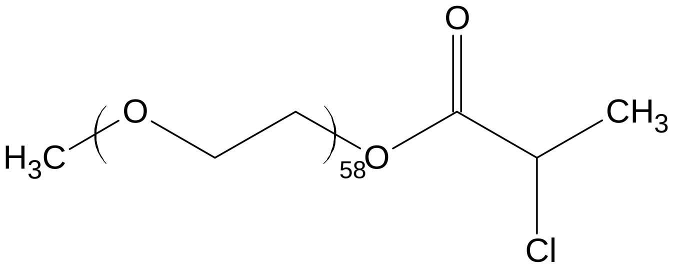
8.3 Calculate mass (*m*) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A_{65}-graft-C_{100})-stat-B_{34} means that chains of polymer C are grafted on units A in the statistic copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P_1 and P_2. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P_1 consisted of styrene (C), and in P_2 of p-chloromethylstyrene (D) units.

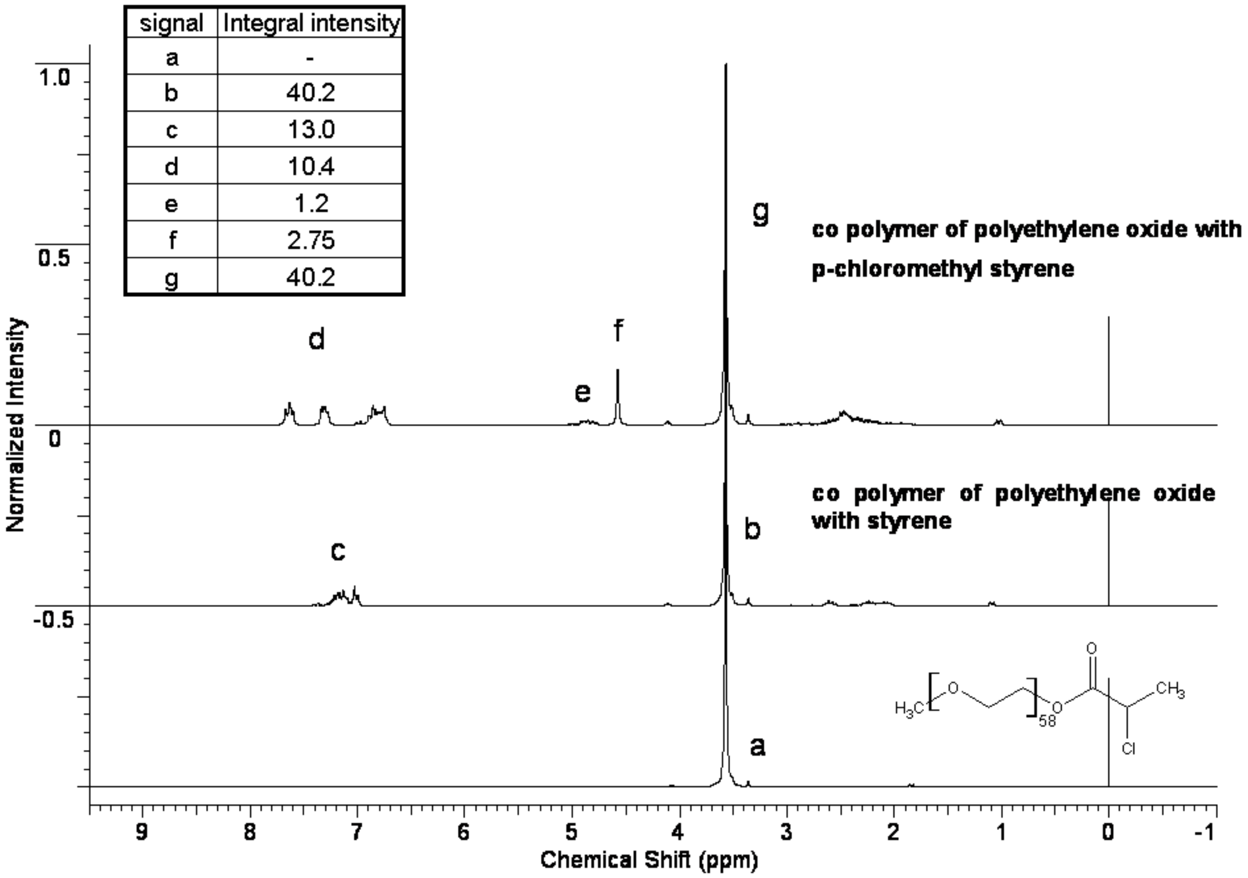
^{1}H NMR spectra of the macroinitiator, P_1 and P_2 are given below. Integral intensities of characteristic signals can be found in the table.

8.6 Assign ^{1}H NMR signals to substructures given in the Answer Sheet.

8.7 Determine molar fractions of units C and D and molecular weights of P_1 and P_2.

8.8 Write down all possible reactions of activation occurring during the synthesis of P_1 and P_2. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.

8.9 Draw the structure of P_1 and one of possible structures of P_2 representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.



signal	Integral intensity
a	-
b	40.2
c	13.0
d	10.4
e	1.2
f	2.75
g	40.2

SOLUTION

8.1 Expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t)

$v_{act} = k_{act}$ [R-Hal] [CuHal(Ligand)$_k$]

$v_{deact} = k_{deact}$ [R•] [CuHal$_2$(Ligand)$_k$]

$v_p = k_p$ [R•] [M]

$v_t = 2\ k_t\ [R•]^2$

8.2 Comparison of rates of ATRP elementary stages

Since all the chains grow with equal rate, the process proceeds as living polymerization. Living radical polymerization is possible only if concentration of active radicals is low to prevent chain transfer and termination.

Thus:

$$v_{\text{deact}} >> v_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$v_{\text{deact}} >> v_{\text{p}}$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$v_{\text{deact}} >> v_{\text{t}}$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$v_{\text{deact}} >> v_{\text{act}}$$

$$v_{\text{deact}} >> v_{\text{p}}$$

$$v_{\text{deact}} >> v_{\text{t}}$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$[\text{M}] = [\text{M}]_0 \exp(-k_\text{P}[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_\text{P}[\text{R}\bullet]\,t)$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$31.0 \times \exp(-1616 \times 1.76 \times 10^{-7} \times 1400) = 20.8$ mmol.

Quantity of monomer consumed during polymerization: 31 – 20.8 = 10.2 mmol

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = \frac{10.2}{1000} \times 100.1 = 1.03 \text{ g}$$

2nd variant

$[\text{M}] = [\text{M}]_0 \exp(-\,k_P[\text{R}\bullet]\,t)$ or $n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_P[\text{R}\bullet]\,t)$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\Delta n(\text{MMA}) = n_0(\text{MMA})\,(1\text{-} \exp(-k_p \times [\text{R}\bullet] \times t)) = 31.0 \times (1\text{-}1616 \times 1.76 \times 10^{-7} \times 1400) =$$

$$= 10.2 \text{ mmol}$$

Mass of the obtained polymer is:

$m = \Delta n(\text{MMA}) \times M(\text{MMA})$ = $(10.2 / 1000) \times 100.1 = 1.03\,\text{g}$

3rd variant

$$\ln\left(\frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) = -\,k_P\,[\mathrm{R}\bullet]\,t = -1616\times1.76\times10^{-7}\times1400 = -\,0.398$$

$$\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = \mathrm{e}^{-0.398} = 0.672$$

$$\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = \frac{n(\mathrm{MMA})}{n_0(\mathrm{MMA})}$$

$$n(\mathrm{MMA}) = 0.672\times n_0(\mathrm{MMA}) = 20.8\ \mathrm{mmol}$$

Quantity of monomer consumed during polymerization is 31 – 20.8 = 10.2 mmol.

Mass of the obtained polymer is

$$m\ = \Delta n(\mathrm{MMA})\times M(\mathrm{MMA}) = (10.2\,/\,1000)\times100.1 = 1.03\ \mathrm{g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is 23.7 + 23.7 = 47.4 mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1-\exp(-k_P\,[\mathrm{R}\cdot]\,t)) = 47.4\ (1-\exp(-1616\times1.76\times10^{-7}\times1295)) = 14.6\,\mathrm{mmol}.$$

Totally 7.3 + 14.6 = 21.9 mmol of monomers was polymerized during two stages.

DP = 21.9 / 0.12 = 182.5

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

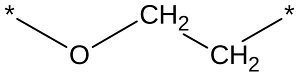
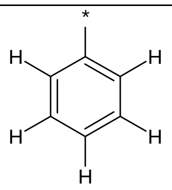
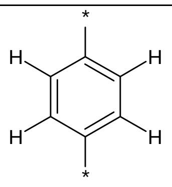
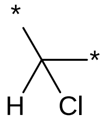
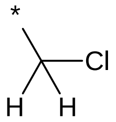
The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is 7.3 / 0.12 = 60.8 ≈ 61 monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning of the 2nd stage were equal. The DP of the 2nd block is 183 – 61 = 122 monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A_{61}-block-(A-stat-B)$_{61}$-Cl or Ts-A_{61}-block-(A_{61}-stat-B_{61})-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P_1 and P_2.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is 40.2 / 4 / 58 = 0.173 for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to 13.0 / 0.173 = 75 protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is 75 / 5 = 15.

Molar fraction of styrene units in P1 is 15 / (15 + 58) = 20.5 %

Intensity of multiplet d is 10.4, which is equivalent to 10.4 / 0.173 = 60 protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is 60 / 4 =15.

Molar fraction of D is 15 / (15 + 58) = 20.5%

$M(P_1)$ = 15.03 + 58 × 44.05 + 72.06 + 15 × 104.15 + 35.45 = **4240**

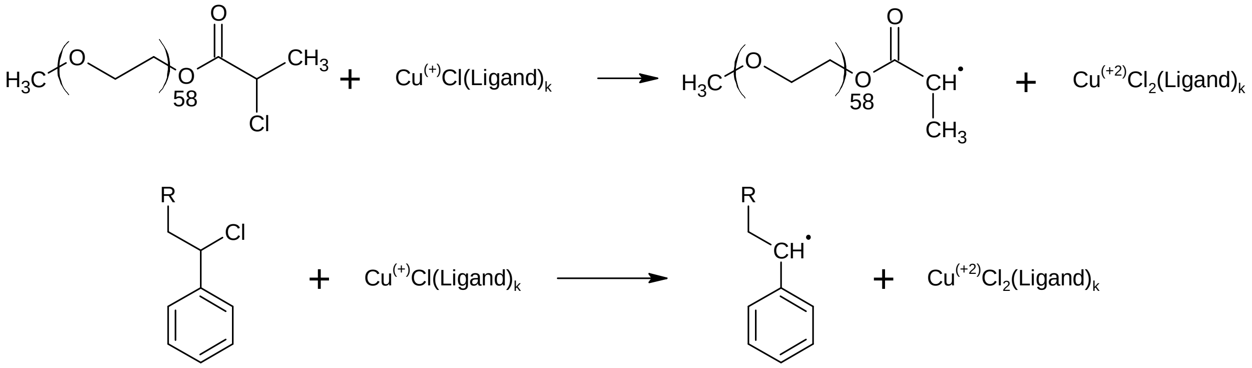
$M(P_2)$ = 15.03 + 58 × 44.05 + 72.06 + 15 × 152.62 + 35.45 = **4967**

$M(P_1)$ = 4240 ; $M(P_2)$ = 4967

n(C) = 20.5 %; n(D) = 20.5 %

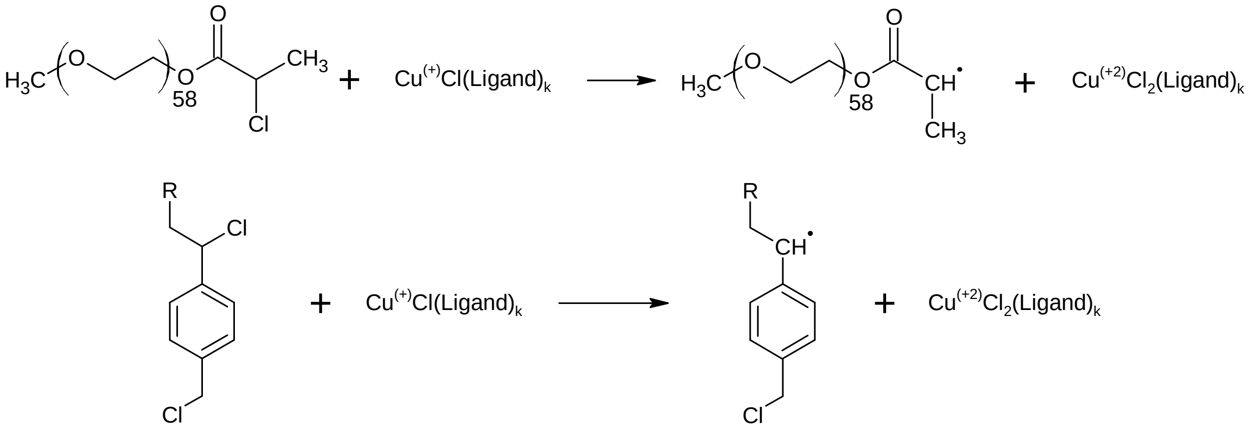
8.8 All possible reactions of activation occurring during the synthesis of P_1 and P_2.

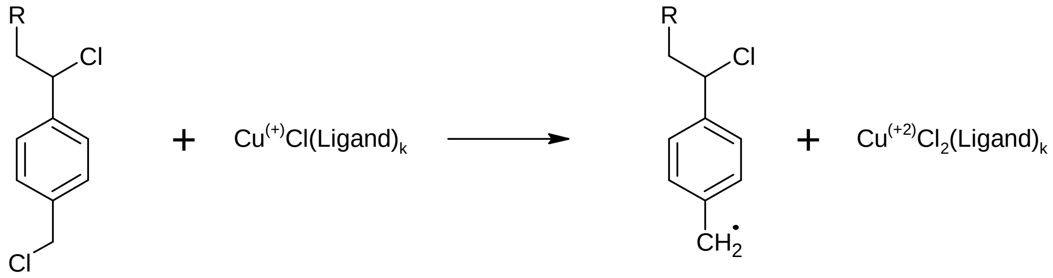
P1:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P_2:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

8.9 The structure of P_1 and one of possible structures of P_2

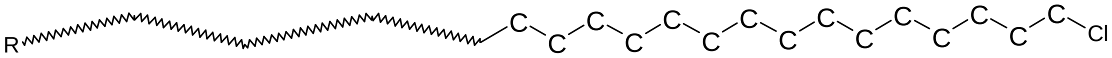
P_1 is a block copolymer of PEO and PS. The PS block contains 15 units.

P_2 is a block copolymer composed of PEO block and branched styrene block.

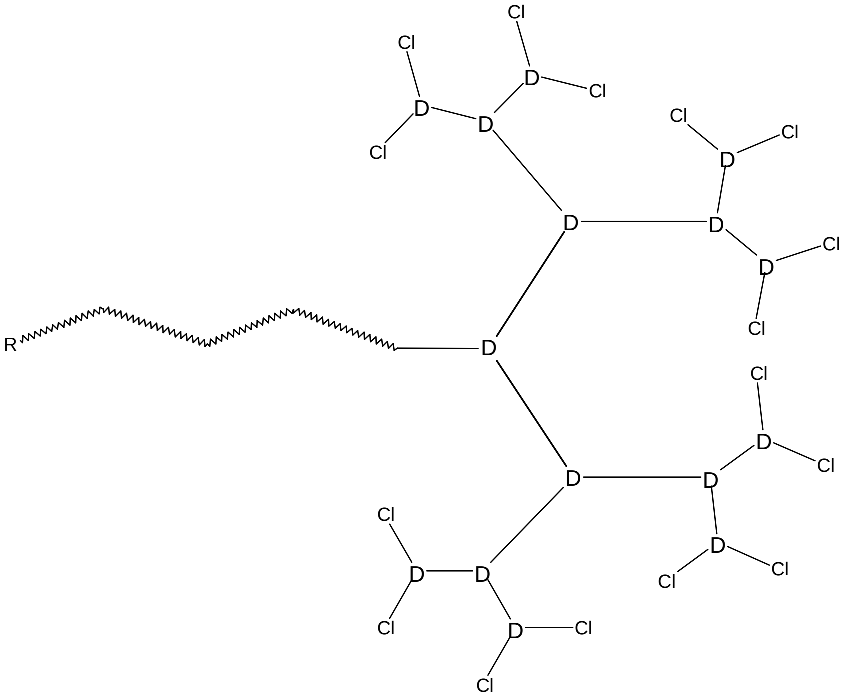
The integral intensity of multiplet f is 2.75, so 2.75/0.173=15.9, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P_2, it would contain 15 choromethyl groups. Each branching reduces the number of such groups by 1. Thus P_2 has 15 – 8 = 7 branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units

P_1



P_2

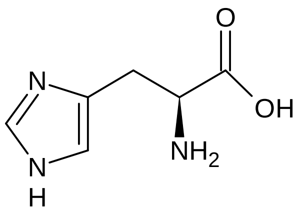


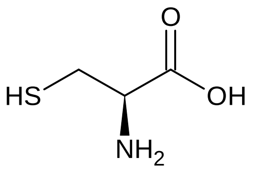
PRACTICAL PROBLEMS

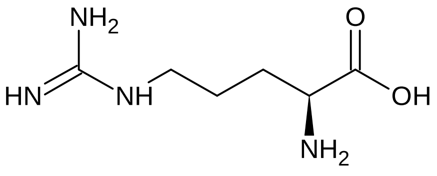
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.


His


Cys


Arg

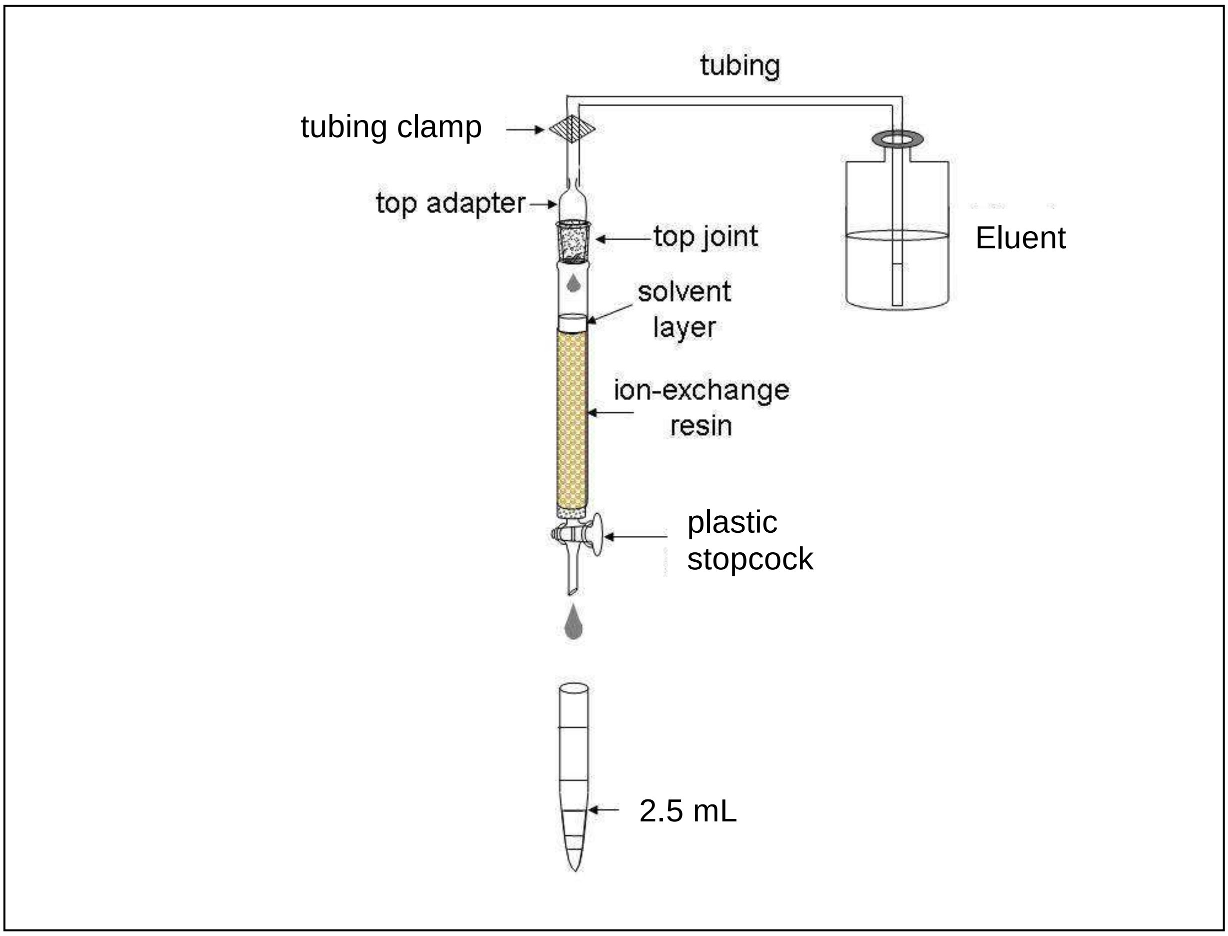
Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

Procedure

Chromatography. Step 1

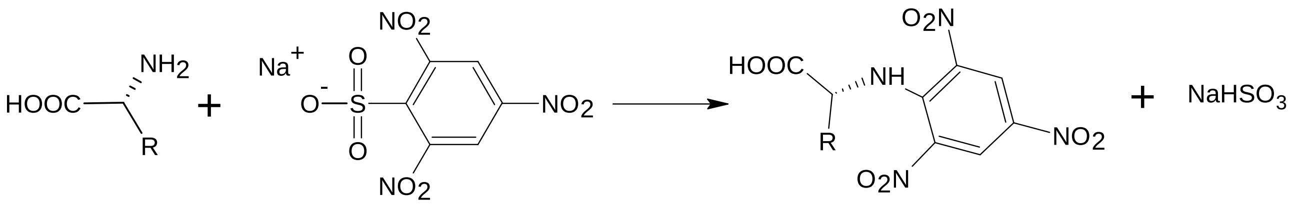
Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled “Waste” so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the “Waste” flask). Close the stopcock and add about 1 cm^3 of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm^3 (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α-amino groups with sodium 2,4,6–trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm^3 of TNBS solution with 10 cm^3 of carbonate buffer solution and place 0.1 cm^3 of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm^3 of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm^3 should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled “Peak 1”, “Peak 2”, “Peak 3”. Prepare samples for quantitative spectrophotometric analysis as described below.

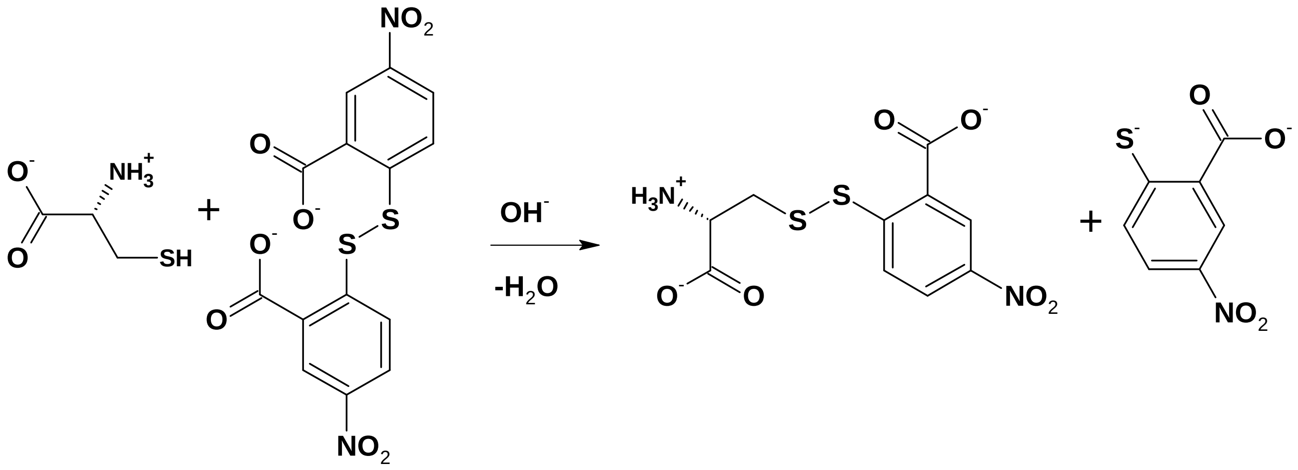
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A_1 (Reference).

Place 0.1 cm^3 of Eluent 1 from plastic microtube into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Test tube B_1 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 2.9 cm^3 of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_1 (for reference) and B_1 (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A_2 (Reference).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of Eluent 2 from plastic microtube and 0.1 cm^3 of Pauli reagent.

Test tube B_2 (Sample).

Place 2.8 cm^3 of Tris-HCl buffer solution into a test tube, add 0.1 cm^3 of the analyzed solution and 0.1 cm^3 of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A_2 (for reference) and B_2 (for sample).

Assay 3 (peak 3).

Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions (Sakaguchi reaction).

Test tube A_3 (Reference).

Place 0.1 cm^3 of Eluent 3 into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 of 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Test tube B_3 (Sample).

Place 0.1 cm^3 of the analyzed solution into a test tube and add 1.5 cm^3 of 10 % NaOH solution, 1 cm^3 8-hydroxyquinoline solution and 0.5 cm^3 of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm^3 of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm^3 of each mixture to the corresponding cells labelled A_3 (for reference) and B_3 (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 M^{-1}cm^{-1} at 410 nm Product of Pauli reaction: 6400 M^{-1}cm^{-1} at 470 nm Product of Sakaguchi reaction: 7700 M^{-1}cm^{-1} at 500 nm	Molar masses of the amino acids. Cysteine: 121 g mol^{-1} Histidine: 155 g mol^{-1} Arginine: 174 g mol^{-1}

1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

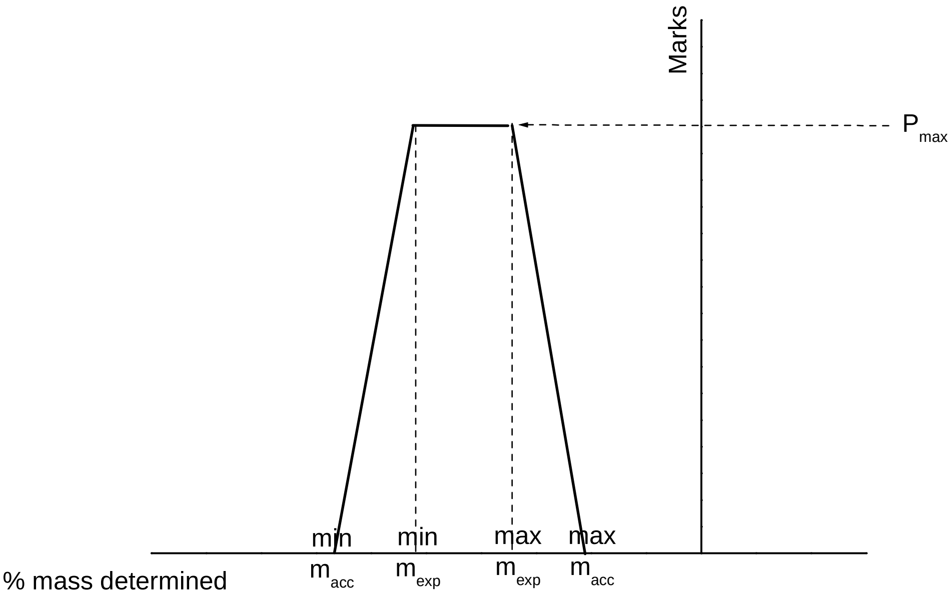
SOLUTION

1.2 – 1.3

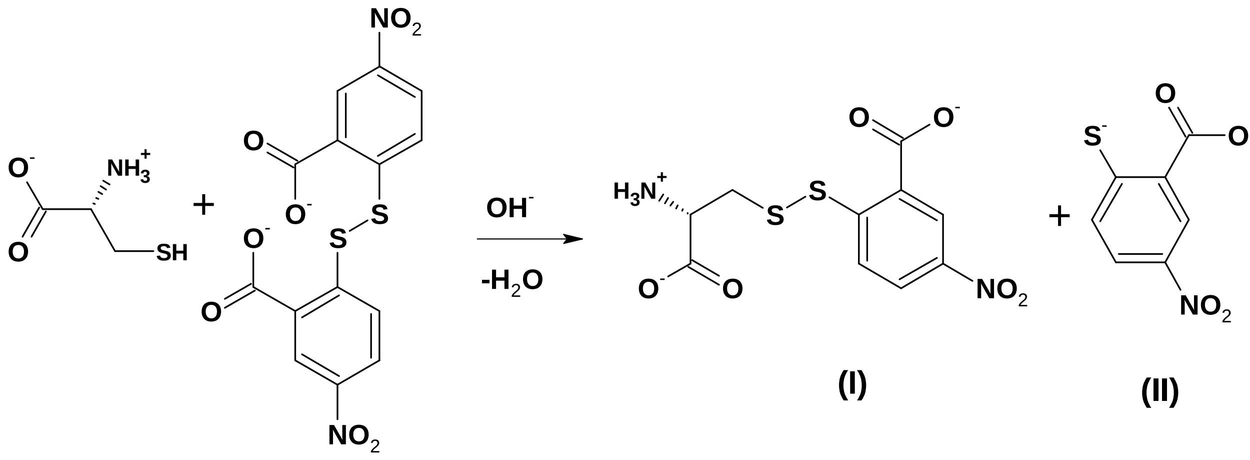
Content of an amino acid = $\frac{A_\lambda n\ V\ M}{\varepsilon\, l}$,

A_λ is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm^3) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

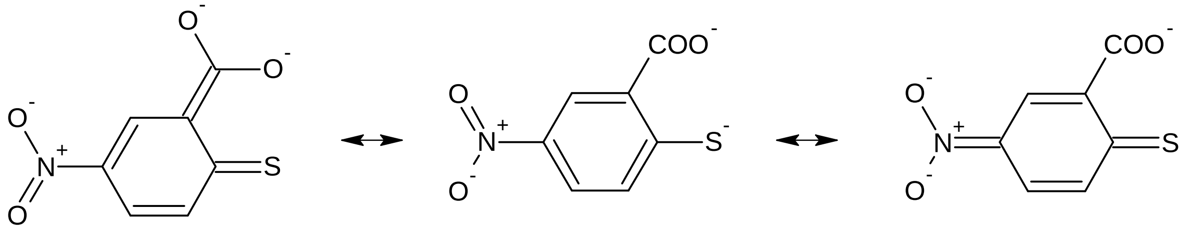
Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).



1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



Under slightly alkaline conditions, thiol group of (**II**) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (**I**) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing C=S bond).

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3, $CaCO_3$ and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4, whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to $H_2PO_4^-$ ion, the endpoint lying in slightly acidic medium (*pH* of ~4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, *pH* of ~10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

a) the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and

b) the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. Dissolution of the sample and removal of CO_2

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm^3 of 15 % $K_2C_2O_4$ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm^3 of HCl solution into a 100 cm^3 volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm^3 of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm^3. Report all the final volume values with 0.01 cm^3 accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm^{-3}).

Step 4. Filtering off calcium oxalate

After the most part of CaC_2O_4 precipitates filter the precipitate off collecting the filtrate into a 100 cm^3 volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+}.

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet. Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+”or “–“ if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	ΔV, cm^3	
	expected	acceptable
$V_{1,\text{f}}$	**0.10**	**0.25**
$V_{2,\text{f}}$	**0.15**	**0.40**
$V_{3,\text{f}}$	**0.15**	**0.40**

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl})\times V(\text{HCl})\times V(\text{aliquot})}{V(\text{flask})\times V(\text{NaOH})} = \frac{1.214\ \text{mol dm}^{-3}\times 10.00\ \text{cm}^3\times 10.00\ \text{cm}^3}{100.0\ \text{cm}^3\times V_{1,\text{f}}\text{cm}^3}$$

2.4 Calculation of the mass of CO_3^{2-}

$$\text{m}(\text{CO}_3^{2-}) = M(\text{CO}_3^{2-})\times 1/2\times\frac{c(\text{NaOH})\times(V_{1,f}-V_{3,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 60.01\ \text{g mol}^{-1}\times 1/2\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{1,f}-V_{3,f})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\,\text{dm}^3/\text{cm}^3 =$$

2.5 Calculation of the mass of HPO_4^{2-}

$$m(\text{HPO}_4^{2-}) = M(\text{HPO}_4^{2-})\times\frac{c(\text{NaOH})\times(V_{3,f}-V_{2,f})\times V(\text{flask})}{V(\text{aliquot})} =$$

$$= 95.98\ \text{g mol}^{-1}\times\frac{c(\text{NaOH})\ \text{mol dm}^{-3}\times(V_{3,\text{f}}-V_{2,\text{f}})\ \text{cm}^3\times 100.0\ \text{cm}^3}{10.00\ \text{cm}^3}\times 0.001\ \text{dm}^3/\text{cm}^3 =$$

2.6 a

$\text{Ca}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{CaHPO}_4 + \text{H}^+$

or

$3\ \text{Ca}^{2+} + 2\ \text{HPO}_4^{2-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 2\ \text{H}^+$

40th

International Chemistry Olympiad

9 theoretical problems
3 practical problems

THE FORTIETH
INTERNATIONAL CHEMISTRY OLYMPIAD
12–21 JULY 2008, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A *pH* meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the *pH* changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

☐ Yes ☐ No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

☐ Yes ☐ No

If yes, calculate the concentration.

SOLUTION

1.1 Any univalent, strong acid (HCl, HBr, HI, HNO_3, $HClO_4$) is acceptable. HF is not!

1.2 ☐ Yes ☑ No

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > c_{acid.}$

No text or calculations are needed.

1.3 ☑ Yes ☐ No

Yes, but it can happen only in quite dilute solutions.

$c = [HA] + [A^–] = [H^+]$

$[H^+] = [A^–] + [OH^–]$

This means that $[HA] = [OH^–]$

$$K = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]([H^+] - [OH^-])}{[OH^-]} = \frac{[H^+]^3}{K_w} - [H^+]$$

The *pH* of the solution must be acidic, but close to 7.

6.5 is a good guess.

A good approximation is: $[H^+] = \sqrt[3]{(K\,K_w)}$

The full equation can be solved through iteration: $[H^+] = \sqrt[3]{(K + [H^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64\times10^{–7}$ mol dm^{-3} as the required concentration. Exact *pH* is 6.25.

1.4 ☑ Yes ☐ No

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. The following equations are thus true:

$c = [H_4A] + [H_3A^–] + [H_2A^{2–}] = [H^+]$

$[H^+] = [H_3A^–] + 2\,[H_2A^{2–}]$

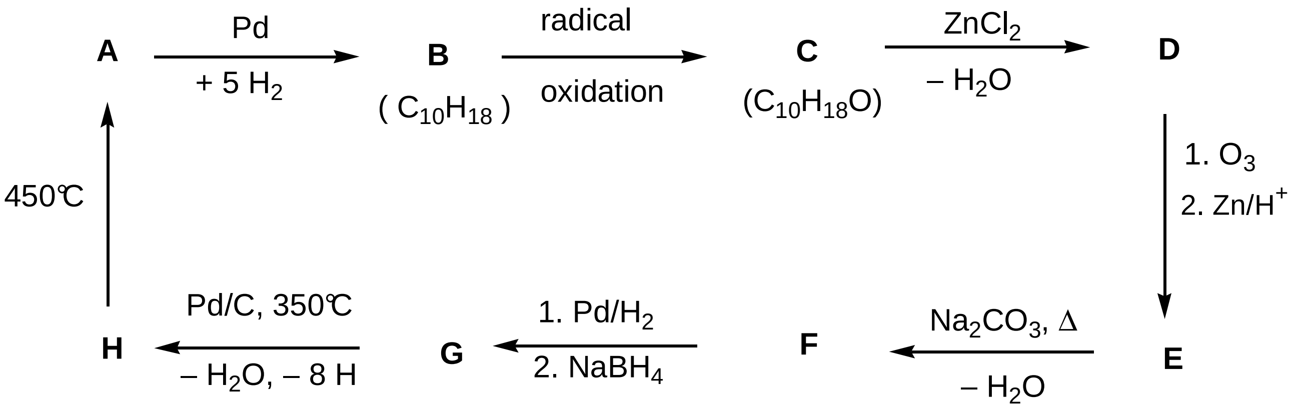
This means that $[H_4A] = [H_2A^{2–}]$

$$K_1 K_2 = \frac{[H^+]^2[H_2A^{2-}]}{[H_4A]} = [H^+]^2$$ (or $pH = (pK_1 + pK_2)\,/\,2 = 2.15$)

$c = 0.0071$ mol dm^{-3}

PROBLEM 2

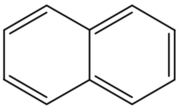
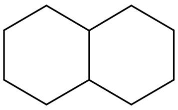
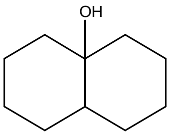
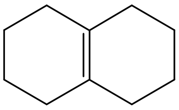
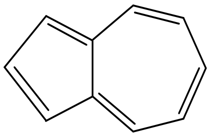
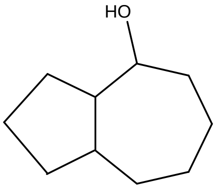
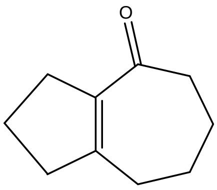
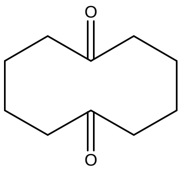
Determine the structure of the compounds **A** - **H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

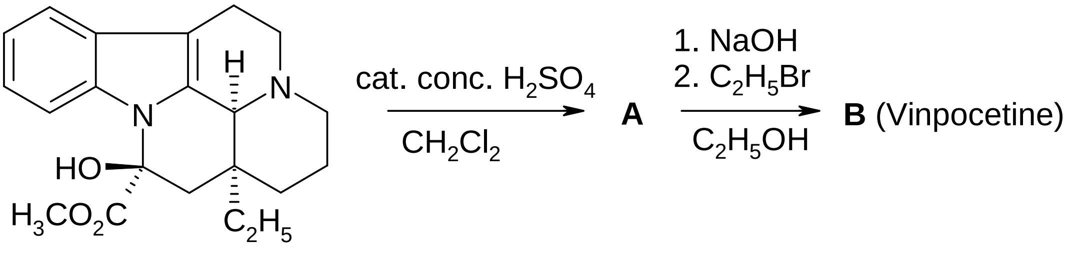
- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

SOLUTION

A 	**B** 	**C**  	**D** 
H 	**G**  	**F**  	**E** 

PROBLEM 3

Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}\ N_2O_3$), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



Vincamine

All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

3.1 Propose structures for the intermediate **A** and vinpocetine (**B**).

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

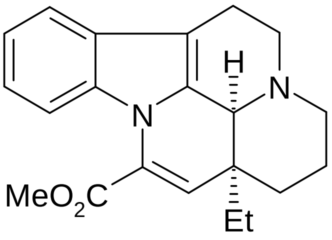
- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**: C 72.11 %, H 7.15 %, N 7.64 %, O 13.10 %.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

3.2 Propose one <u>possible</u> structure for each of the metabolites **C**, **D**, **E** and **F**!

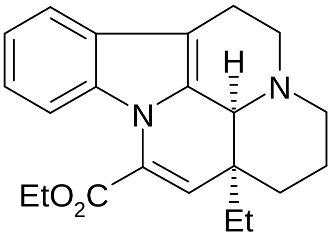
3.3 Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.

SOLUTION

3.1



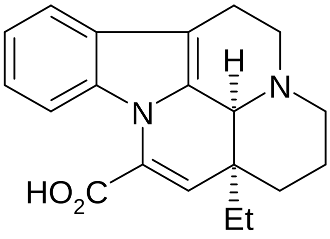
A



B

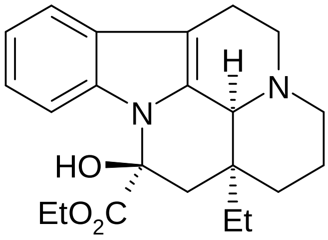
3.2

C



apovincaminic acid

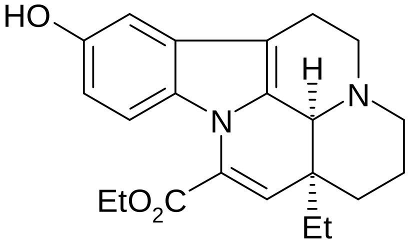
D



ethyl vincaminate

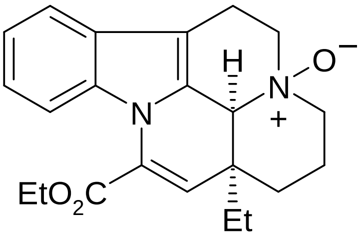
Both stereoisomers around the new chiral center are acceptable.

E



10-hydroxyvinpocetine

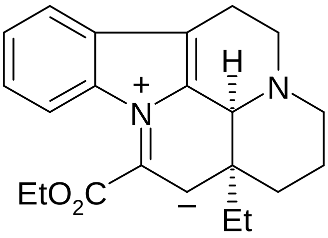
F



vinpocetine N-oxide

All aromatic positions for the OH are acceptable in **E**.

3.3



All aromatic positions for the OH are acceptable in **E**.

PROBLEM 4

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

On base catalysis the sterically less hindered C–O bond is cleaved predominantly. Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the ◀ ⦙⦙⦙ — bond symbols and nothing else where necessary.

4.1 Draw the structure of the reactant and the predominant products when 2,2-dimethyloxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

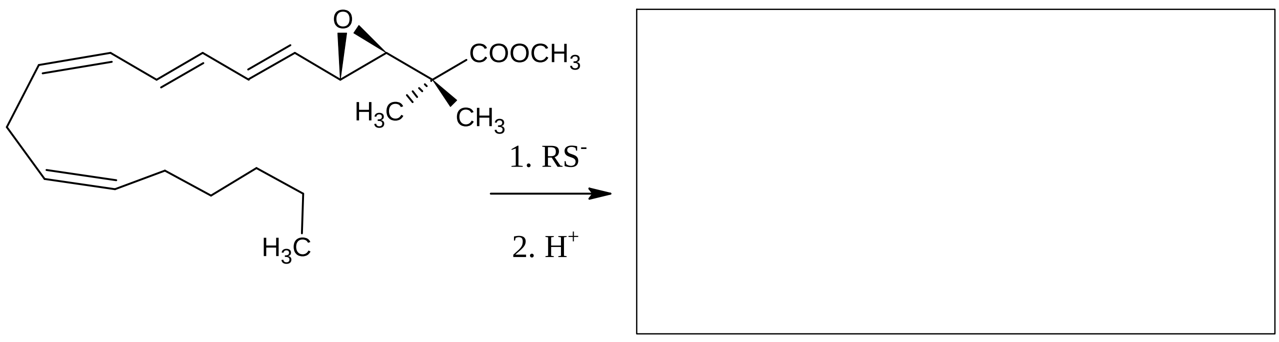
(i) sulphuric acid

(ii) $NaOCH_3$.

2,2-dimethyloxirane

$$\xleftarrow[CH_3OH]{H^+} \qquad\qquad \xrightarrow[CH_3OH]{NaOCH_3}$$

4.2 Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS^-).



Different porous acidic aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

4.3 Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane). Give the structure of the reactant as well.

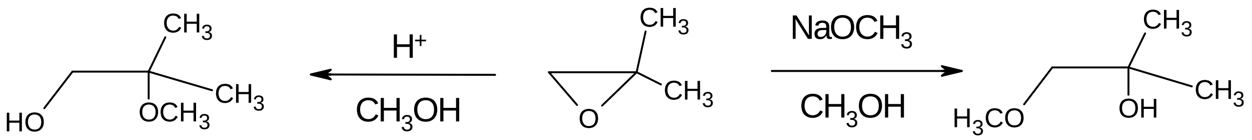
4.4 Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.

4.5 Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

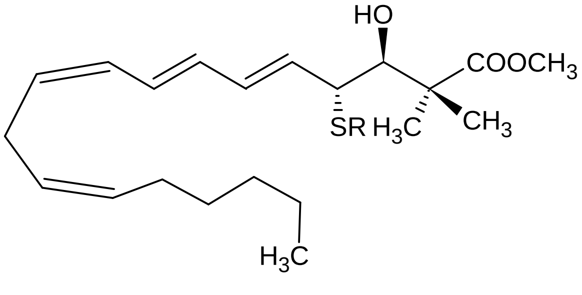
SOLUTION

4.1

2,2-dimethyloxirane



4.2



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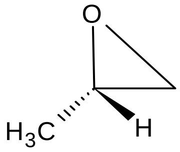
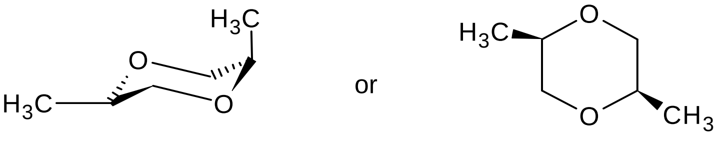
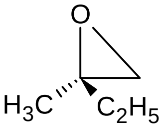


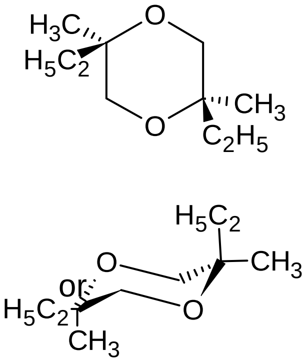
(*S*)-2-methyloxirane



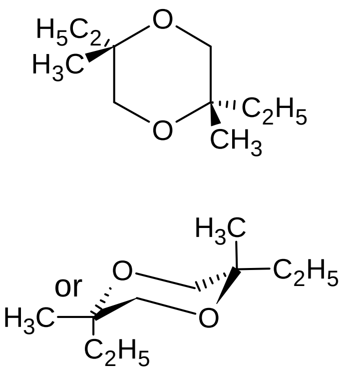
product

4.4 (*R*)-1,2-epoxy-2-methylbutane:

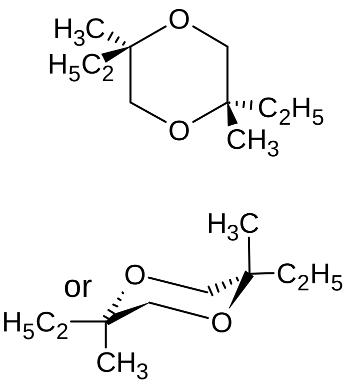




R,R

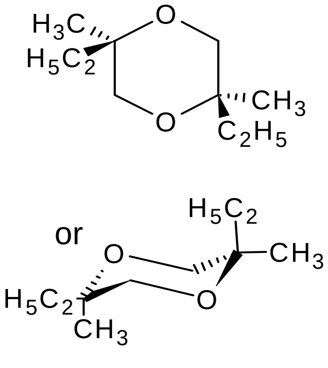


S,S

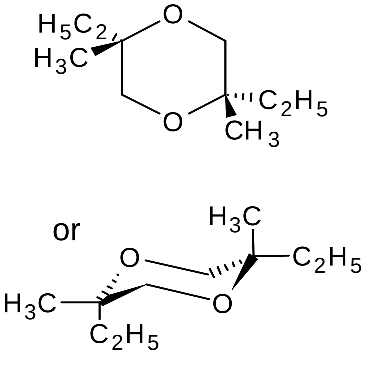


R,S

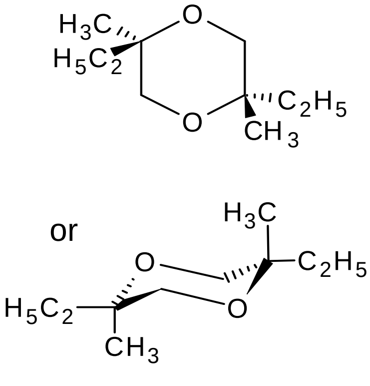
4.5



R,R



S,S



R,S

PROBLEM 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 ℃) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, *pH* ≈ 8.5-9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, *pH* ≈ 4.5-5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 ℃ produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 ℃ is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances **A** - **F**

5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

SOLUTION

5.1 The formulae of the substances **A** – **F:**

A	**B**	**C**
$Ba(NO_2)_2$	$(NH_4)_2SO_4$	$BaSO_4$
D	**E**	**F**
BaO	$BaCO_3$	BaO_2

5.2 Equations:

$Ba(NO_2)_2 = BaO + NO + NO_2$

$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$

$Ba^{2+} + SO_4^{2-} = BaSO_4$

$2\ NO_2^- + 2\ I^- + 4\ H^+ = 2\ NO + I_2 + 2\ H_2O$

$NH_4^+ + NO_2^- = N_2 + 2\ H_2O$

$BaO + H_2O = Ba^{2+} + 2\ OH^-$

$Ba^{2+} + 2\ OH^- + CO_2 = BaCO_3 + H_2O$

$BaO + CO_2 = BaCO_3$

$2\ BaO + O_2 = 2\ BaO_2$

$BaO_2 + 2\ I^- + 4\ H^+ = Ba^{2+} + I_2 + 2\ H_2O$

$BaCO_3 = BaO + CO_2$

$NH_4^+ + OH^- = NH_3 + H_2O$

Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400 °C, probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because $Ca(OH)_2$ is poorly soluble while the solubilities of Li_2CO_3 and Tl_2CO_3 are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either M_{Ca} + 45.8, or M_{Sr} + 39.05, or M_{Ba} + 32. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO_2. This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with $Ba(OH)_2$ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO_4^{2-} or HPO_4^{2-} but the acidity of **B** is consistent with the former and, in addition, $(NH_4)_2HPO_4$ would not give the same $BaHPO_4$ precipitate with $Ba(OH)_2$ as with $Ba(NO_2)_2$. If we accept that **B** is $(NH_4)_2SO_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

PROBLEM 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

6.1 How many type **A** cavities can be found in a unit cell?

6.2 How many water molecules are there in a unit cell?

6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

6.4 Methane hydrate is formed with the structure in **c)** at temperatures between 0-10 ℃. What is the density of the clathrate?

6.5 The density of chlorine hydrate is 1.26 g/cm^3. What is the ratio of the number of water and guest molecules in the crystal?

Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

☐ Some **A** ☐ Some **B** ☐ All **A** ☐ All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes

$H_2O(l) \rightarrow H_2O(s)$ (1)

x $CH_4(g) + H_2O(l) \rightarrow$ x $CH_4.1H_2O$(clathrate) (2)

6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

SOLUTION

6.1 The number of **A** cavities in a unit cell: $\boxed{2}$

6.2 The number of water molecules in a unit cell?

46 = 20 x 2 (dodecahedra) + 6 x 2 /2 (faces)

6.3 The number of water to the number of guest molecules?

46 : 8 = 5.75

6.4 A unit cell has a volume of 1.182^3 nm^3 = 1.651 nm^3.

It contains 8 methane and 46 water molecules with a mass of 957 g mol^{-1}/ N_A = 1.589×10^{-21} g.

The density is 1.589 / 1.651 = 0.962 g/cm^3.

6.5 The mass of a unit cell with this density is: 1.651 nm^3 × 1.26 g cm^{-3} = 2.081×10^{-21} g, meaning 1253 g/mol for the contents.

Substracting the waters, this means 424.3 g mol^{-1} for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell.

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68.

It is expected that only the 6 larger B type cavities contain chlorine. Thus:

☐ Some **A** ☐ Some **B** ☐ All **A** ☑ All **B**

6.6 Methane fits in both cavities, its radius is approximately 37 + 77 + 120 pm = 234 pm.

The chlorine molecule, with a radius of 180 + 99 pm = 279 pm, fits only in **B**.

Thus 234 pm < *r*(**A**) < 279 pm and 279 pm < *r*(**B**)

6.7

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	–
$\Delta H_m(1)$	–
$\Delta H_m(2)$	–
$\Delta S_m(1)$	–
$\Delta S_m(2)$	–
$\Delta S_m(2) - \Delta S_m(1)$	–
$\Delta H_m(2) - \Delta H_m(1)$	–

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$\Delta G_m(1) > \Delta G_m(2)$

$\Delta H_m(1) - T\,\Delta S_m(1) > \Delta H_m(2) - T\,\Delta S_m(2)$

$T\,(\Delta S_m(2) - \Delta S_m(1)\,) > \Delta H_m(2) - \Delta H_m(1)$

a negative quantity > $\Delta H_m(2) - \Delta H_m(1)$

PROBLEM 7

The dithionate ion ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3.

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3.

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with $BaCl_2$ solution. When the solid is heated and maintained at 130 °C, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with $BaCl_2$ solution. When another sample of the original crystals is kept at 300 °C for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with $BaCl_2$ solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 °C, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at 75 °C.

$[Br_2]_0$ (mmol dm^{-3})	$[Na_2S_2O_6]_0$ (mol dm^{-3})	$[H^+]_0$ (mol dm^{-3})	v_0 (nmol dm^{-3}s^{-1})
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2, H^+ and $S_2O_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($Cr_2O_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

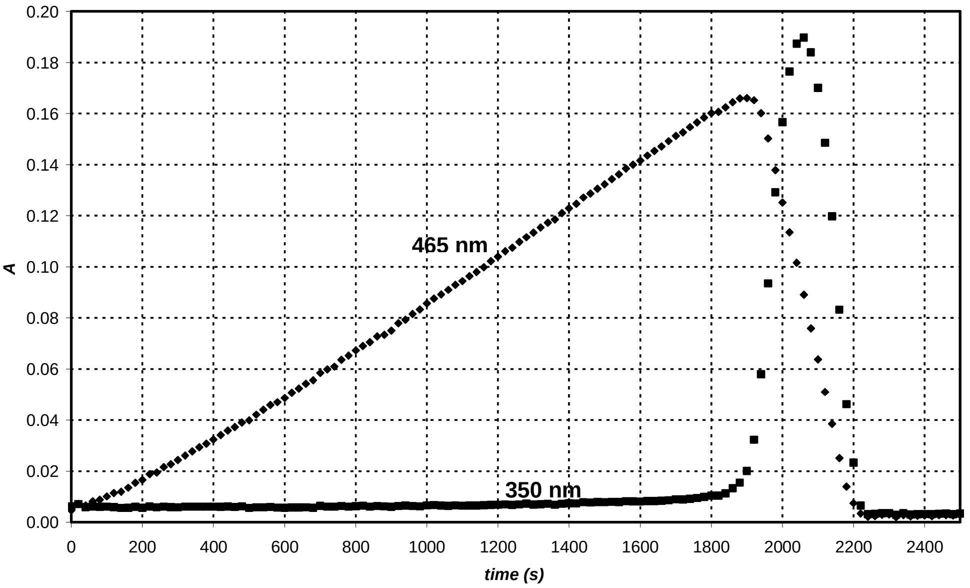
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: [$Na_2S_2O_6$] = 0.0022 mol dm^{-3}, [$HClO_4$] = 0.70 mol dm^{-3}, and the temperature was 75 ℃. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as $H_4IO_6^-$ in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 ℃ in the same experiment at two different wavelengths. The initial concentrations were [$H_4IO_6^-$] = 5.3·10^{-4} mol dm^{-3}, [$Na_2S_2O_6$] = 0.0519 mol dm^{-3}, [$HClO_4$] = 0.728 mol dm^{-3}. At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 dm^3 mol^{-1} cm^{-1}. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 dm^3 mol^{-1} cm^{-1}. The optical path length was 0.874 cm.



7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

SOLUTION

7.1 $MnO_2 + 2\ SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-}$

$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-}$

7.2 $MnS_2O_6 + Na_2CO_3 \rightarrow Na_2S_2O_6 + \underline{MnCO_3}$

7.3 Formula: $Na_2S_2O_6 \cdot 2\ H_2O$

Equation (130 ℃): $Na_2S_2O_6 \cdot 2\ H_2O \rightarrow Na_2S_2O_6 + 2\ H_2O$

Equation (300 ℃): $Na_2S_2O_6 \rightarrow Na_2SO_4 + SO_2$ or with H_2O

7.4 $S_2O_6^{2-} + Br_2 + 2\ H_2O \rightarrow 2\ SO_4^{2-} + 2\ Br^{-} + 4\ H^{+}$

7.5 Reaction order for Br_2: 0 for H^+: 1 for $S_2O_6^{2-}$: 1

Experimental rate equation: $v = k\,[HSO_4^{-}]\,[H^+]$

$k = 2.56 \cdot 10^{-5}$ dm^3 mol^{-1} s^{-1}

7.6 Species: SO_2 (or H_2SO_3)

Reaction: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^{-} + SO_2$

7.7 $t_{½} = 10$ h 45 min $= 3.87 \cdot 10^4$ s

$k_{obs} = \ln 2 / t_{½} = 1.79 \times 10^{-5}$ s^{-1}

$k = k_{obs} / [H^+] = 2.56 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}

Rate determining step: $S_2O_6^{2-} + H^+ \rightarrow HSO_4^{-} + SO_2$

7.8 Increase: $2\ H_4IO_6^{-} + 7\ S_2O_6^{2-} + 2\ H_2O + 2\ H^+ \rightarrow 14\ HSO_4^{-} + I_2$

Decrease: $I_2 + S_2O_6^{2-} + 2\ H_2O \rightarrow 2\ HSO_4^- + 2\ I^- + 2\ H^+$

The expected time for the maximum absorbance of the kinetic curve measured at 465 nm:

$$t_{\max} = \frac{7}{2}\frac{[H_4IO_6^-]_0}{k[S_2O_6^{2-}]_0[H^+]_0} = \frac{7 \times 5.3 \times 10^{-4}\ M}{2 \times 2.56 \times 10^{-5}\ M^{-1}s^{-1} \times 0.0519\ M \times 0.728\ M} = 1900\ s$$

The expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm: 1; –7 (it reflects the stoichiometry).

PROBLEM 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified $CeCl_3$ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm^3)	E (mV)
0.1000	26.9
1.000	–32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce^{3+} (ε = 35.2 dm^3 mol^{-1}cm^{-1}) at 295 nm, and, as a precaution, also for Ce^{4+} (ε = 3967 dm^{3}mol^{-1}cm^{-1}).

8.2 Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (A) measured in a solution containing $CeCl_3$ (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained 0.0100 mol/dm^3 $CeCl_3$ and 0.1050 mol/dm^3 HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance (A_{295nm}) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectophotometric measurements is ±0.002 and the accuracy of the voltage measurements is ±0.3 mV.

time (min)	0	120	240	360	480
$A_{295\ \mathrm{nm}}$	0.3496	0.3488	0.3504	0.3489	0.3499
E (mV)	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+}, Cl^{-}, and H^{+}. $d[Ce^{3+}]/dt = d[Cl^{-}]/dt = d[H^{+}]/dt$ = ?

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic $CeCl_3$ solution she had used before. She measured the molar absorption coefficient for Ce^{3+} (ε = 2400 dm^3 mol^{-1} cm^{-1}) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3. The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0 °C.

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.

8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

SOLUTION

8.1 $[\text{Cl}^-] = 10^{-(E+32.2\,mV)/59.1\,mV}$

8.2 $[\text{Ce}^{3+}] = \dfrac{A_{295nm}}{35.2\,\text{dm}^3\text{mol}^{-1}}$

8.3 $[\text{Ce}^{3+}]$ = 0.0100 mol/dm^3 $\Rightarrow$ $A_{295\text{nm}}$= 0.352

$[\text{Cl}^-]$ = 3·0.0100 mol/dm^3 + 0.1050 mol/dm^3 = 0.1350 mol/dm^3 $\Rightarrow$ E = 19.2 mV

8.4 HCl, Cl_2, (O_3, ClO_2) (no oxidation of indicator)

8.5 $d[\text{Ce}^{3+}]/dt$ = ? $d[\text{Cl}^-]/dt$ = ? $d[\text{H}^+]/dt$ = ?

No significant change in either Cl^- or Ce^{3+} concentrations.

$[\text{H}^+] = [\text{Cl}^-] - 3\,[\text{Ce}^{3+}]$, no significant change.

All three values are zero.

8.6 What percentage of the light is absorbed in this experimental setup?

A = 2400 dm^3 mol^{-1} cm^{-1} × 5 cm × 0.0100 M = 120 $\Rightarrow$ (100 – 10^{-118}) % ≈ 100 %

8.7 $p_{\text{partial}} = p_{\text{final}} - p_{\text{initial}}$ = 114075 Pa – 102165 Pa = 11910 Pa

$n = p_{\text{partial}}V/(RT)$ = 11910 Pa·0.000068 m^3 / (8.314 J mol^{-1} K × 295.15 K) =

= 3.3×10^{-4} mol

identity of gases: H_2, O_2

8.8 reaction: $2\ H_2O \xrightarrow{h\nu} 2\ H_2 + O_2$

8.9 Final pressure: 104740 Pa (saturated water vapour)

8.10 Quantum yield:

3.3×10^{-4} mol gas formed altogether: 2.2×10^{-4} mol H_2 and 1.1×10^{-4} mol O_2.

Light beam intensity 0.0500 J s^{-1} $\Rightarrow \dfrac{0.0500\ \text{Js}^{-1}\lambda}{h\,c\,N_A} = 1.06\times10^{-7}\text{mol s}^{-1}\text{photon}$

Total time 18.00 h = 64800 s

Total number of absorbed photons: 64800 s × 1.06×10^{-7} mol s^{-1} = 6.87×10^{-3} mol

Quantum yield for H_2 production: Φ = 2.2×10^{-4} mol / 6.87×10^{-3} mol = 0.032

Quantum yield for O_2 production: Φ = 1.1×10^{-4} mol / 6.87×10^{-3} mol = 0.016

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

PROBLEM 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+}. Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

The standard redox potentials for some relevant reactions are:

$Tl^+(aq) + e^- \rightarrow Tl(s)$ $E^o_1 = -0.336$ V

$Tl^{3+}(aq) + 3e^- \rightarrow Tl(s)$ $E^o_2 = +0.728$ V

$I_2(s) + 2e^- \rightleftharpoons 2\,I^-(aq)$ $E^o_3 = +0.540$ V

The equilibrium constant for the reaction $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$: $K_1 = 0.459$.

Use T=25 ℃ throughout this problem.

9.1 Calculate the redox potentials E^o_4 and E^o_5 for the following reactions:

$Tl^{3+}(aq) + 2\,e^- \rightarrow Tl^+(aq)$ E^o_4

$I_3^-(aq) + 2\,e^- \rightarrow 3\,I^-(aq)$ E^o_5

9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

SOLUTION

9.1 $E_4^0 = \dfrac{3\,E_2^0 - E_1^0}{2} = 1.26\ \text{V}$

$E_5^0 = E_3^0 + 0.059 / 2 \log(1 / K_1) = 0.550$ V

9.2 Tl I, Tl I_3, Tl I_5, Tl I_7, Tl I_9

Tl I_3 can be either $Tl^{3+}(I^-)_3$ or $Tl^+(I_3^-)$

More stable: $Tl^+(I_3^-)$

as $E_4^0 > E_5^0$ or E_3^0,

Isomerisation: $Tl^{3+} + 3\ I^- = Tl^+ + I_3^-$

9.3 Reaction: $Tl^+ + I_3^- + I^- \rightarrow Tl\ I_4^-$

This reaction could be regarded as sum of three reactions:

$Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ $E_4^0 = -1.26$ V, thus $\Delta_r G_4^o = n\ F\ E_4^0 = 243.1$ kJ mol^{-1}

$I_3^-(aq) + 2\ e^- \rightarrow 3\ I^-(aq)$ $E^o_5 = 0.550$ V, thus $\Delta_r G_5^o = -n\ F\ E_5^o = -106.1$ kJ mol^{-1}

$Tl^{3+} + 4I^- \rightarrow Tl\ I_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^o = -R\ T \ln\beta_4 = -203.8$ kJ mol^{-1}

The net free enthalpy change is $\Delta_r G_7^o = \Delta_r G_4^o + \Delta_r G_5^o + \Delta_r G_6^o = -66.8$ kJ mol^{-1}

Thus $K_2 = \exp\left(-\dfrac{\Delta_r G_7}{RT}\right) = 4.96 \cdot 10^{11}$

9.4 Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

From the values *b* = 1, 3 and *a* = 1, 2, 3 only *b* = 3, *a* = 2 gives a realistic:

$M_X = 16.0$ g mol^{-1}.

X is oxygen.

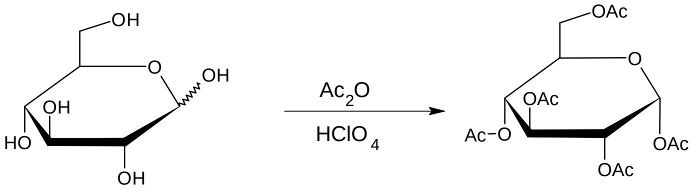
Formula: Tl_2O_3.

Equation: $2\ Tl\ I_3 + 6\ OH^- \rightarrow Tl_2O_3 + 6\ I^- + 3\ H_2O$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α-D-glucopyranose pentaacetate

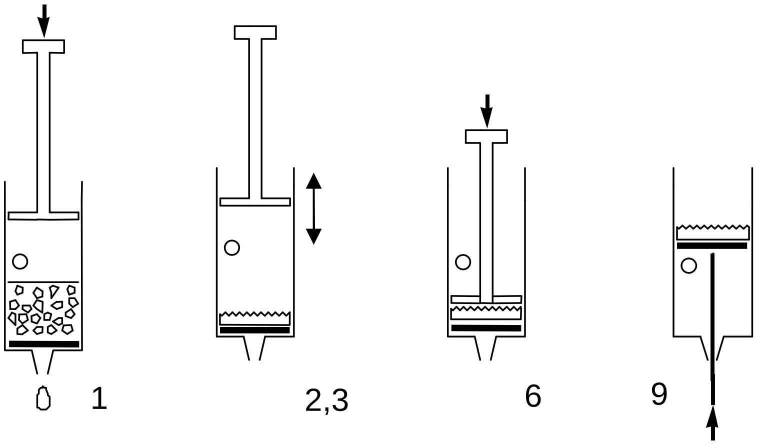


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm^3 of pure acetic acid to 12 cm^3 of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% $HClO_4$ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm^3 of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm^3 of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



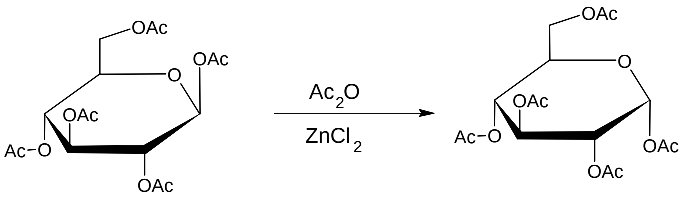
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm^3 of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

1.1 Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

1.2 Calculate the theoretical yield (mass) of your product in g. (M(C) = 12 g mol^{-1}, M(O) = 16 g mol^{-1}, M(H) = 1.0 g mol^{-1}

Synthesis of α-D-glucopyranose pentaacetate from β-D-glucopyranose pentaacetate

An alternative synthesis of α-D-glucopyranose pentaacetate starts from readily available β-D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous $ZnCl_2$ (preweighed in a test tube). Add 100 mg of pure β-D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm^3 methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70ºC. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm^3 of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

1.3 Copy your plate on the answer sheet and place your plate in the labelled zip lock bag.

1.4 Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

The isomerisation reaction of β-D-glucopyranose pentaacetate can be used for the preparation of pure α-D-glucopyranose pentaacetate.

☐ a) Yes
☐ b) No
☐ c) Cannot be decided based on these experiments

SOLUTION

1.1 Yield of the product in g, measured by the organizer.

The samples are dried by the organisers. The typical yield is 70 %.

Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.

1.1 Calculation of the theoretical yield of the product in g:

$C_6H_{12}O_6 \rightarrow C_{16}H_{22}O_{11}$

$$m = \frac{3.00\,\text{g} \times 390\,\text{g}\,\text{mol}^{-1}}{180\,\text{g}\,\text{mol}^{-1}} = 6.50\,\text{g}$$

1.3 The developed TLC plate was expected to be sketched on the answer sheet.

Full points were given if both standards and all samples are present.

1.4 Solutions: a), a).

PROBLEM 2 (Practical)

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6].3H_2O$ (M = 422.41 g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm^3 volumetric flask. Take 10.00 cm^3 portions of the hexacyanoferrate(II) solution. Add 20 cm^3 1 mol/dm^3 sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm^3 Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

2.1 Report the Ce^{4+} solution volumes consumed.

2.2 Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6].3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm^3 of the hexacyanoferrate(II) solution and add 20 cm^3 1 mol/dm^3 sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

2.3 Report the zinc solution volumes consumed.

2.4 Interpret the titration answering the questions on the answer sheet.

Mark the correct answer:

The diphenyl amine indicator changes in colour at the end point

☐ a) because the concentration of the Zn^{2+} ions increases.

☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.

☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.

☐ d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

☐ a) Oxidized

☐ b) Reduced

☐ c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

☐ a) True

☐ b) False

2.5 Determine the formula of the precipitate.

____

SOLUTION

2.1 Ce^{4+} consumptions:

Full marks if V_1 is within 0.15 cm^3 of the expected value recalculated from the $K_4[Fe(CN)_6]$ mass. Zero marks if deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.2 The titration reaction:

$Ce^{4+} + [Fe(CN)_6]^{4-} = Ce^{3+} + [Fe(CN)_6]^{3-}$

$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$

2.3 Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $K_4[Fe(CN)_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3. Linear scale is applied in between.

2.4 Solutions: b), b), a)

2.5 Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc : hexacyanoferrate(II) in the precipitate can be evaluated as:

$$\frac{n(\text{Zn})}{n(\text{Fe(CN)}_6)} = \frac{10\, c(\text{Zn})\, V_2\, M}{m}$$

Values for c(Zn) are distributed according to a certain plan.

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $K_2Zn_3[Fe(CN)_6]_2$.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($H_2Zn_3[Fe(CN)_6]_2$ or $KHZn_3[Fe(CN)_6]_2$) is also acceptable.

PROBLEM 3 (Practical)

Caution:

Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.

The heat gun heats the expelled air up to 500 ℃. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+, NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Ba^{2+}, Pb^{2+}, Bi^{3+}

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, HSO_4^-, S^{2-}, HS^-, Cl^-, ClO_4^-, MnO_4^-, Br^-, I^-

You have test tubes and heating at your disposal but no additional reagents apart from distilled water and *pH* paper.

Identify the compounds in the solutions **1**-**8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks: The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

SOLUTION

The solutions received by the students contain the following compounds in eight test-tubes: $AgNO_3$, BaI_2, $KHCO_3$, $MgSO_4$, NaHS, NaOH, NH_4ClO_4, $Pb(CH_3COO^-)_2$ ($Pb(OAc)_2$). There were eight sets of samples differing in order of the compounds in particular test tubes.

The problem can be approached in many ways. A systematic solution is given here for one of the sets of test tubes with the following order of the compounds:

Test tube No	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Compound	$AgNO_3$	$KHCO_3$	NH_4ClO_4	NaOH	NaHS	$Pb(OAc)_2$	BaI_2	$MgSO_4$

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (*pH* paper reading about 5-6). Solution **2** is basic (*pH* = 9) while solutions **4** and **5** are very strongly basic (*pH* > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and MnO_4^-. (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Bi^{3+}, and HSO_4^- with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Ba^{2+}, Pb^{2+}.

Anions: OH^-, CO_3^{2-}, HCO_3^-, CH_3COO^-, $C_2O_4^{2-}$, NO_2^-, NO_3^-, F^-, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, SO_4^{2-}, S^{2-}, HS^-, Cl^-, ClO_4^-, Br^-, I^-.

The unknown solutions react with each other as follows (↓ = precipitate; ↑ = volatile product; “no change” means even when boiled, unless indicated otherwise):

	1 $AgNO_3$	**2** $KHCO_3$	**3** NH_4ClO_4	**4** $NaOH$	**5** $NaHS$	**6** $Pb(OAc)_2$	**7** BaI_2	**8** $MgSO_4$
1 $AgNO_3$	—	—	—	—	—	—	—	—
2 $KHCO_3$	↓ light yellow ↑ neutral, odourles	—	—	—	—	—	—	—
3 NH_4ClO_4	no change	↓ white crystals (*)	—	—	—	—	—	—
4 $NaOH$	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 $NaHS$	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH_3, H_2S	no change	—	—	—	—
6 $Pb(OAc)_2$	↓ white crystals	↓ white ↑ neutral, odourles	no change	↓ white	↓ black	—	—	—
7 BaI_2	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 $MgSO_4$	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH_3 is detectable by its odour and by *pH* paper.

(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H_2S appears.

$2\ Ag^+ + 2\ HCO_3^- = Ag_2CO_3 + CO_2 + H_2O$

$Pb^{2+} + 2\ HCO_3^- = PbCO_3 + CO_2 + H_2O$

$Ba^{2+} + 2\ HCO_3^- = BaCO_3 + CO_2 + H_2O$

$Mg^{2+} + 2\ HCO_3^- = MgCO_3 + CO_2 + H_2O$ (more accurately, basic carbonates of variable composition are formed)

$Ag^+ + I^- = AgI$; $2\ Ag^+ + SO_4^{2-} = Ag_2SO_4$; $Ag^+ + CH_3COO^- = CH_3COOAg$

$Pb^{2+} + 2\ OH^- = Pb(OH)_2$; $Pb^{2+} + 2\ I^- = PbI_2$; $Pb^{2+} + SO_4^{2-} = PbSO_4$

$K^+ + ClO_4^- = KClO_4$; $Ba^{2+} + SO_4^{2-} = BaSO_4$; $Mg^{2+} + 2\ OH^- = Mg(OH)_2$

$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$

$2\ Ag^+ + HS^- = Ag_2S + H^+$; $Pb^{2+} + HS^- = PbS + H^+$; $CH_3COO^- + H^+ = CH_3COOH$

$NH_4^+ + OH^- = NH_3 + H_2O$

$NH_4^+ + HCO_3^- = NH_3 + CO_2 + H_2O$

Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2. Thus **2** contains CO_3^{2-} or HCO_3^-.

Second, there are only 3 dark precipitates that can be formed from the given ions: Ag_2O, Ag_2S, and PbS. This fact, together with the *pH* of the solutions, instantly identifies the cation of **1** as $\mathbf{Ag^+}$, the cation of **6** as $\mathbf{Pb^{2+}}$, the anion of **4** as $\mathbf{OH^-}$, and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the *pH* of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is $\mathbf{HS^-}$.

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as $\mathbf{HCO_3^-}$. (in accord with the moderately basic *pH*)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is $\mathbf{NH_4^+}$.

2+**4** form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+.

2+**5** do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+. Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+. Thus the anion of **3** is $\mathbf{ClO_4^-}$ and the cation of **2** is $\mathbf{K^+}$. **4** does not give a precipitate with NH_4ClO_4. The cation of **4** is $\mathbf{Na^+}$.

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of $KHCO_3$ and NaOH (Li^+). The cation of **5** is **Na^+**.

7 forms no precipitate or ammonia with NaOH but gives a precipitate with $KHCO_3$. **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is **Ba^{2+}** and the anion of **7** is **I^-**.

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and $H_2PO_4^-$ are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+. This excludes both HCO_3^- and $H_2PO_4^-$. Thus the anion of **8** is **SO_4^{2-}**. This instantly identifies the cation of **8** as **Mg^{2+}**.

6 is a soluble compound of lead. The anion could be CH_3COO^-, NO_2^-, NO_3^-, or ClO_4^-. The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+. It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is **CH_3COO^-**.

Soluble salts of silver are even less numerous, the only choices are NO_3^-, F^-, and ClO_4^-. The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH. The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^-. The solubility of $KClO_4$ is quite significant;
therefore the absence of a precipitate with $KHCO_3$ is inconclusive. The anion of **1** is therefore either **NO_3^-** or **ClO_4^-**.

QUANTITIES AND THEIR UNITS USED IN THIS PUBLICATION

SI Basic Units

Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol

Special names and symbols for certain derived SI Units

Force	F	Newton	N
Pressure	p	pascal	Pa
Energy	E	joule	J
Power	P	watt	W
Electric charge	Q	coulomb	C
Electric potential difference	U	volt	V
Electric resistance	R	ohm	Ω

Other derived SI Units used in chemistry

Area	S	square metre	m^2
Volume	V	cubic metre	m^3
Density	ρ	kilogram per cubic metre	kg m^{-3}
Concentration	c	mole per cubic metre	mol m^{-3} (mol dm^{-3})
Molar mass	M	kilogram per mole	kg mol^{-1} (g mol^{-1})

Some other quantities and constants

Relative atomic mass of an element	A_r
Relative molecular mass of a compound	M_r
Molar fraction	x
Mass fraction	w
Volume fraction	φ
Enthalpy	H
Entropy	S
Gibbs energy	G
Temperature in Celsius scale	℃

Elementary charge, e	$1.6021892 \times 10^{-19}$ C
Planck constant, h	6.626176×10^{-34} J s
Avogadro constant, A	6.022045×10^{23} mol^{-1}
Faraday constant, F	9.648456×10^{4} C mol^{-1}
Gas constant, R	8.31441 J mol^{-1} K^{-1}
Zero of Celsius scale, T_0	273.15 K (exactly)
Normal pressure, p_0	1.01325×10^{5} (exactly)
Standard molar volume of ideal gas, V_0	2.241383×10^{-2} m^3 mol^{-1}

Abbreviations and Mathematical symbols

ICHO	International Chemistry Olympiad
STP	Standard temperature and pressure (T_0, p_0)
M	molar, mol dm^{-3}
N	normal
≙	corresponds to
≈	approximately equal to
∼	proportional to
⇒	implies