32nd

ICHO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE THIRTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
2--11 JULY 2000, COPENHAGEN, DENMARK
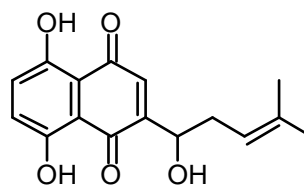
THEORETICAL PROBLEMS

PROBLEM 1

Synthesis of Compounds with Wound Healing Properties

Shikonin is a red compound found in the roots of the plant *Lithospermum erythrorhizon* which grows in Asia. Extracts of the root have been used for centuries in folk medicine and are used today in ointments for healing of wounds.
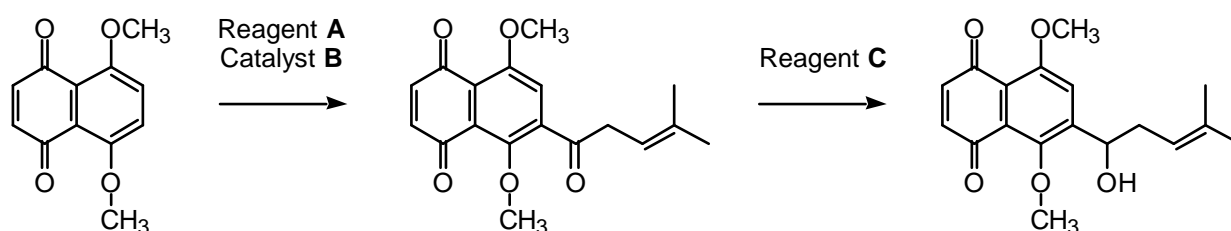

Shikonin

1.1 How many stereoisomers of Shikonin are possible ?

1.2 Do all stereoisomers of Shikonin have the same melting point? Mark with an X.

yes	no

The following sequence is part of a synthetic route to Shikonin:

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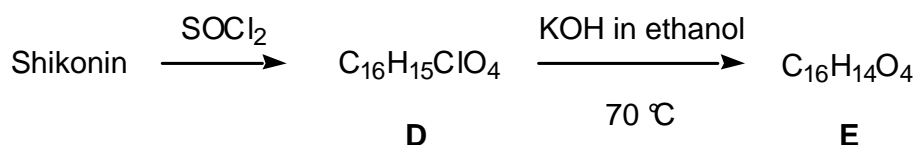ICHO International Information Centre, Bratislava, Slovakia

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1.3 Draw the structural formula of reagent **A**.

1.4 Indicate (by means of an X in the appropriate check-box) the correct IUPAC name for reagent **A**.

|	
2-Methyl-2-pentenoyl chloride	❑
1-Chloro-4-methyl-3-pentene	❑
4-Methyl-3-pentenoyl chloride	❑
4-Methyl-3-pentene-1-ol	❑
4,4-Dimethyl-3-butenoyl chloride	❑

1.5 Write the molecular formula of reagent **C**.

Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:

$$\text{Shikonin} \xrightarrow{\text{SOCl}_2} \underset{\textbf{D}}{C_{16}H_{15}ClO_4} \xrightarrow[70\,°C]{\text{KOH in ethanol}} \underset{\textbf{E}}{C_{16}H_{14}O_4}$$

1.6 Draw the structural formula of compound **E**.

1.7 How many stereoisomers of compound **E**, if any, are possible

Another route to useful Shikonin analogues is the following:
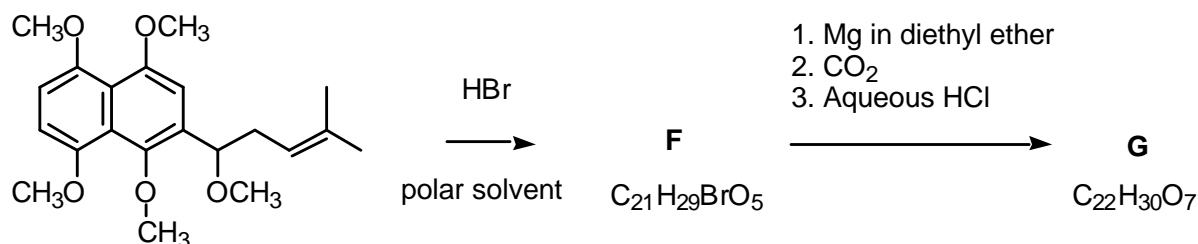
1.8 Draw the structural formula of compound **F**.

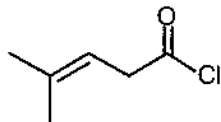**1.9** Draw the structural formula of compound **G**.

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SOLUTION

1.1 2 stereoisomers.

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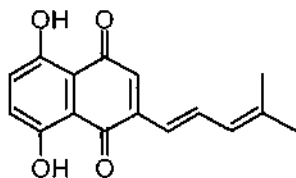**1.2** Stereoisomers of Shikonin have the same melting point.

1.3 The structural formula of reagent **A**:

1.4 The correct IUPAC name for reagent **A** is 4-Methyl-3-pentenoyl chloride.

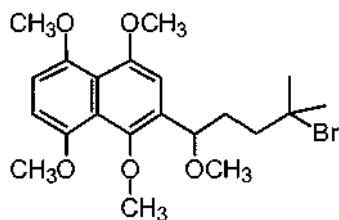**1.5** NaBH₄ (LiAlH4 will be acccepted)

1.6 The structural formula of compound **E**:

1.7 **2** stereoisomers

1.8 The structural formula of compound **F**:

1.9 The structural formula of compound **G**:

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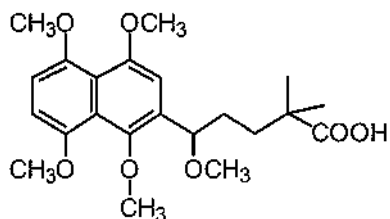
PROBLEM 2

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2\,H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot \frac{1}{2}\,H_2O$. Consider the following reaction:

$$CaSO_4 \cdot 2\,H_2O(s) \rightarrow CaSO_4 \cdot \frac{1}{2}\,H_2O(s) + 1\frac{1}{2}\,H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

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Compound	$\Delta_f H$ (kJ mol^{-1})	S (J K^{-1} mol^{-1})
CaSO$_4$ ·2 H$_2$O(s)	−2021.0	194.0
CaSO$_4$ · ½ H$_2$O(s)	−1575.0	130.5
H$_2$O(g)	−241.8	188.6

Gas constant: R = 8.314 J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}
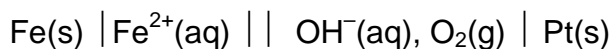
0 °C = 273.15 K.

2.1   Calculate ΔH (in kJ) for transformation of 1.00 kg of CaSO$_4$ · 2 H$_2$O(s) to hemihydrate CaSO$_4$. ½ H$_2$O(s). Is this reaction endothermic or is it exothermic?

2.2   Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing CaSO$_4$ · 2 H$_2$O(s), CaSO$_4$ · ½ H$_2$O(s) and H$_2$O(g) at 25 °C.

2.3   Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH and ΔS are temperature independent.

 Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

(1)   Fe(s) $\rightarrow$ Fe^{2+}(aq) + 2 e$^-$

(2)   O$_2$(g) + 2 H$_2$O(l) + 4 e$^-$ $\rightarrow$ 4 OH$^-$(aq)
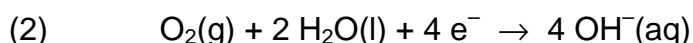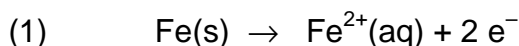
An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 ºC. The cell is represented by the following cell diagram:

Fe(s) $|$Fe^{2+}(aq) $||$ OH$^-$(aq), O$_2$(g) $|$ Pt(s)

Standard electrode potentials (at 25 ºC):

Fe^{2+}(aq) + 2 e$^-$ $\rightarrow$ Fe(s) E = − 0.44 V

O$_2$(g) + 2 H$_2$O(l) + 4 e$^-$ $\rightarrow$ 4 OH$^-$(aq) E = 0.40 V

Nernst factor: RT ln10 / F = 0.05916 volt (at 25 ºC)

Faraday constant: F = 96485 C mol^{-1}

2.4   Calculate the standard electromotive force (the standard cell voltage), E, at 25 ºC.

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2.5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.

2.6 Calculate the equilibrium constant at 25 °C for th e overall cell reaction.

2.7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

2.8 Calculate E for the cell at 25 °C for the following conditions :
[Fe^{2+}] = 0.015 M, $pH_{\text{right-hand half-cell}}$ = 9.00, p(O$_2$) = 0.700 bar.

_____

SOLUTION

2.1 ΔH^0 = −1575.0 kJ mol^{-1} + 1.5× (−241.8) kJ mol^{-1} − (−2021.0 kJ mol^{-1}) = 83.3 kJ mol^{-1}

$n = m / M$ = 1000g / 172.18 g mol^{-1} = 5.808 mol

ΔH^0 = 484 kJ

The reaction is endothermic.

2.2 ΔS^0 = 130.5 J K^{-1} mol^{-1} + 3/2 $\times$ 188.6 J K^{-1} mol^{-1} − 194.0 J K^{-1} mol^{-1}

$\qquad$ = 219.4 J K^{-1} mol^{-1}

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ = 17886 J mol^{-1}

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

$K = (p(\text{H}_2\text{O}))^{3/2}$ = 7.35 $\times$ 10^{-4} (pressure in bar)

p(H$_2$O) = 8.15 $\times$ 10^{-3} bar

2.3 p(H$_2$O) = 1.00 bar implies K = 1.00 and $\Delta G^0 = - RT \ln K$ = 0

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

0 = 83300 J K^{-1} − T 219.4 J K^{-1} mol^{-1}

T = 380 K or 107 °C

2.4 E^0(cell) = E^0(right) − E^0(left) = 0.40 V − (− 0.44 V) = 0.84 V

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2.5 Oxidation takes place at the negative, left half-cell.

Left half: $2\ Fe \rightarrow 2\ Fe^{2+} + 4\ e^-$ (multiplied by 2)

Right half: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Overall: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ OH^-$
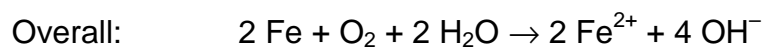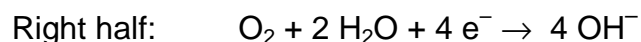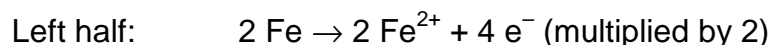
2.6 $K = [Fe^{2+}]^2\ [OH^-]^4 / p(O_2)$ (conc. in M and pressure in bar)

$\Delta G = -\ n\ F\ E$ (cell) $= -\ RT\ \ln K$

$K = 6.2 \times 10^{56}$

2.7 $Q = I\ t = 0.12\ A \times 24 \times 60 \times 60\ s = 10\ 368\ C$

$n(e^-) = Q\ /\ F = 10\ 368\ C\ /\ 96485\ C\ mol^{-1} = 0.1075\ mol$

$m(Fe) = n(Fe)\ M(Fe) = 1/2 \times 0.1075\ mol \times 55.85\ g\ mol^{-1} = 3.0\ g$

2.8 $E(\text{cell}) = E^0(\text{cell}) - \dfrac{0.05916\ V}{n} \log \dfrac{[Fe^{2+}]^2\ [OH^-]^4}{p(O_2)}$

$pH = 9.00$ implies $[H^+] = 1 \times 10^{-9}$ and $[OH^-] = 1 \times 10^{-5}$

$E(\text{cell}) = 0.84\ V - \dfrac{0.05916\ V}{4} \log \dfrac{0.015^2\ [1 \times 10^{-5}]^4}{0.700} = 1.19\ V$

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PROBLEM 3

Bioinorganic Chemistry

The square planar complex *cis*-diammine dichloroplatinum(II) is an important drug for the treatment of certain cancers.

3.1 Draw the structures of *cis*- and *trans*-diammine dichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds also have the empirical formula $Pt(NH_3)_2Cl_2$.

3.2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has
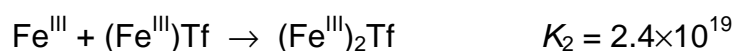
1) empirical formula $Pt(NH_3)_2Cl_2$,

2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,

3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound

3.3 How many *5d* electrons are there in the platinum(II) ion?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3.4 Which of the five *5d* orbitals attain the highest energy (*i. e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 °C corresponding to the react ions:

$Fe^{III} + Tf \rightarrow (Fe^{III})Tf$　　　　　$K_1 = 4.7 \times 10^{20}$

$Fe^{III} + (Fe^{III})Tf \rightarrow (Fe^{III})_2Tf$　　　　$K_2 = 2.4 \times 10^{19}$

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In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III} . Tf\}$ and $\{Tf . Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant

$K = [\{Tf . Fe^{III} \}] [\{Fe^{III} . Tf \}]^{-1} = 5.9$.

3.5 Calculate the values of the two constants $K_1' = [\{Fe^{III} . Tf\}] [Fe^{III}]^{-1} [Tf]^{-1}$ and $K_1'' = [\{Tf . Fe^{III} \}] [Fe^{III}]^{-1} [Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

**3.6** Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Fe^{III} . Tf \}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Tf . Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms.

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

_____

SOLUTION

3.1 The structures of *cis*- and *trans*-diammine dichloroplatinum(II)
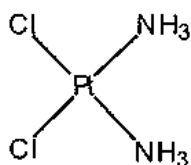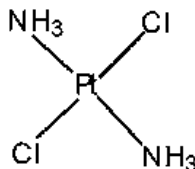
cis	*trans*

3.2 [Pt(NH₃)₄] [PtCl₄]

$[Pt(NH_3)_4] [PtCl_4]$

$[Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

$[Pt(NH_3)_3Cl]_2 [PtCl_4]$

$[Pt(NH_3)_4] [Pt(NH_3)Cl_3]_2$

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3.3 Eight *d*-electrons.

3.4 Orbital $5\,d_{x^2-y^2}$. In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

3.5 The concentration of monoferric forms of transferrin is

$[(Fe^m)Tf = [\{Fe^m\text{-}Tf\}] + [\{Tf\text{-}Fe^{III}\}]$
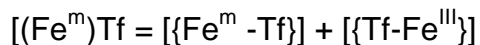
$K_1^{'} + K_1^{"} = K_1 \qquad K_1^{'} K = K_1^{"}$

$K_1^{'} = \dfrac{K_1}{1+K} = \dfrac{4.7 \times 10^{20}}{1+5.9} = 6.8 \times 10^{19}$

$K_1^{"} = K_1 - K_1^{'} = (4.7 - 0.68) \times 10^{20} = 4.0 \times 10^{20}$

3.6 $K_1^{'} K_2^{'} = K_1^{"} K_2^{"} = K_1 K_2$

$K_1^{'} = \dfrac{K_1 K_2}{K_1^{'}} = \dfrac{4.7 \times 10^{20} \times 2.19 \times 10^{19}}{6.8 \times 10^{19}} = 1.7 \times 10^{20}$

$K_1^{"} K_2^{"} = K_1 K_2$

$K_2^{"} = \dfrac{K_1 K_2}{K_1^{"}} = \dfrac{4.7 \times 10^{20} \times 2.4 \times 10^{19}}{4.0 \times 10^{20}} = 2.8 \times 10^{19}$

3.7 $(= 2\ (CO_3^{2-}) + 1\ (Asp(O^-)) + 2\ (2 \times Tyr(O^-))$

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PROBLEM 4

A Naturally Occurring Compound

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %,   H: 5.3%,   O: 31.5%.

4.1 Derive the empirical formula of compound **A**.
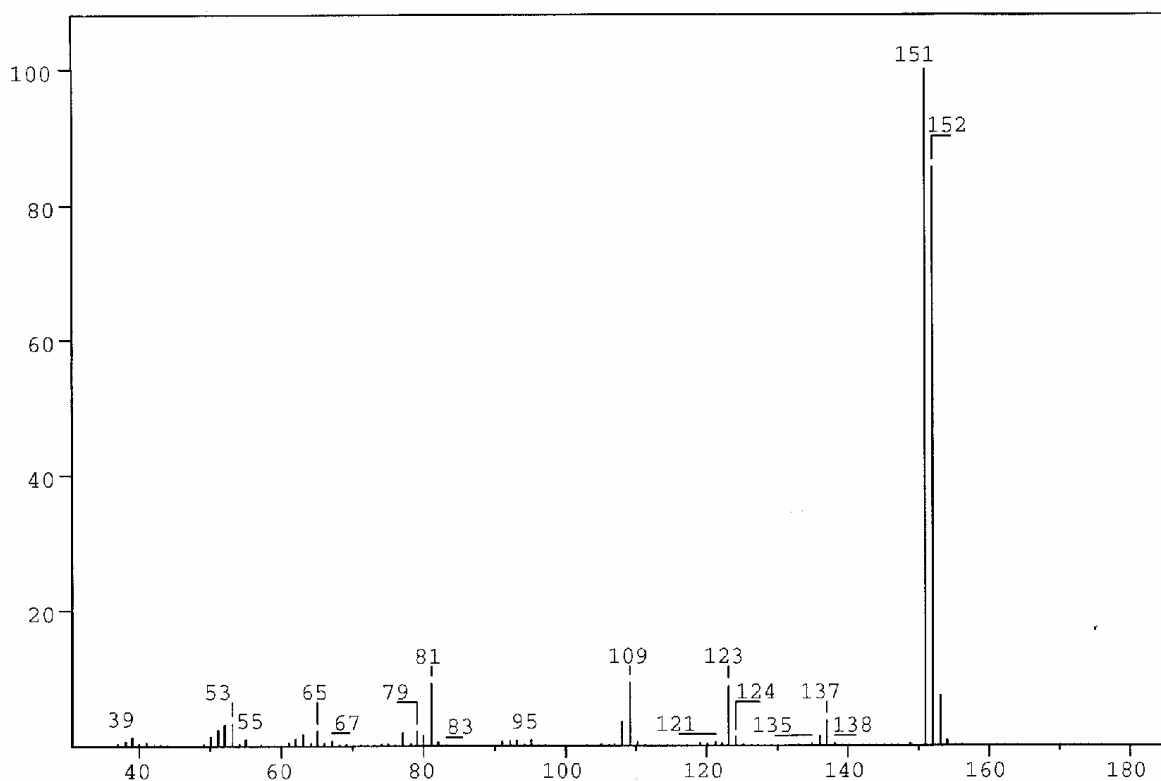
Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4.2 What is the molecular formula for compound **A**?

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase. Another solution of **A** in ether is shaken with an aqueous solution of NaHCO$_3$. **A** remains in the ether phase.

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4.3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

alcohol ❑   phenol ❑   aldehyde ❑   ketone ❑

acid   ❑   ester   ❑   ether   ❑

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($Ag(NH_3)_2^+$).

4-1 Which of the following functional groups does this indicate the presence of in **A**? Mark with an X.

hydroxy group of an alcohol   ❑   hydroxy group of a phenol   ❑

carbonyl group of an aldehyde   ❑   carbonyl group of a ketone   ❑

carboxylic group   ❑   ester group   ❑

alkoxy group of an ether   ❑


```
Table of Integrals
     FROM            TO          VALUE
   10.00 PPM      9.69 PPM       0.94
    7.56 PPM      7.32 PPM       1.91
    7.15 PPM      6.92 PPM       0.93
    6.41 PPM      6.20 PPM       0.94
    4.02 PPM      3.89 PPM       3.10
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Figure 2a

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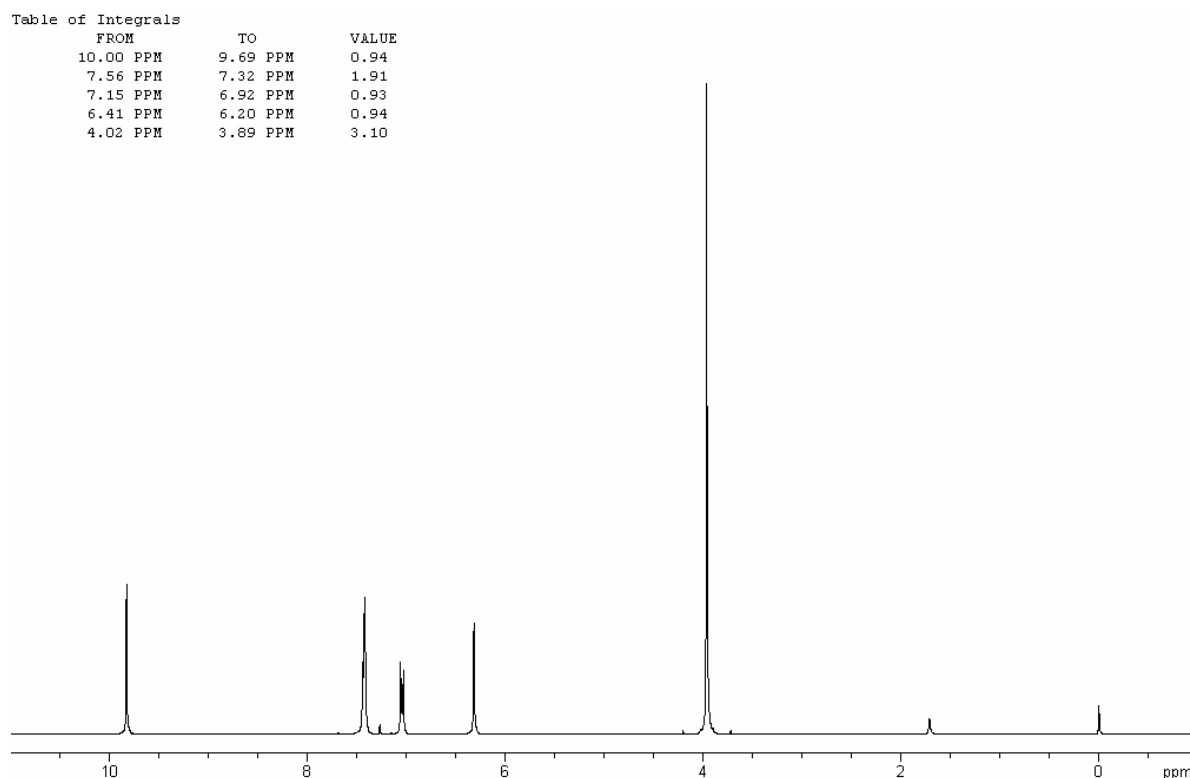
The ^{1}H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent $CDCl_3$ (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 – 7.6 ppm.
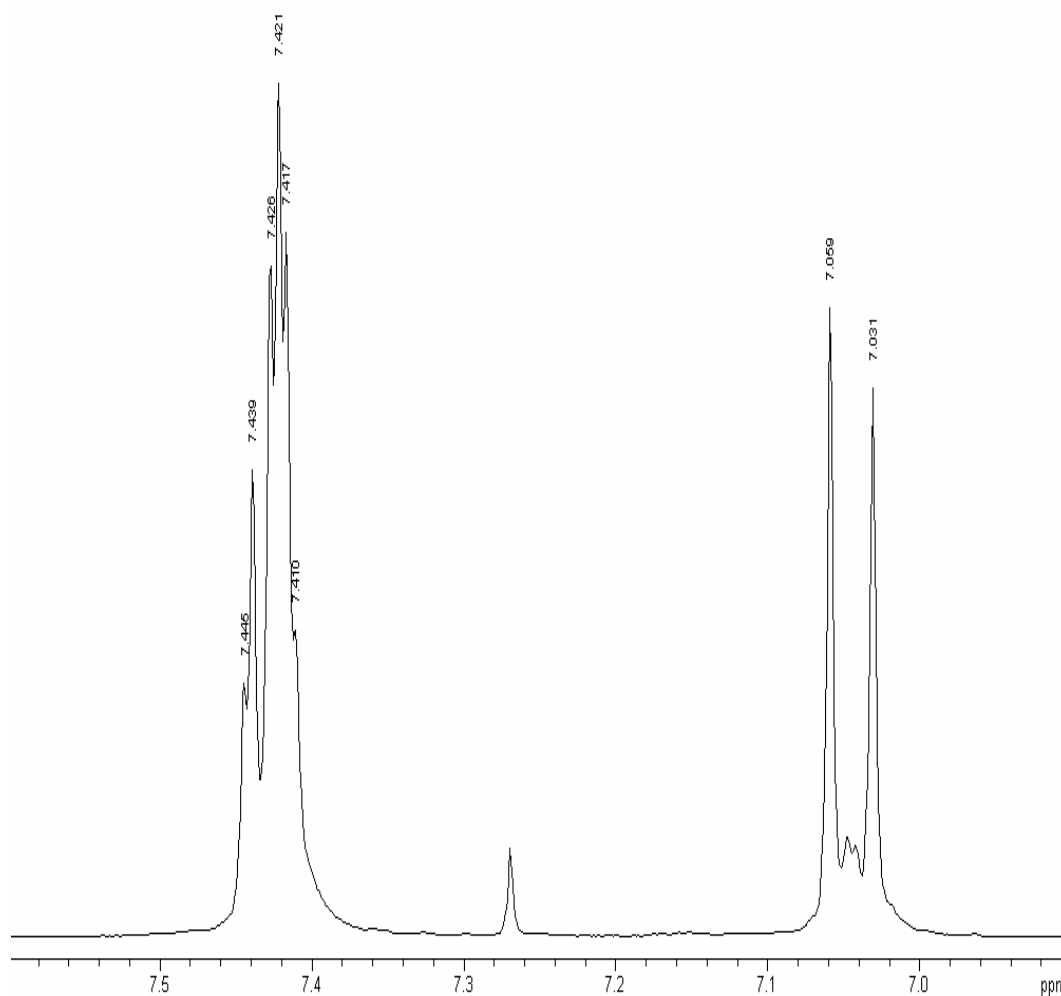

Figure 2b

Selected chemical shift and coupling constant values are given in Table 1.

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4.5   Which of the following does this indicate? Mark with an X.

Exchange of carbon-bonded hydrogen ❑

Exchange of oxygen-bonded hydrogen ❑

Dilution effect ❑

Hydrolysis ❑

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The same signal moves to a lower ppm value upon dilution with $CDCl_3$.

4.6 Which of the following does this indicate?

Indicate the true statements (more than one).

Increased hydrogen bonding ❑

Decrease in hydrogen bonding ❑

Intermolecular hydrogen bonding ❑

Intramolecular hydrogen bonding ❑

No hydrogen bonding ❑

4.7 Draw the four possible structural formulas for compound **A** based on the information given above

4.8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.

4.9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.
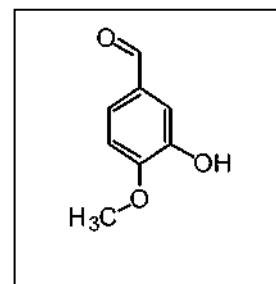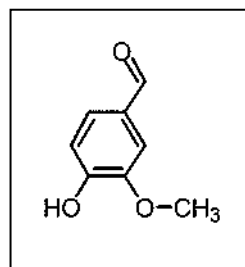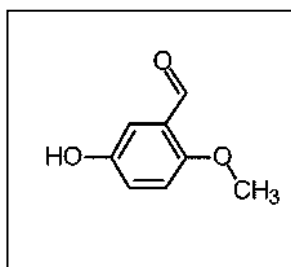
Table 1. ^{1}H Chemical Shift δ

Hydrogens attached to carbon		
Methyl	CH_3-C- $CH_3-C=O-$ CH_3-O-R CH_3-OCOR	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
Methylene	CH_2-C- $CH_2-C=O-$ CH_2-OR CH_2-OCOR	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
Methine	$CH-$	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
Alkene		4.0 – 7.3 ppm depending on the substituent
Aldehyde	$R-CHO$	9.0 – 10.0 ppm

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Table 1 (continued) ^{1}H Chemical Shift δ

Hydrogens attached to oxygen		
Alcohols	ROH	0.5 – 5.0 ppm
Phenols	ArOH	4.0 – 7.0 ppm
Carboxylic acids	RCOOH	10.0 – 13.0 ppm
Selected spin-spin coupling constants		
Alkanes (free notation)	H-C-C-H vicinal	6 – 8 Hz
Alkenes	trans cis geminal	11 – 18 Hz 6 – 12 Hz 0 – 3 Hz
Aromates	ortho meta para	6 – 10 Hz 1 – 4 Hz 0 – 2 Hz

_____

SOLUTION

4.1   The empirical formula of **A** is $C_8H_8O_3$.

4.2   The molecular formula of compound A: $C_8H_8O_3$.

4.3   The compound **A** is a phenol.

4.4   Compound **A** forms a mirror with Tollen's reagent. This indicates the presence of carbonyl group of an aldehyde.

4.5   It indicates exchange of oxygen-bonded hydrogen.

4.6   It indicates:

decrease in hydrogen bonding,

intermolecular hydrogen bonding.

4.7   Four possible structural formulas for compound **A**:

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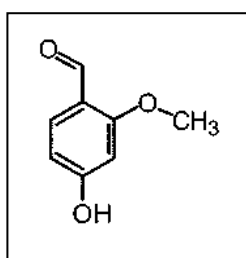
4.8 Formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum: CH_3,   HC=O.

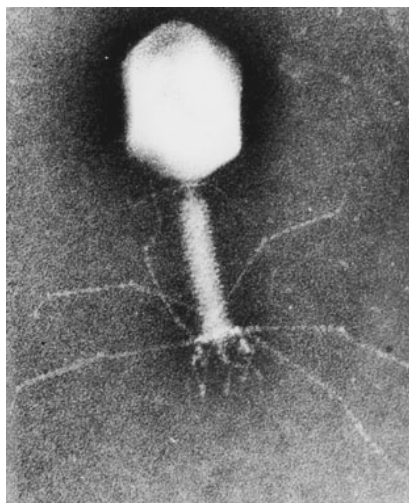**4.9** Two isomers having a lower pK_a value than the others:

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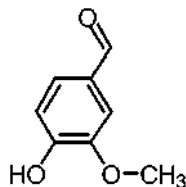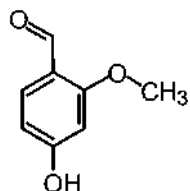
PROBLEM 5

Protein and DNA

DNA is composed of 2'-deoxy-nucleotides carrying the bases adenine (A), guanine (G), cytosine (C) and thymine (T). The molar mass of the 2'-deoxy-nucleotide-5'-triphosphates is given in table 2:

Table 2

dNTP	Molar mass /g mol^{-1}
dATP	487
dGTP	503
dCTP	464
dTTP	478

5.1 Calculate the molar mass of a double stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat stable DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. Under optimal conditions the number of double-stranded DNA copies doubles in each cycle. Using the PCR method you perform 30 cycles starting from a single double stranded DNA molecule.

5.2 Calculate the approximate mass of the DNA you obtain from this experiment.

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The bacteria-virus T4 enzyme - polynucleotide kinase (PNK) catalyzes the transfer of the terminal phosphate of ATP (γ-orthophosphate) to the 5'-hydroxyl termini of ribo- and deoxyribonucleotides:
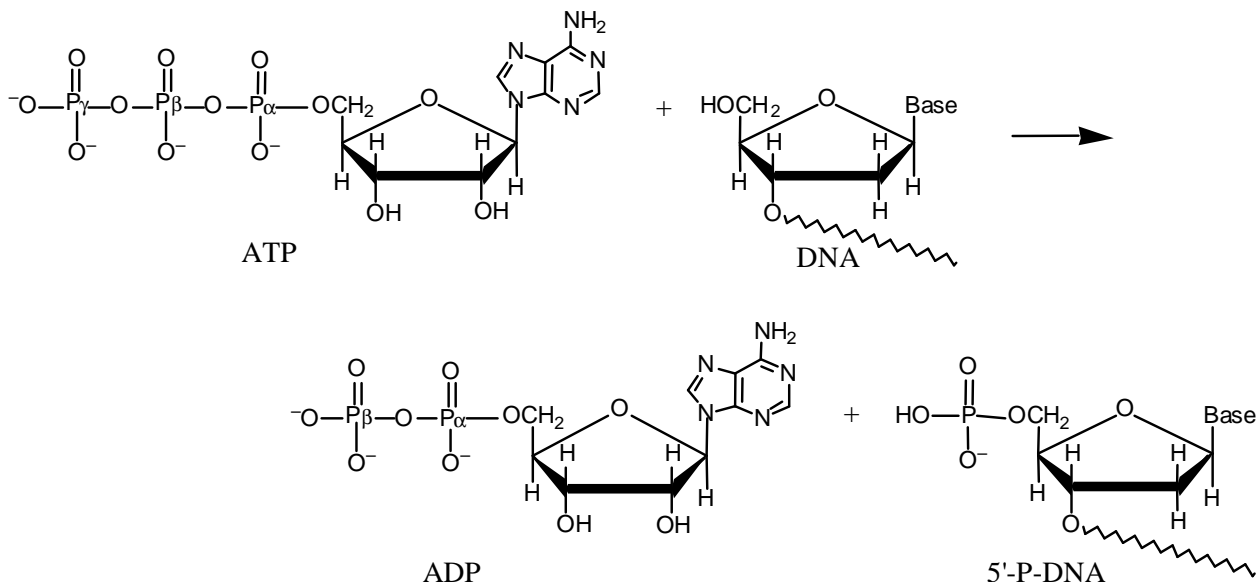
PNK is commonly used to label DNA at the 5'-end with the radioactive phosphorus isotope ^{32}P using ATP in which the γ-P (the outermost of the phosphorus atoms) is replaced with ^{32}P. The amount of ^{32}P and thus the amount of labelled DNA can be measured.

A 10 µL solution containing double stranded DNA is labelled 100 % with [γ-^{32}P]ATP by PNK. 37 days ago, the specific activity of [γ-^{32}P]ATP was 10 Ci/mmol or 370 ·10^9 Bq/mmol. ^{32}P has a half-life of 14.2 days, and during the decay a β-particle is emitted. Now the labelled DNA emits 40000 β-particles/s.

5-3 Calculate the concentration of the DNA solution.

In an experiment in which PNK is incubated with [γ-^{32}P]ATP and single stranded DNA, the reaction can be monitored by isolating labeled DNA and measuring the β-particle emission. Using this kind of measurements in a 1 cm^3 experimental mixture, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant (turnover number) of 0.05 s^{-1} and molar mass of 34620 g mol^{-1}.

5.4 Calculate the concentration (in mg/cm3) of PNK in the experimental mixture.

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Aromatic amino acids, tryptophan, tyrosine and phenylalanine absorb UV light of a wavelength between 240 nm and 300 nm. In a protein containing several aromatic amino acids, the sum of the molar absorptivity per amino acid $\Sigma\varepsilon_{amino\ acid}$, is approximately equal to the molar absorptivity, $\varepsilon_{protein}$, for the protein. The molar absorptivity, $\varepsilon_{amino\ acid}$, at 280 nm for tyrosine, tryptophan and phenylalanine is 1400 M^{-1} cm^{-1}, 5600 M^{-1} cm^{-1} and 5 M^{-1} cm^{-1}, respectively. The absorbance of a 10 µM solution of PNK is 0.644 at 280 nm and with 1.00 cm light path. The amino acid sequence of PNK contains 14 tyrosines and 9 phenylalanines.

(M = mol dm^{-3})

5.5 Calculate the number of tryptophan residues in a PNK molecule.

_____

SOLUTION

5.1 Calculation of the molar mass of a double stranded DNA fragment under given conditions:

dNTP average mass = 483 g mol^{-1}; $M(HP_2O_7^{2-})$ = 175 g mol^{-1};

1000 bp double stranded DNA M(DNA) = $((483 - 175) \times 2 \times 1000 + 2 \times 17)$ g mol^{-1} = 616034 g mol^{-1}.

5.2 Calculation of the approximate mass of the DNA you obtaining from the described experiment.

2^{30} copies = 1073741824 copies

Total mass of DNA: m(DNA) = 1073741824 / N$_A$ $\times$ 616350 g mol^{-1} = 1.1 ng

5.3 Calculation of the concentration of the DNA solution.

$$A = A_0\,e^{-kt} \text{ and } k = \frac{\ln 2}{t_{1/2}} \implies A_0 = \frac{40000}{e^{-0.0488 \times 37}}\text{ dps} = 243464\text{ dps}$$

It corresponds to $\dfrac{243464}{370}$ pmol $5'-^{32}$ P-DNA = 658 pmol $5'-^{32}$ P-DNA .

Since volume of the labelled DNA is 10 µL, the concentration of the DNA is thus approx. 66 µM.

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5.4 Since 9 nmol DNA is labelled per min and the turnover number is 0.05 s^{-1} the amount of PNK that catalyses the labelling is:

$$\frac{9 \, \text{nmol}\,\text{min}^{-1}}{0.05 \times 60 \, s} = 3 \, \text{nmol}$$

which corresponds to 3 nmol $\times$ 34620 g mol^{-1} = 0.1 mg.

The concentration of the PNK in mg cm^{-3} is is thus 0.1 mg cm^{-3}-

5-5 $\varepsilon_{\text{Tryptophan}}$ = 5600 M^{-1} cm^{-1};

$\varepsilon_{\text{Tyrosine}}$ = 1400 M^{-1} cm^{-1};

$\varepsilon_{\text{Phenylalanine}}$ = 5 M^{-1} cm^{-1}

$$\varepsilon = \frac{A}{c \, l} \;\Rightarrow\; \varepsilon_{\text{PNK}} = \frac{0.644}{10 \, \mu\text{M} \times 1.00 \, \text{cm}} = 64400 \, \text{M}^{-1} \, \text{cm}^{-1}$$

$\Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}}) = (14 \times 1400) + (9 \times 5)$ M^{-1} cm^{-1} = 19645 M^{-1} cm^{-1}

$\Sigma\varepsilon_{\text{Tryptophan}} = \varepsilon_{\text{PNK}} - \Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}}) \;\Rightarrow$

$\Sigma\varepsilon_{\text{Tryptophan}} = (64400 - 19645)$ M^{-1} cm^{-1} = 44755 M^{-1} cm^{-1}

The number of tryptophan residues in a PNK molecule is thus:

$$\frac{44755 \, \text{M}^{-1} \, \text{cm}^{-1}}{5600 \, \text{M}^{-1} \, \text{cm}^{-1}} = 8 \, \text{residues}$$

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PROBLEM 6

Hard Water

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO_2, is a diprotic acid in aqueous solution. The pK_a-values at 0 ℃ are:

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^- (aq) + H^+(aq) \qquad pK_{a1} = 6.630$$

$$HCO_3^- (aq) \rightleftharpoons CO_3^{2-} (aq) + H^+(aq) \qquad pK_{a2} = 10.640$$
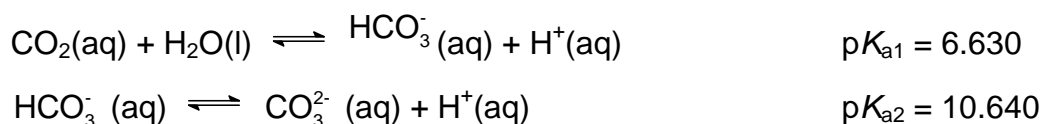
The liquid volume change associated with dissolution of CO_2 may be neglected for all of the following problems. The temperature is to be taken as being 0 ℃.

6.1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 mol dm^{-3}. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant $R = 8.314$ J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO_2 in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

6.5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 cm3 of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

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The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\ HCO_3^-(aq)$$
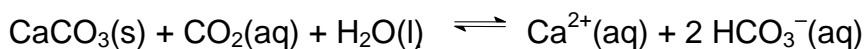
The equilibrium constant, K, for this reaction is $10^{-4.25}$ at 0 °C.

6.6 Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.

6.7 A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6.6.

6.8 The calcium hydroxide solution referred to in problem 6.7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2.

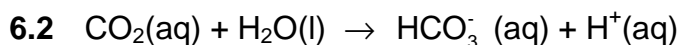**6.9** Calculate the solubility product constant for calcium carbonate from the data given above.

_____

SOLUTION

6.1 $c(CO_2) = 0.0752$ M $n(CO_2) = 0.0752$ mol

The ideal gas equation: $p\,V = n\,R\,T$

1.00 bar $\times\ V = 0.0752$ mol $\times\ 0.08314$ dm^3 bar mol^{-1} K$^{-1} \times 273.15$ K

$V = 1.71$ dm^3

6.2 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-\ (aq) + H^+(aq)$

$[H^+] = [HCO_3^-] = x$ and $[CO_2] + [HCO_3^-] = 0.0752$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x^2}{0.0752 - x}$$

$[H^+] = 0.000133$ and $[CO_2] = 0.0751$

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6.3 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$
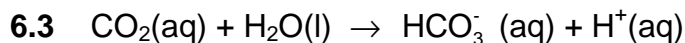
$[CO_2] = 0.0751$ and $[HCO_3^-] = 0.0100$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \ 0.0100}{0.0751}$$

$\underline{x = [H^+] = 1.76 \times 10^{-6}}$

6.4 $CO_2(aq) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2 \ HCO_3^-(aq)$ $[HCO_3^-] = 0.0200$

$CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$
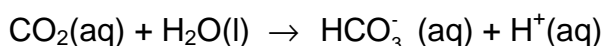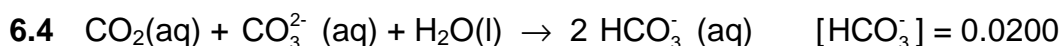
$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \ 0.0200}{0.0751}$$
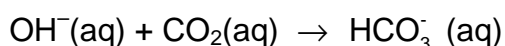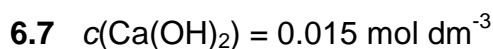
$x = [H^+] = 8.8 \times 10^{-7}$

6.5 $0.0012 \ g \ CaCO_3$ in $100 \ cm^3$ of water
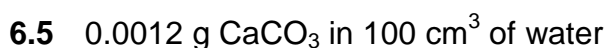
$0.0012 \ g \ /100 \times 0872 \ g \ mol^{-1} = 0.000012 \ mol \ CaCO_3$ in $100 \ cm^3$ of water

$[Ca^{2+}] = 1.2 \times 10^{-4}$ $c(Ca^{2+}) = 1.2 \times 10^{-4} \ mol \ dm^{-3}$

6.6 $K = \dfrac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = 10^{-4.25}$ and $2 \ [Ca^{2+}] = [HCO_3^-]$

$\dfrac{4 \ [Ca^{2+}]}{0.0751} = 10^{-4.25}$ $[Ca^{2+}] = 1.02 \times 10^{-2}$ $c(Ca^{2+}) = 1.02 \times 10^{-2} \ mol \ dm^{-3}$

6.7 $c(Ca(OH)_2) = 0.015 \ mol \ dm^{-3}$

$OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

All hydroxide has been consumed $(K = 10^{7.37})$.

From problem 6.6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of $CaCO_3$

$[Ca^{2+}] = 1.02 \times 10^{-2}$ $c(Ca^{2+}) = 1.02 \times 10^{-2} \ mol \ dm^{-3}$

6.8 $c(Ca(OH)_2) = 0.0075 \ mol \ dm^{-3}$
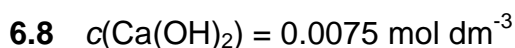
From problem 6.6 we found that the maximum possible calcium ion concentration we can have, is $1.02 \times 10^{-2} \ mol \ dm^{-3}$, *i.e.* no precipitation of $CaCO_3$ occurs.

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$[Ca^{2+}] = 0.75 \times 10^{-2}$ $c(Ca^{2+}) = 0.75 \times 10^{-2}$ mol dm^{-3}

6.9

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} \times \frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}][H^+]} = \frac{K_{sp}\,K_{a1}}{K_{a2}}$$

$$K_{sp} = 10^{-8.26}$$

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PRACTICAL PROBLEMS
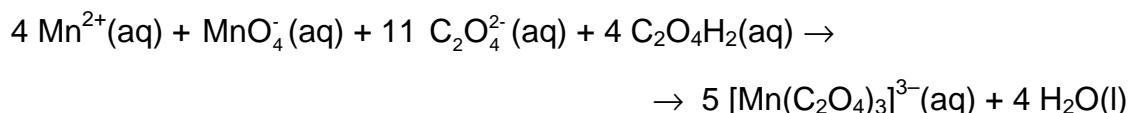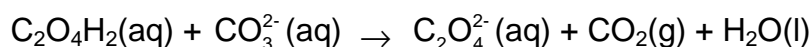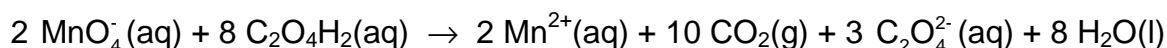
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PROBLEM 1 (Practical)

This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a "classic" within inorganic photo chemistry.

Preparation of Potassium tris(oxalato)manganate(III) Hydrate, $K_3[Mn(C_2O_4)_3] \cdot x H_2O$

Note 1: The $[Mn(C_2O_4)_3]^{3-}$ ion is photosensitive and should therefore be protected from light as far as possible. Also, the thermal stability of the title compound is low.

Note 2: Before starting the synthesis, write down the thermometer reading in ice-water.

The synthesis comprises a reduction of manganese(VII) to manganese(II) with oxalic acid at 70 – 75 °C. After the addition of the suffi cient amount of potassium ions in form of potassium carbonate, manganese(III) is formed by the addition of manganese(VII) at a temperature below 2 °C.

$2\ MnO_4^-(aq) + 8\ C_2O_4H_2(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 3\ C_2O_4^{2-}(aq) + 8\ H_2O(l)$

$C_2O_4H_2(aq) + CO_3^{2-}(aq) \rightarrow C_2O_4^{2-}(aq) + CO_2(g) + H_2O(l)$

$4\ Mn^{2+}(aq) + MnO_4^-(aq) + 11\ C_2O_4^{2-}(aq) + 4\ C_2O_4H_2(aq) \rightarrow$

$$\rightarrow 5\ [Mn(C_2O_4)_3]^{3-}(aq) + 4\ H_2O(l)$$

Dissolve 5.00 g of $C_2O_4H_2 \cdot 2\ H_2O$ in 35 cm^3 of water in a 150 cm^3 beaker by heating to 70 °C. Slowly add 1.00 g of KMnO $_4$ with magnetic stirring. The temperature must not exceed 70 - 75 °C. When the mixture is colourless, add 1.10 g of K_2CO_3 in small portions and cool the mixture in ice. When the temperature of the mixture has fallen to 25 - 30 °C, add 25 g of crushed ice. Meanwhile, cool the hotplate with a beaker containing ice.

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Maintain the temperature of the reaction mixture not more than 2 ℃ above your reported temperature of ice-water while adding 0.24 g of KMnO$_4$ in small portions with vigorous stirring. Stir for another 10 min and filter off the white precipitate and unmelted ice, if any, using the 60 cm^3 filter syringe (see procedure A). Collect the filtrate in a 250 cm^3 beaker cooled in ice. Add 35 cm^3 of ice-cold ethanol to the cherry-red filtrate (just swirl the beaker; stirring will lead to the formation of tiny crystals), wrap the beaker in aluminium foil and cool it in ice for 2 h (swirl the beaker three or four times during this period).

Clean the filter - first with 4 ᴍ HCl, then with water. Collect the cherry-red crystals by filtration using a 60 cm^3 filter syringe, then wash them two times 5 cm3 of ethanol and then two times with 5 cm^3 of acetone, and dry the product in air and protect it from light for at least one hour. A brown vial with lid should be taken to be tared by the lab assistant. When dry, the product is placed in the vial. Write name and student code on the vial. Then close the vial and take it and your answer sheet to the lab. assistant who will weigh your sample. The theoretical yield is 7.6 mmol.
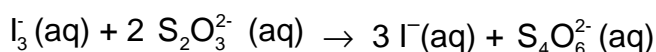
1.1 Record the yield in grams.

1.2 Suggest a molecular formula of the white precipitate which is removed in the first filtration.

_____

Analysis of the Provided Sample of K$_3$[Mn(C$_2$O$_4$)$_3$] · x H$_2$O for Oxidizing Ability

Note 3: The burette contains a cleanser and should therefore be rinsed 3 - 4 times with water before use.

Manganese(III) is reduced to manganese(II) by iodide ions and the triiodide ions formed are then titrated with thiosulfate.

$$2\,Mn^{III}(aq) + 3\,I^-(aq) \rightarrow 2\,Mn^{II}(aq) + I_3^-(aq)$$

$$I_3^-(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$
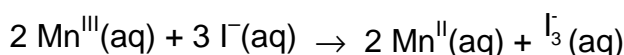
In a 250 cm^3 conical flask dissolve 1.0 g of KI in 25 cm^3 of demineralized water and add 10 cm^3 of 4 ᴍ HCl. Immediately after an accurately preweighed sample (approx. 200 mg) of the provided complex is transferred (as much as possible is poured directly into the

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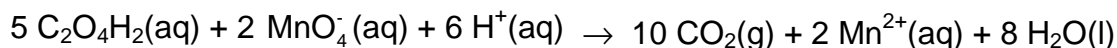liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I$_3^-$ formed with the standardized, approx. 0.025 **M** Na$_2$S$_2$O$_3$ solution. When the brown colour has faded to light yellow, add 2 cm^3 of starch indicator solution and continue the titration until the colour changes from blue to colourless.

1.3 Calculate the molar mass of the analyzed compound from the titration data.

_____

Analysis of the Provided Sample of K$_3$[Mn(C$_2$O$_4$)$_3$] · x H$_2$O for Reducing Ability

Note 4: The burette should be rinsed 2 - 3 times with water before this titration.

Manganese(III) is reduced to manganese(II) by the oxalate ligands, and excess oxalate is titrated with permanganate.

2 [Mn(C$_2$O$_4$)$_3$]$^{3-}$(aq) + 10 H$^+$(aq) $\rightarrow$ 2 Mn^{2+}(aq) + 2 CO$_2$(g) + 5 C$_2$O$_4$H$_2$(aq)

5 C$_2$O$_4$H$_2$(aq) + 2 MnO$_4^-$(aq) + 6 H$^+$(aq) $\rightarrow$ 10 CO$_2$(g) + 2 Mn^{2+}(aq) + 8 H$_2$O(l)

Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm^3 conical flask. Add 25 cm^3 of 2 **M** sulphuric acid and heat the solution to 75 – 80 ℃. Without further heating, titrate with the standardized, approx. 0.025 **M** KMnO$_4$ solution. Near the end of the titration add the titrant slowly, until one drop gives the solution a rose colour which does not fade on standing for 0.5 min.

1.4 Calculate the molar mass of the analyzed compound from the titration data.

The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with KMnO$_4$ for the following calculation.

1.5 Calculate the value of x in the formula K$_3$[Mn(C$_2$O$_4$)$_3$] · x H$_2$O and the yield of your preparation in percent of the theoretical yield.

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PROBLEM 2   (Practical)

Synthesis of Amino Acid Methyl Ester Hydrochloride

In the synthesis of peptides, one amino acid is reacted with another to form an amide bond between them. In order to ensure that the individual amino acids do not form amide bonds with themselves and that only one product is formed, the amino group in the first amino acid and the carboxyl group in the second amino acid are masked before the peptide synthesis.

The procedure described below can be used for masking the carboxylic acid groups in amino acids before peptide formation.
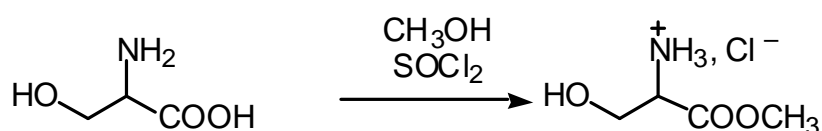
The experiment should be performed in a ventilated hood since thionyl chloride is an irritant and since irritating gases are evolved during the reaction.

Thionyl chloride is a corrosive acid chloride. Avoid contact with skin and eyes. Splashes in eyes or on skin should be flushed immediately with water. Thionyl chloride in larger amounts reacts violently with water.

Procedure

Absolute methanol (2.0 cm^3) is transferred quickly to a dry test tube which is then closed with a piece of aluminium foil. The foil is used as a lid throughout the subsequent manipulations with the tube. This protects the content from moisture from the air. The methanol is cooled in an ice-bath for 1 – 2 min. Thionyl chloride, handle with care, see above (0.52 cm^3) is drawn up into a 1 cm^3 graduated syringe with polyethylene tube tip, as described in separate procedure B, and is cautiously added to the methanol over a period of approximately 5 min.

The mixture is kept at 0 °C for approx. 2 min. (S)-Serine (0.210 g, weighed sample provided) is added and the mixture is kept at room temperature for approx. 2 min before gently heating to boiling (using a sand bath) for 10 min. All material should then have dissolved.

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The mixture is cooled in an ice-bath for approx. 2 min. Dry *tert.*-butyl methyl ether (10 cm^3) is then added. The inside wall of the test tube is scratched at the surface region of the solution with a glass spatula for about 1 min. and the test tube is then left in the ice-bath for a further 5 –15 min for crystallization. The separated crystals are then isolated by filtration as described in separate procedure A. The filtrate is collected in a 100 cm^3 beaker.

The crystals are washed two times on the filter, each time with 1 cm^3 of *tert.*-butyl methyl ether. The filter cake is finally pressed with the piston, and the crystals are pre-dried by pumping air through the filter cake with the piston.
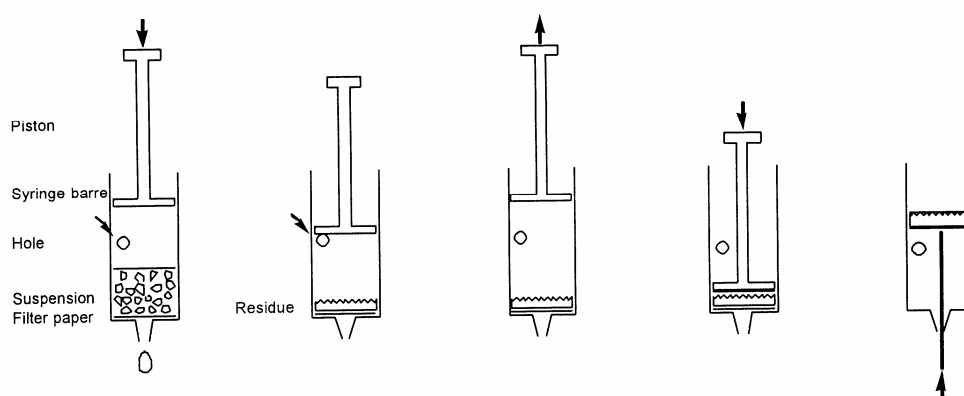
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm^3 syringe with a disc of porous polypropylene is used in task 1, while a 10 cm^3 syringe with a disc of filtration paper is used in task 2. The procedure is sketched on Fig. 1.

Fig. 1: Micro-scale filtration in plastic syringe

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Procedure:

1.   Fill the syringe from above with suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.

2.   Close hole and press piston for filtration.

3.   Stop before passing the hole.

4.   Open hole and draw piston back.

5.   Repeat steps 2-4 a couple of times.

6.   Remove piston and place filter paper on top of the filter cake.

7.   Press piston against filter cake.

8.   Push filter cake out with straightened- out paper clip.

Filtration procedure for practical problem 1

The provided filter syringe to be used in this experiment is made from a 60 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm^3 mark. With a plastic spatula a disc of porous polypropylene, which fits tightly inside the syringe, is pressed down to be positioned at the base of the syringe. The mixture to be filtered is applied without the piston inserted. Drops of solution may be moved downwards by tapping the syringe against a solid surface,

The piston is now placed in the syringe and gently pressed down while keeping the hole closed with a finger so to promote the passage of solvent through the filter. When the piston reaches just above the hole, the finger is removed from the hole, and the piston is drawn back again to the top position. This cycle can then be repeated a couple of times, until the filter cake looks dry. Remember to close the drilled hole, then the piston is moved downwards and to open the hole, when the piston is moved upwards. The filter cake can be washed and the washing solution pressed out using similar cycles.

Solvent remaining in the outlet can be sucked up with a small piece of tissue paper. The solid is then removed from the syringe and collected on a piece of weighing paper for drying.
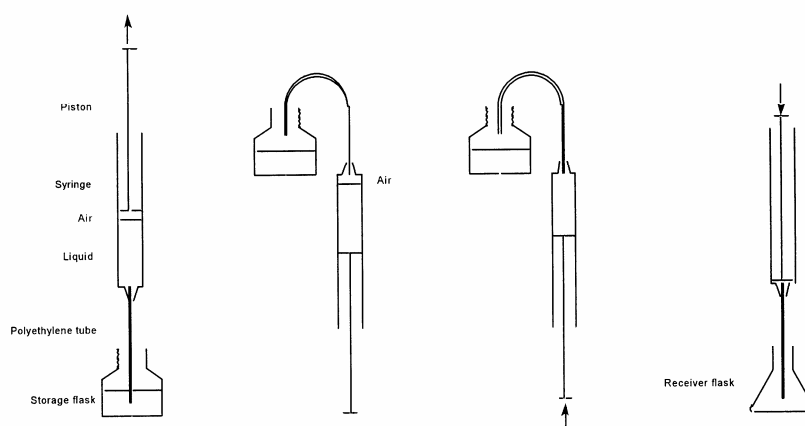
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Filtration procedure for practical problem 2

The provided filter syringe to be used in this experiment is made from a 10 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm^3 mark. A piece of filter paper which fits snugly in the syringe is pressed down to the bottom with the piston. Filtration and washing are then performed as described for task 1. Before removing the filter cake the piston is withdrawn. A piece of filter paper fitting the syringe is then pressed all the way down to the filter cake using the piston. The filter cake is pressed by means of the piston. Then the piston is then drawn back and out the syringe (slowly, until the hole is reached).

This leaves the filter cake between two pieces of filter paper. Solvent remaining in the outlet can be sucked up with a small piece of tissue paper.

The filter cake is cautiously pushed out of the syringe using an straightened-out metal paper clip introduced through the outlet of the syringe. The solid material is then removed from the syringe, if possible as a coherent plug. The residue is collected on a piece of filter paper for drying by using a small metal spatula. Filter paper from the filtration can be fixed with the paper clip tip while adhering solid is removed using the spatula.

PROCEDURE B

Fig. 2. Measuring volumes of liquids using a syringe

Procedure:

1. Suck up a slight excess of liquid in syringe.

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2. Turn syringe upside down; the tip of the tube is kept in the storage nottle. Air in the syringe is accumulated at its top.

3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.

4. Turn the syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.

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