

26th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE TWENTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 3--11 JULY 1994, OSLO, NORWAY

THEORETICAL PROBLEMS

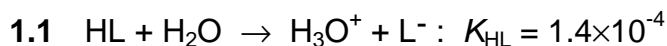
PROBLEM 1

Lactic acid is formed in the muscles during intense activity (anaerobic metabolism). In the blood, lactic acid is neutralized by reaction with hydrogen carbonate. This will be illustrated by the following calculations:

Lactic acid written as HL is monoprotic, and the acid dissociation constant is $K_{\text{HL}} = 1.4 \times 10^{-4}$.

The acid dissociation constants for carbonic acid are: $K_{\text{a1}} = 4.5 \times 10^{-7}$ and $K_{\text{a2}} = 4.7 \times 10^{-11}$. All carbon dioxide remains dissolved during the reactions.

- 1.1 Calculate pH in a 3.00×10^{-3} M solution of HL.
- 1.2 Calculate the value of the equilibrium constant for the reaction between lactic acid and hydrogen carbonate.
- 1.3 3.00×10^{-3} mol of lactic acid (HL) is added to 1.00 dm^3 of 0.024 M solution of NaHCO_3 (no change in volume, HL completely neutralized).
 - i) Calculate the value of pH in the solution of NaHCO_3 before HL is added.
 - ii) Calculate the value of pH in the solution after the addition of HL.
- 1.4 pH in the blood of a person changed from 7.40 to 7.00 due to lactic acid formed during physical activity. Let an aqueous solution having $pH = 7.40$ and $[\text{HCO}_3^-] = 0.022$ represent blood in the following calculation. How many moles of lactic acid have been added to 1.00 dm^3 of this solution when its pH has become 7.00?
- 1.5 In a saturated aqueous solution of $\text{CaCO}_3(\text{s})$ pH is measured to be 9.95. Calculate the solubility of calcium carbonate in water and show that the calculated value for the solubility product constant K_{sp} is 5×10^{-9} .
- 1.6 Blood contains calcium. Determine the maximum concentration of "free" calcium ions in the solution ($pH = 7.40$, $[\text{HCO}_3^-] = 0.022$) given in 1.4.

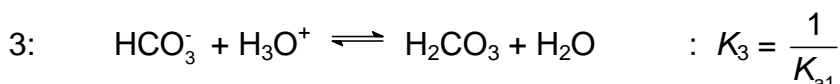
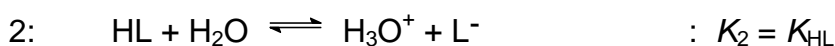
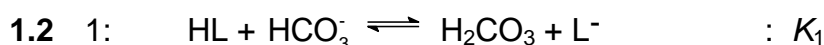
SOLUTION

$$c_0 - x \qquad \qquad x \qquad x$$

$$K_a = \frac{x^2}{c_0 - x} = 1.4 \times 10^{-4} \qquad c_0 = 3.00 \times 10^{-3}$$

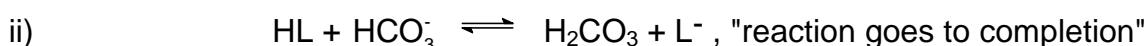
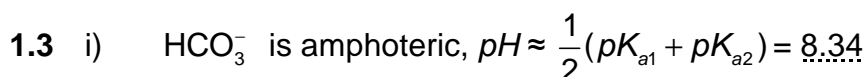
Assumption $c_0 \gg x$ gives $x = 6.5 \cdot 10^{-4}$, not valid

Quadratic formula: $x = 5.8 \times 10^{-4}$, $[\text{H}_3\text{O}^+] = 5.8 \times 10^{-4}$, $\text{pH} = 3.24$



Reaction 1 = 2 + 3, $K_1 = K_2 \cdot K_3 = 311 \quad (3.1 \times 10^2)$

$$\text{Alternative: } K_1 = \frac{[\text{H}_2\text{CO}_3][\text{L}^-]}{[\text{HL}][\text{HCO}_3^-]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]} \times \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}$$

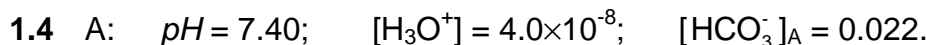


Before: 0.0030 0.024 0 0

After: 0 0.021 0.0030 0.0030

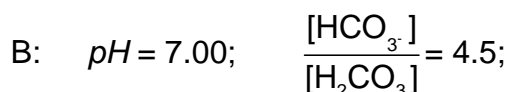
Buffer: $\text{pH} \approx \text{p}K_{a1} + \log \frac{0.021}{0.0030} = 6.35 + 0.85 = 7.20$

(Control: $\frac{K_{\text{HL}}}{[\text{H}_3\text{O}^+]} = \frac{[\text{L}^-]}{[\text{HL}]} = 2.2 \times 10^3$, assumption is valid)



From K_{a1} : $[\text{H}_2\text{CO}_3]_{\text{A}} = 0.0019$;

(1) $[\text{HCO}_3^-]_{\text{B}} + [\text{H}_2\text{CO}_3]_{\text{B}} = 0.0239 \quad (0.024)$



$$(2) \quad [\text{HCO}_3^-]_{\text{B}} = 4.5 [\text{H}_2\text{CO}_3]_{\text{B}}$$

$$\text{From (1) and (2):} \quad [\text{HCO}_3^-]_{\text{B}} = 0.0196$$

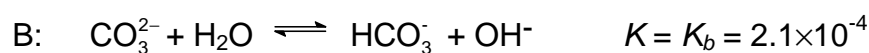
$$[\text{H}_2\text{CO}_3]_{\text{B}} = 0.0043$$

$$n(\text{HL}) = \Delta n(\text{H}_2\text{CO}_3) = \Delta c(\text{H}_2\text{CO}_3) \times 1.00 \text{ dm}^3 = 2.4 \times 10^{-3} \text{ mol}$$

$$1.5 \quad [\text{OH}^-] = 8.9 \times 10^{-5} \quad [\text{H}_2\text{CO}_3] \text{ of no importance}$$



$$c_0 \qquad c_0$$



$$c_0 - x \qquad x \qquad x$$

$$\text{From B:} \quad [\text{HCO}_3^-] = [\text{OH}^-] = 8.9 \times 10^{-5}$$

$$[\text{CO}_3^{2-}] = \frac{[\text{HCO}_3^-][\text{OH}^-]}{K_b} = 3.8 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 1.3 \times 10^{-4}$$

$$c_0(\text{Ca}^{2+}) = 1.3 \times 10^{-4} \text{ mol dm}^{-3} = \text{solubility}$$

$$1.6 \quad K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 1.3 \times 10^{-4} \times 3.8 \times 10^{-5} = 4.9 \times 10^{-9} = 5 \times 10^{-9}$$

$$\text{From } K_{a2}: \quad [\text{CO}_3^{2-}] = \frac{K_{a2} [\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = 2.6 \times 10^{-5}$$

$$Q = [\text{Ca}^{2+}][\text{CO}_3^{2-}]; \quad \text{Precipitation when } Q > K_{sp} = 5 \times 10^{-9}$$

No precipitation when $Q < K_{sp}$

Max. concentration of "free" Ca^{2+} ions:

$$[\text{Ca}^{2+}]_{\text{max}} = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = 1.9 \times 10^{-4}$$

PROBLEM 2

Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulphuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

- 2.1** 0.2515 g of a grain sample was treated with sulphuric acid, sodium hydroxide was then added and the ammonia distilled into 50.00 cm³ of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 cm³ of 0.1050 M sodium hydroxide. Calculate the concentration of nitrogen in the sample, in percent by mass.
- 2.2** Calculate the *pH* of the solution which is titrated in 2.1 when 0 cm³, 9.65 cm³, 19.30 cm³ and 28.95 cm³ of sodium hydroxide have been added. Disregard any volume change during the reaction of ammonia gas with hydrochloric acid. *K_a* for ammonium ion is 5.7×10^{-10} .
- 2.3** Draw the titration curve based on the calculations in b).
- 2.4** What is the *pH* transition range of the indicator which could be used for the back titration.
- 2.5** The Kjeldahl method can also be used to determine the molecular weight of amino acids. In a given experiment, the molecular weight of a naturally occurring amino acid was determined by digesting 0.2345 g of the pure acid and distilling ammonia released into 50.00 cm³ of 0.1010 M hydrochloric acid. A titration volume of 17.50 cm³ was obtained for the back titration with 0.1050 M sodium hydroxide. Calculate the molecular weight of the amino acid based on one and two nitrogen groups in the molecule, respectively.

SOLUTION

$$\mathbf{2.1} \quad [(50.00 \times 0.1010) - (19.30 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2515} = 16.84 \% \text{ N}$$

$$\mathbf{2.2} \quad 0 \text{ cm}^3 \text{ added:} \quad [\text{H}^+] = \frac{19.30 \cdot 0.1050}{50} = 0.04053$$

$$pH = 1.39$$

$$9.65 \text{ cm}^3 \text{ added: } [\text{H}^+] = 0.01699$$

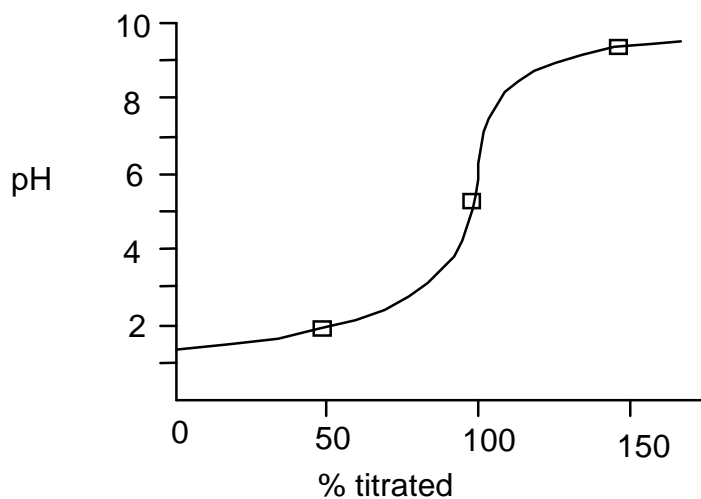
$$pH = 1.77$$

$$19.30 \text{ cm}^3 \text{ added: } [\text{H}^+] = \sqrt{5.7 \cdot 10^{-10} \times \frac{50.000 \times 101019 \times 300 \times 1050}{50 + 19.30}}$$

$$pH = 5.30$$

$$28.95 \text{ cm}^3 \text{ added: } pH = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.24 + \log \frac{1.01}{2.01} = 8.94$$

2.3



2.4 Indicator pH transition range: $pH 5.3 \pm 1$

$$2.5 \quad [(50.00 \times 0.1010) - (17.50 \times 0.1050)] \frac{14.01}{1000} \times \frac{100}{0.2345} = 19.19 \% \text{ N}$$

$$1 \text{ N: } M_r = 73.01$$

$$2 \text{ N: } M_r = 146.02$$

PROBLEM 3

Sulphur forms many different compounds with oxygen and halogens (sulphur as the central atom). These compounds are mainly molecular, and many are easily hydrolysed in water.

- 3.1** Write Lewis structures for molecules SCl_2 , SO_3 , SO_2ClF , SF_4 , and SBrF_5 .
- 3.2** Carefully draw the geometries of the 5 molecules. (Disregard small deviations from "ideal" angles.)
- 3.3** A compound, consisting of sulphur (one atom per molecule), oxygen and one or more atoms of the elements F, Cl, Br, and I, was examined. A small amount of the substance reacted with water. It was completely hydrolyzed without any oxidation or reduction, and all reaction products dissolved. 0.1 M solutions of a series of test reagents were added to separate small portions of a diluted solution of the substance.

Which ions are being tested for in the following tests?

- i) Addition of HNO_3 and AgNO_3 .
- ii) Addition of $\text{Ba}(\text{NO}_3)_2$.
- iii) Adjustment to $\text{pH} = 7$ with NH_3 and addition of $\text{Ca}(\text{NO}_3)_2$.

Write the equations for the possible reactions in the tests:

- iv) Addition of KMnO_4 followed by $\text{Ba}(\text{NO}_3)_2$ to an acid solution of the substance.
- v) Addition of $\text{Cu}(\text{NO}_3)_2$.

- 3.4** In practice, the tests in 3.3 gave the following results:

- i) A yellowish precipitate.
- ii) No precipitate.
- iii) No visible reaction.
- iv) The main features were that the characteristic colour of permanganate disappeared, and a white precipitate was formed upon addition of $\text{Ba}(\text{NO}_3)_2$.
- v) No precipitate.

Write the formulas of the possible compounds, taking the results of these tests into account.

- 3.5** Finally, a simple quantitative analysis was undertaken:

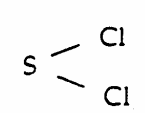
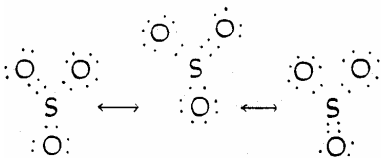
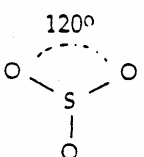
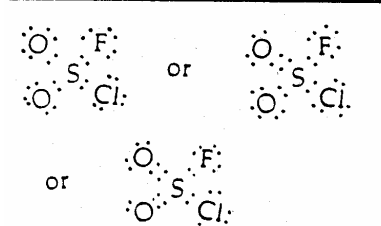
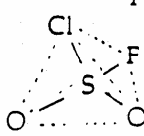
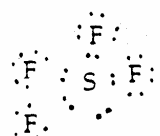
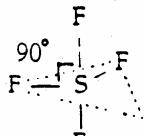
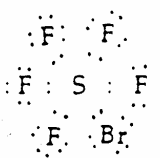
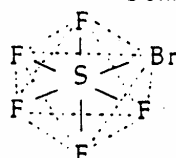
7.190 g of the substance was weighed out and dissolved in water to give 250.0 cm³ of a solution. To 25.00 cm³ of this solution, nitric acid and enough AgNO_3 was added

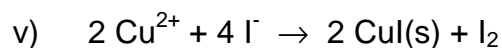
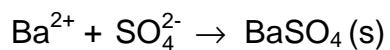
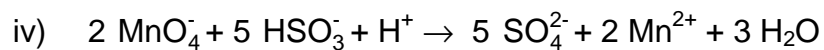
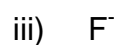
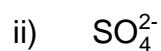
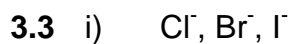
to secure complete precipitation. After washing and drying the precipitate weighed 1.452 g. Determine the formula of the compound.

3.6 Write the equation describing the reaction of the substance with water.

If you have not found the formula for the compound, use SOClF.

SOLUTION

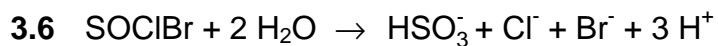
	3.1	3.2
SCl ₂	$\begin{array}{c} \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \end{array} : \begin{array}{c} \cdot\cdot \\ \text{S} \\ \cdot\cdot \end{array} : \begin{array}{c} \cdot\cdot \\ \text{Cl} \\ \cdot\cdot \end{array}$	 <p>Bent</p>
SO ₃		 <p>120°</p> <p>Trigonal planar</p>
SO ₂ ClF		 <p>Tetrahedral</p>
SF ₄		 <p>90°</p> <p>Trigonal bipyramidal - 1 corner</p>
SBrF ₅		 <p>Octahedral</p>



3.4 SOClBr and SOBr_2

3.5 SOClBr

[SOClBr : 1.456g, and SOBr_2 : 1.299g]



PROBLEM 4

Platinum(IV) oxide is not found in the nature, but it can be prepared in a laboratory. Solid platinum(IV) oxide is in equilibrium with platinum metal and oxygen gas at 1 atm ($= 1.01325 \times 10^5$ Pa) and 650 °C.

4.1 This suggests that the conditions on the Earth, when the minerals we know were formed, were:

[1] $p(\text{O}_2) = 1$ atm, $t = 650$ °C;

[2] $p(\text{O}_2) < 1$ atm, $t < 650$ °C;

[3] $p(\text{O}_2) > 1$ atm, $t < 650$ °C;

[4] $p(\text{O}_2) < 1$ atm, $t > 650$ °C;

[5] $p(\text{O}_2) > 1$ atm, $t > 650$ °C

Mark the most probable alternative [1] – [5] on the answer sheet. Please note that the marking of only one alternative will be accepted.

4.2 What are ΔG and K_p for the formation of platinum(IV) oxide at oxygen pressure of 1 atm and temperature of 650 °C?

The preparation of platinum(IV) oxide involves boiling of a solution which contains hexachloroplatinate(IV) ions with sodium carbonate. In this process $\text{PtO}_2 \cdot n \text{H}_2\text{O}$ is formed and this is in turn converted to platinum(IV) oxide upon subsequent filtering and heat treatment. In the following we assume $n = 4$.

$\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$ or $\text{Pt}(\text{OH})_4 \cdot 2 \text{H}_2\text{O}$ can be dissolved in acids and strong bases.

4.3 Write the balanced equations for the preparation of platinum(IV) oxide according to the procedure given above.

4.4 Write the balanced equations for the dissolution of $\text{PtO}_2 \cdot 4 \text{H}_2\text{O}$ in both hydrochloric acid and sodium hydroxide.

Platinum is mainly found in the nature as the metal (in mixture or in alloying with other precious metals). Platinum is dissolved in aqua regia under the formation of hexachloroplatinate(IV) ions. Aqua regia is a mixture of concentrated hydrochloric and nitric acids in proportion 3 : 1, and of the nitrosylchloride (NOCl) and the atomic chlorine which are formed upon the mixing. The latter is believed to be the active dissolving component.

The hexachloroplatinate(IV) ions can be precipitated as diammonium hexachloroplatinate(IV) and by thermal decomposition of this compound, finely powdered platinum and gaseous products are formed.

- 4.5** Write the balanced equations for the formation of aqua regia and its reaction with platinum.
- 4.6** Write the balanced equation of the thermal decomposition of diammonium hexachloroplatinate(IV) at elevated temperature.

From diammonium hexachloroplatinate(IV) we can prepare $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ which occurs in *cis* ($\Delta H_f^0 = -467.4 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -228.7 \text{ kJ mol}^{-1}$) and *trans* ($\Delta H_f^0 = -480.3 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -222.8 \text{ kJ mol}^{-1}$) form.

- 4.7** The occurrence of the isomers shows that $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has geometry:
- [1] linear,
 - [2] planar,
 - [3] tetrahedral,
 - [4] octahedral geometry.

Mark the correct alternative of [1] – [4] on the answer sheet.

- 4.8** Is the *cis* form or *trans* form thermodynamically more stable?

Platinum is used as a catalyst in modern automobiles. In the catalyst carbon monoxide ($\Delta H_f^0 = -110.5 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -137.3 \text{ kJ mol}^{-1}$) reacts with oxygen to carbon dioxide ($\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -394.4 \text{ kJ mol}^{-1}$).

- 4.9** Is the reaction spontaneous at 25 °C?

[1] yes, or

[2] no.

Is the reaction:

[3] endothermic, or

[4] exothermic?

Calculate ΔS° for the reaction.

Establish whether the entropy of the reaction system

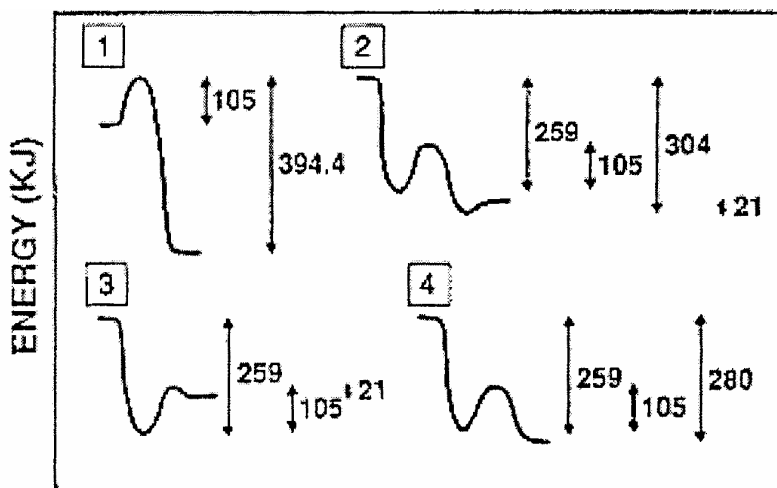
[5] increases, or

[6] decreases.

4.10 Establish an expression for the temperature dependence of the equilibrium constant in this case.

The overall catalytic reaction is simple, whereas the reaction mechanism in the homogeneous phase is very complicated with a large number of reaction steps, and the course is difficult to control owing to a distinct chain character. With platinum as catalyst the significant reaction steps are: (i) Adsorption of CO and adsorption/dissociation of O₂ ($\Delta H = -259$ kJ per mol CO + O), (ii) their activation (105 kJ per mol CO + O) and (iii) the reaction and the desorption of CO₂ ($\Delta H = 21$ kJ per mol CO₂).

A one-dimensional energy-diagram for the platinum catalyzed oxidation of carbon monoxide to dioxide can be represented as:

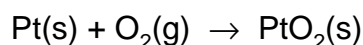


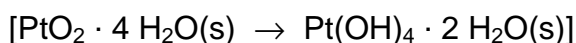
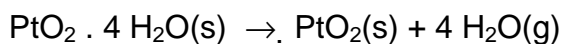
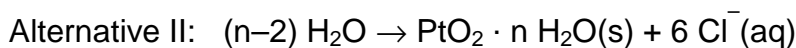
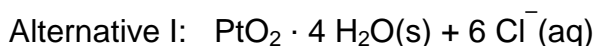
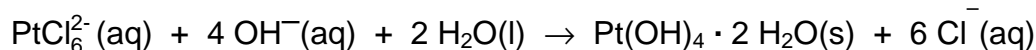
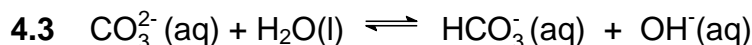
4.11 Mark the correct alternative of [1] – [4] on the answer sheet.

SOLUTION

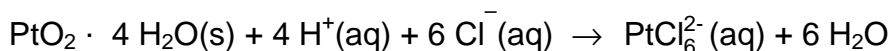
4.1 Correct answer is No 4.

4.2 $\Delta G = 0$ kJ and $K_p = 1$ according to the chemical equation

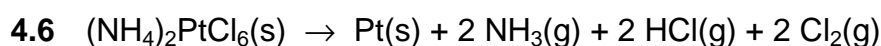
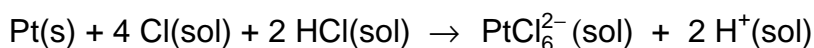
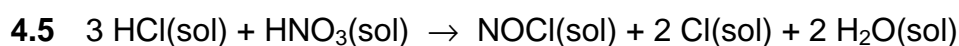
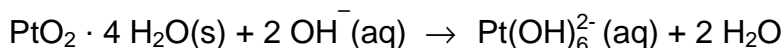




4.4 In hydrochloric acid:

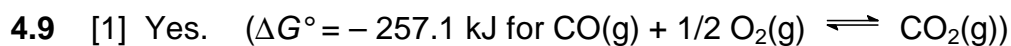


In sodium hydroxide:

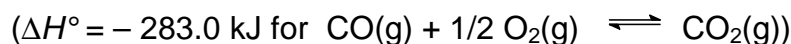


4.7 Correct is No 2.

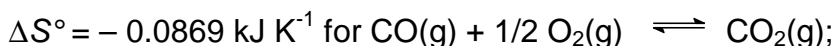
4.8 The cis form is thermodynamically more stable.



[4] The reaction is exothermic.



[6] is correct.



As seen from the sign for ΔS° as well as for the reaction enthalpy the entropy of the system decreases.

4.10 $\ln K_p = 34037 / T - 10.45$ for $\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$

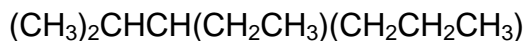
Alternative: $K_p = \exp^{(34037 / T - 10.45)}$

4.11 No 2 is correct.

PROBLEM 5

There is only one correct answer to each question

5.1 What is the correct systematic name (IUPAC name) for the compound below?

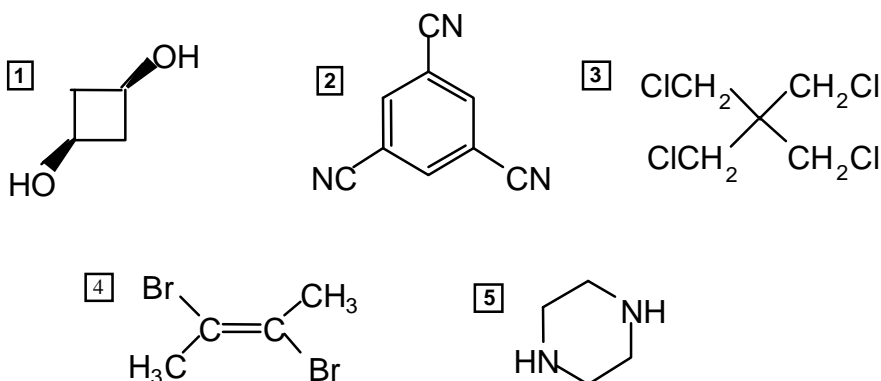


- 1 3-Isopropylhexane
- 2 2-Methyl-3-propylpentane
- 3 Ethyl isopropyl propyl methane
- 4 3-Hexylpropane
- 5 3-Ethyl-2-methylhexane

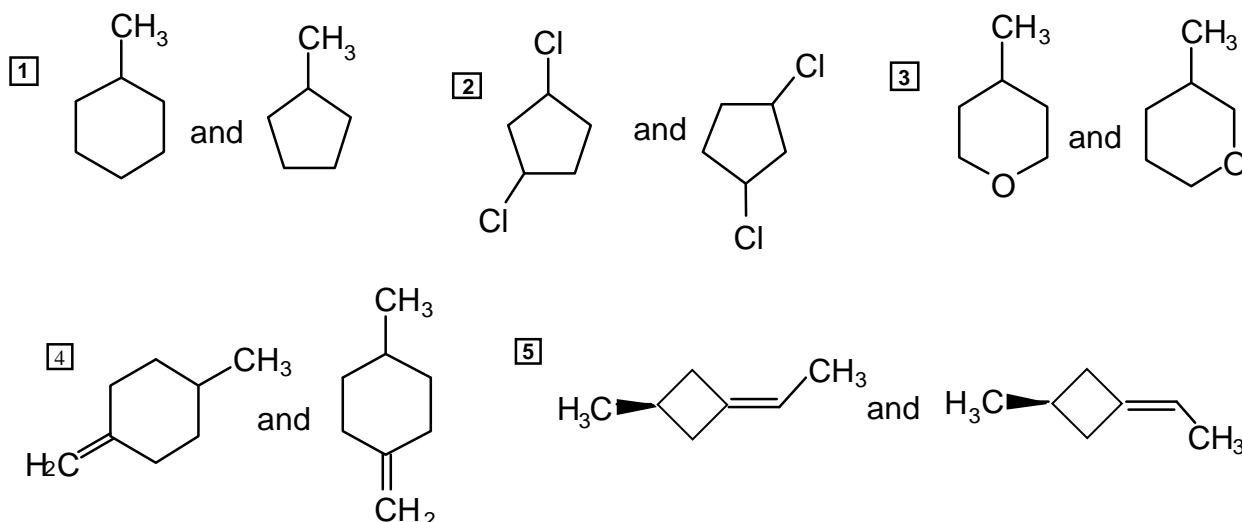
5.2 How many isomers, including stereoisomers, containing only saturated carbon atoms, are there for C_5H_{10} ?

- 1 4 isomers 2 5 isomers 3 6 isomers
- 4 7 isomers 5 8 isomers

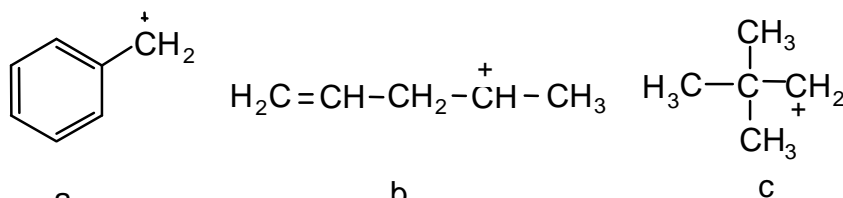
5.3 Which one of the following compounds has a dipole moment significantly different from zero?



5.4 Which of the following is a pair of structural isomers?

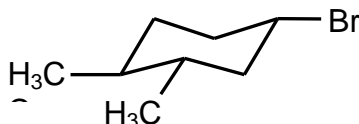


5.5 Which of the following five options is the correct order of relative stabilities of cations a, b and c as written below (most stable first)?



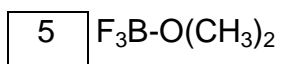
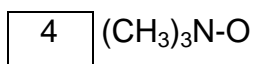
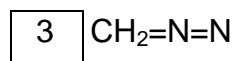
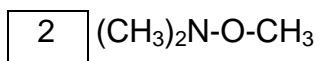
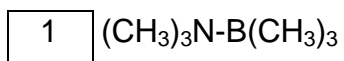
- 1 a>b>c 2 b>c>a 3 c>a>b 4 a>c>b 5 b>a>c

5.6 What is the correct stereochemical descriptor of the optically active compound drawn below?



- 1 1*R*,3*R*,4*R* 2 1*R*,3*R*,4*S* 3 1*R*3*S*,4*R* 4 1*S*,3*S*,4*R* 5 1*S*,3*S*,4*S*

5.7 All the molecules drawn below are neutral compounds. Which one does not contain a formal positive charge and a formal negative charge?



SOLUTION

	1	2	3	4	5
5.1	X				X
5.2				X	
5.3	X				
5.4			X		
5.5	X				
5.6					X
5.7		X			

PROBLEM 6

An optical active compound **A** ($C_{12}H_{16}O$) shows amongst other a strong IR-absorption at $3000 - 3500\text{ cm}^{-1}$, and two medium signals at 1580 and 1500 cm^{-1} . The compound does not react with 2,4-dinitrophenylhydrazine (2,4-D). Upon treatment with $I_2/NaOH$, **A** is oxidized and gives a positive iodoform reaction.

Ozonolysis of **A** (1. O_3 ; 2. Zn, H^+) gives **B** ($C_9H_{10}O$) and **C** ($C_3H_6O_2$). Both **B** and **C** give precipitation when treated with 2,4-D, and only **C** gives positive reaction with Tollens reagent. Nitration of **B** (HNO_3/H_2SO_4) may give two mono-nitro compounds **D** and **E**, but in practical work only **D** is formed.

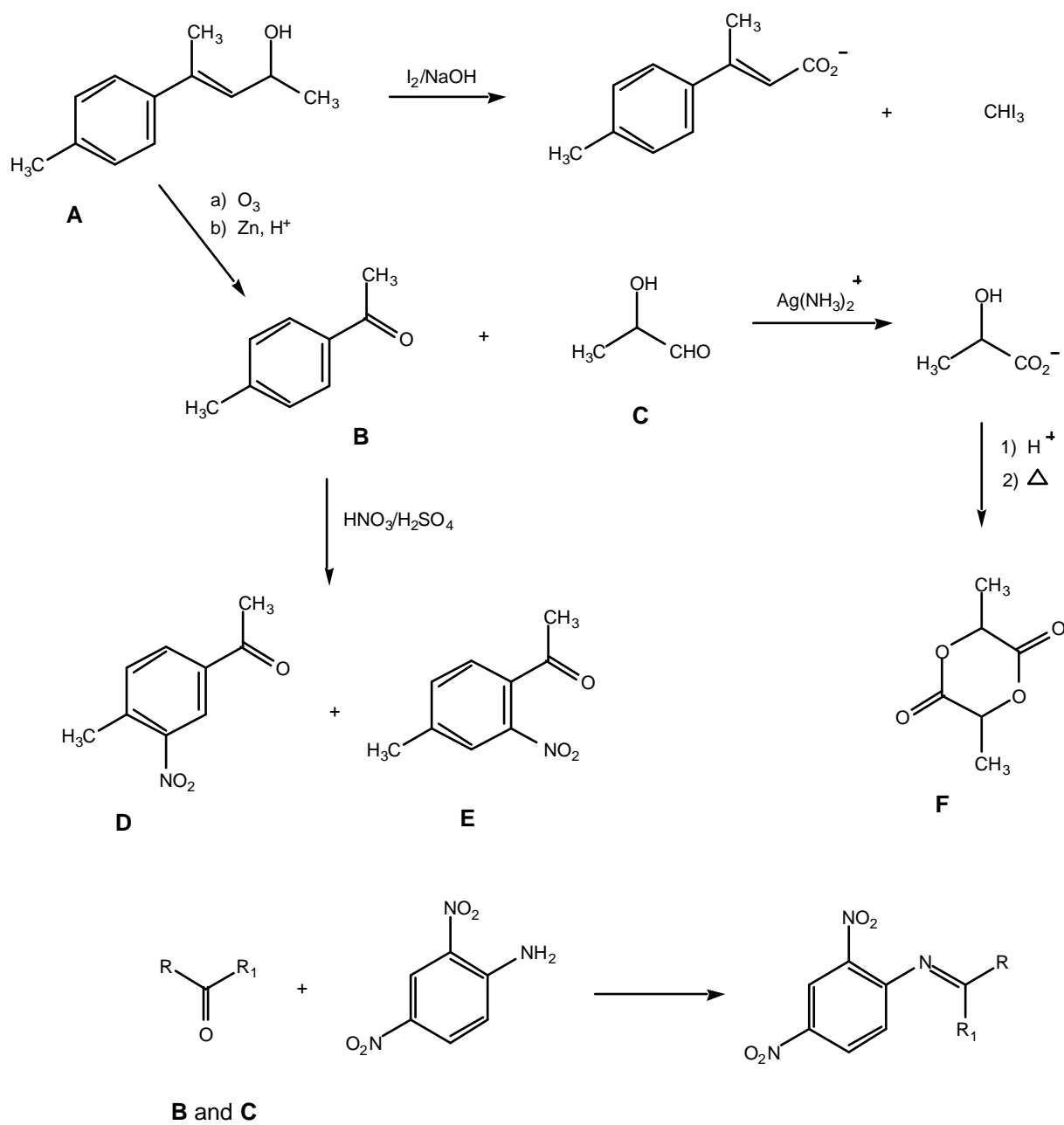
Acidification followed by heating of the product formed by the Tollens reaction on **C** gives compound **F** ($C_6H_8O_4$). The compound gives no absorption in IR above 3100 cm^{-1} .

- 6.1** Based on the above information draw the structure formula(e) for the compounds **A** – **F** and give the overall reaction scheme, including the (2,4-D) and the products of the Tollens and iodoform reactions.
- 6.2** Draw **C** in an R-configuration. Transform this into a Fischer projection formula and state whether it is a **D** or L configuration.

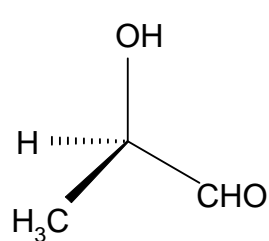
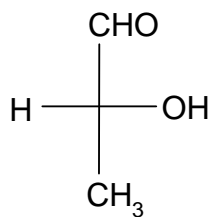
SOLUTION

(See the next page.)

6.1



6.2


R-configuration

D-configuration

PROBLEM 7

7.1 When an ideal, monatomic gas expands reversibly from a volume V_1 to a volume V_2 , a work

$$w = - \int_{V_1}^{V_2} p \, dV$$

is performed on the system by the surroundings. In this equation, w is the work and p is the pressure of the gas.

Determine the performed work when one mole ideal gas expands isothermally from $V_1 = 1.00 \text{ dm}^3$ to $V_2 = 20.0 \text{ dm}^3$ at the temperature $T = 300.0 \text{ K}$.

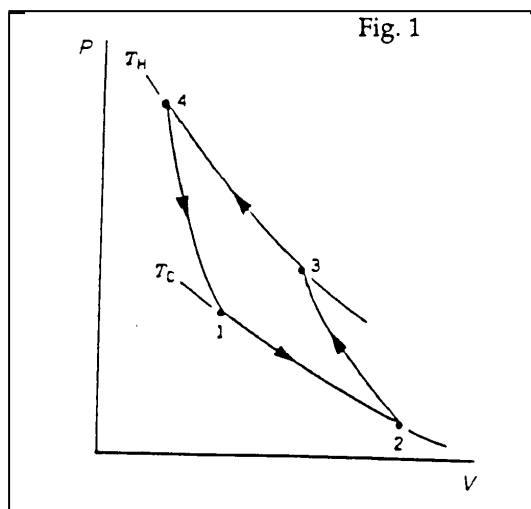
Given: The gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

7.2 Determine how much heat must be added to the gas during the process given under 7.1.

7.3 The gas will perform less work in an adiabatic expansion than in an isothermal expansion. Is this because the adiabatic expansion is characterized by (check the square you think is most important).

1	The volume of the gas is constant
2	The expansion is always irreversible
3	No heat is supplied to the gas

7.4 The cyclic process shown schematically in Figure 1 shows the four steps in a refrigeration system with an ideal gas as working medium. Identify the isothermal and adiabatic steps in the process. Here, T_H and T_C represent high and low temperature, respectively. Specify for each step whether it is adiabatic or isothermal.



SOLUTION

7.1 Work performed on the gas is

$$w = - \int_{V_1}^{V_2} p \, dV = - RT \int_{V_1}^{V_2} \frac{dV}{V} = - RT \ln \frac{V_2}{V_1}$$

$$= -8,314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \ln \frac{20.00}{1.00} = -7472 \text{ J mol}^{-1} = -7.47 \text{ kJ mol}^{-1}$$

7.2 Because this is an isothermal expansion of an ideal monatomic gas, there is no change in internal energy. From the first law of thermodynamics, we then have that $\Delta U = q + w = 0$

where q is the amount of supplied heat and w is performed work. This leads to $\underline{q} = -w = 7.47 \text{ kJ mol}^{-1}$.

7.3 (3) No heat is supplied to the gas.

7.4	isotherm	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
	adiabat	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>

PROBLEM 8

Avogadro's Number: $6.022 \cdot 10^{23}$

8.1 An atom of ^{238}U disintegrates by a series of α -decays and β^- -decays until it becomes ^{206}Pb , which is stable.

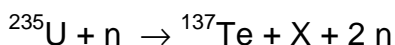
i) How many α -decays and how many β^- -decays does an atom starting as ^{238}U undergo before it becomes stable?

ii) One of the following ten nuclides is formed from a series of disintegrations starting at ^{238}U . Which one ?

^{235}U , ^{234}U , ^{228}Ac , ^{224}Ra , ^{224}Rn , ^{220}Rn , ^{215}Po , ^{212}Po , ^{212}Pb , ^{211}Pb .

8.2 In a thermal neutron-induced fission process, ^{235}U reacts with a neutron and breaks up into energetic fragments and (normally) 2-3 new neutrons.

We consider one single fission event:



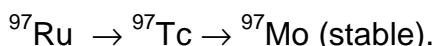
Identify the fragment X.

8.3 The half-life of ^{238}U is 4.5×10^9 years, the half-life of ^{235}U is 7.0×10^8 years. Natural uranium consists of 99.28 % ^{238}U and 0.72 % ^{235}U .

i) Calculate the ratio in natural U between the disintegration rates of these two uranium isotopes.

ii) A mineral contains 50 weight percent uranium. Calculate the disintegration rate of ^{238}U in 1.0 kg of this mineral.

8.4 We have the following radioactive sequence:



Halflives: ^{97}Ru : 2.7 days; ^{97}Tc : 2.6×10^6 years

At $t = 0$ a radioactive source containing only ^{97}Ru has a disintegration rate of 1.0×10^9 Bq.

i) What is the total disintegration rate of the source at $t = 6.0$ days?

ii) What is the total disintegration rate of the source at $t = 6000$ years?

SOLUTION

8.1 i) 8 α 's and 6 β^- 's (only α 's gives ^{206}Os , to come from Os to Pb requires 6 β^- 's).

ii) ^{234}U , all other answers are incorrect.

8.2 ⁹⁷Zr

8.3 i) $D = \lambda N$, i.e. $D_1 / D_2 = \lambda_1 N_1 / \lambda_2 N_2 = \text{abund.}(1)T_{1/2}(2) / \text{abund.}(2)T_{1/2}(1)$
 $= (99.28 \times 7.0 \times 10^8) / (0.72 \times 4.5 \times 10^9) = 21.4$ (0.047 is also of course correct)

ii) $N = (m/AW(U)) \times \text{abundance}(238) \times N_A = (500 / 238.01) \times 0.9928 \times 6.022 \times 10^{23}$
 $= 1.26 \times 10^{24}$

$$D = N \ln 2 / T_{1/2} = 1.26 \times 10^{24} \times \ln 2 / (4.5 \times 10^9 \text{ (y)} \times 3.16 \times 10^7 \text{ (s/y)}) = 6.1 \cdot 10^6 \text{ Bq}$$

8.4 i) $\lambda = \ln 2 / 2.7(\text{d}) = 0.26 \text{ d}^{-1}$

$$D = D_0 e^{-\lambda t} = 1.0 \times 10^9 \times e^{-(0.26 \times 6.0)} = 2.1 \times 10^8 \text{ Bq}$$

ii) Number of ⁹⁷Ru atoms in the source:

$$N = D T_{1/2}({}^{97}\text{Ru}) / \ln 2 = 1.0 \times 10^9 \text{ (Bq)} \times 2.7 \text{ (d)} \times 24 \text{ (h/d)} \times 3600 \text{ (s/h)} / 0.6931 =$$

$$= 3.4 \times 10^{14} \text{ atoms}$$

When all ⁹⁷Ru has disintegrated, these atoms have all become ⁹⁷Tc, and the disintegration rate of this nuclide is

$$D = N \ln 2 / T_{1/2}({}^{97}\text{Tc}) = (3.4 \times 10^{14} \times 0.6931) / (2.6 \cdot 10^6 \text{ y} \times 3.16 \times 10^7 \text{ s y}^{-1}) =$$

$$= 2.9 \text{ Bq}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Determination of Fatty Acids

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 cm³ of this solution contain a total of 1.00 g acid plus ester). By titration the acid number¹⁾, the saponification number²⁾ and the iodine number³⁾ of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 cm³). There will be no supplementation.

- 1) Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.
- 2) Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.
- 3) Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Relative atomic masses:

$$A_r(\text{I}) = 126.90 \quad A_r(\text{O}) = 16.00$$

$$A_r(\text{K}) = 39.10 \quad A_r(\text{H}) = 1.01$$

1) Determination of the Acid Number

Reagents and Apparatus

Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1 : 1 mixture), burette (50 cm³), Erlenmeyer flasks (3 x 250 cm³), measuring cylinder (100 cm³), graduated pipette (2 cm³), funnel.

Procedure:

Pipette out aliquots (2.00 cm³) from the unknown mixture into Erlenmeyer flasks (250 cm³). Add first ca. 100 cm³ of an ethanol/ether mixture (1:1) and then add the indicator (5 drops).

Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the Saponification Number*Reagents and Apparatus*

Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 cm³), round bottom flask (250 cm³), Liebig condenser, burette (50 cm³), Erlenmeyer flasks (3 x 250 cm³), volumetric pipette (25 cm³), volumetric pipette (10 cm³), graduated pipette (2 cm³), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

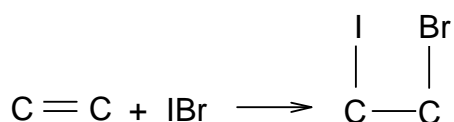
Procedure

Pipette out a 2.00 cm³ aliquot of the unknown sample into a round bottom flask (250 cm³) and add 25.0 cm³ 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for 30 min in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 cm³ volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 cm³ and titrate with 0.1000 M HCl using phenolphthalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the Iodine Number

In this experiment iodobromine adds to the double bond.



The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I₂, (IBr + I⁻ → I₂ + Br⁻) which in turn is determined by standard thiosulphate solution.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus

Unknown sample, 0.2000 M Hanus solution, dichloro-methane, 15 % KI solution in distilled water, distilled water, 0.2000 M sodium thiosulphate, starch indicator, Erlenmeyer flasks (3 x 500 cm³), buret (50 cm³), graduated pipette (2 cm³), measuring cylinders (10 and 100 cm³), volumetric pipette (25 cm³), aluminium foil.

Procedure

Pipette out aliquots (1.00 cm³) of the unknown mixture into Erlenmeyer flasks (500 cm³) and add 10 cm³ of dichloromethane. With a pipette add 25.0 cm³ Hanus solution, cover the opening with aluminium foil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 cm³ of the 15 % KI solution, shake thoroughly and add 100 cm³ of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 cm³) and continue titration until the blue colour entirely disappears.

Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

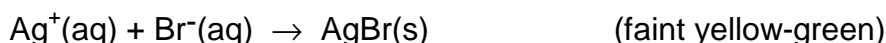
- i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester.
 - ii) Calculate the number of double bonds in the unsaturated acid.
-
-

PROBLEM 2 (Practical)**Volumetric Determination of Bromide by Back-titration with Thiocyanate after Precipitation with Silver Ions in Excess***Moments worth considering:*

- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 cm³ pipette will be at disposal for each candidate.

Principle

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

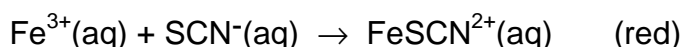


The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place resulting in the precipitation of silver thiocyanate:



Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:

**a) Procedures**

Every candidate has got a 0.5 dm³ brown bottle with screw cap, containing the potassium thiocyanate solution (about 0.08 M) and also a 0.25 dm³ brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

i) Determination of bromide in the unknown sample solution

Fill the 250 cm³ volumetric flask containing the bromide sample solution to the mark with water. Transfer three 25.00 cm³ portions (pipette) of the sample solution to three Erlenmeyer flasks. Add about 5 cm³ of 6 M nitric acid (measuring cylinder) to each flask. Transfer 25.00 cm³ (pipette) of the accurately known silver solution and about 1 cm³ of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquots with the potassium thiocyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

ii) Standardization of the potassium thiocyanate solution

Transfer 25.00 cm³ (pipette) of the silver nitrate solution to an Erlenmeyer flask, add about 5 cm³ of 6 M nitric acid and about 1 cm³ of the iron(III) indicator solution and about 25 cm³ of water (use measuring cylinders for these solutions). Titrate the contents with the thiocyanate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass: $A_r(\text{Br}) = 79.90$

b) Exercise

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar concentration of free (unprecipitated) Br⁻ in this solution:

$$K_{sp}(\text{AgBr}) = 5.00 \times 10^{-13} \quad K_{sp}(\text{AgSCN}) = 1.00 \times 10^{-12}$$

Ignore the effect of *pH* and Fe(III) species.

Note:

On the answer sheet, not only the required final results shall be given, but also exemplifications of how the calculations are carried out.

27th



International Chemistry Olympiad

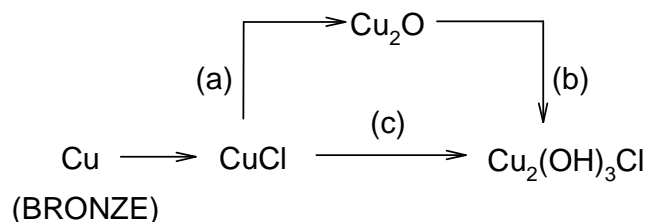
**6 theoretical problems
3 practical problems**

THE TWENTY-SEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 13--20 JULY 1995, BEIJING, CHINA

THEORETICAL PROBLEMS

PROBLEM 1

1.1 Excavated Chinese ancient bronze musical instrument, carillon, was covered entirely by rust. Chemical analysis showed that the rust contains CuCl, Cu₂O and Cu₂(OH)₃Cl. Simulation experiments showed that CuCl was formed first under the action of both air and Cl containing aqueous solution and then Cu₂(OH)₃Cl produced through the following two different ways:



Using the molar standard formation Gibbs free energies of the species concerned answer the following questions:

Species	Cu ₂ O(s)	CuO(s)	CuCl(s)	Cu₂(OH)₃Cl(s)	Cl(aq)	OH(aq)	H ₂ O(l)
$\Delta_f G^0(298 \text{ K})$ (kJ mol ⁻¹)	-146	-130	-120	-1338	-131	-157	-237

- Write balanced equations for reactions (a), (b) and (c).
- Calculate the molar standard Gibbs free energy $\Delta_f G^0(298 \text{ K})$ for reactions (a), (b) and (c).
- Decide the spontaneous direction of reaction (a) in air through calculation, when $T = 298 \text{ K}$, $c(\text{HCl}) = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$.

1.2 Rate constants k_c for reaction (c) were measured at various temperatures in a simulation experiment in order to obtain its kinetic parameters. On the basis of the data given below answer the following questions:

t / °C	25	40
k_c / mol dm ⁻³ s ⁻¹	1.29×10^{-4}	2.50×10^{-4}

- Write the equation for calculating the activation energy of reaction (c) and find the value.
- Assign the overall reaction order of reaction (c).
- Knowing that the rate determining step of reaction (c) is the monolayer adsorption of O₂ (g) on solid CuCl, write the overall rate equation of this heterogeneous reaction (c). Under what condition might the reaction order be the same as that you have given in ii)? Assume only O₂ can be adsorbed.

1.3 A copper plate was divided into two parts, Cu(1) and Cu(2). Cu(1) was then hammered so that Cu(1) and Cu(2) are different in certain thermodynamic properties.

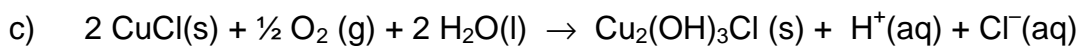
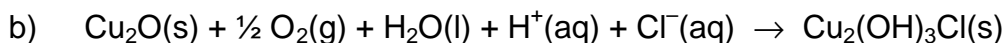
- An galvanic cell with Cu(1) and Cu(2) was designed as Cu(1)|CuSO₄(aq)|Cu(2) and the electromotive force E of the above cell was expressed as $E = \Phi_R - \Phi_L$, where Φ_R and Φ_L being the right and left electrode potentials (i. e. half-cell potentials), respectively. Please choose the correct E value from the following and give the thermodynamic reason for your choice.
(A) $E < 0$ (B) $E = 0$ (C) $E > 0$ (D) It cannot be decided
- Write the net cell reaction for the cell.

1.4 In a Cu-Zn alloy the molar fractions of Cu and Zn are 0.750 and 0.250, respectively. The structure type of the alloy is the same as that of pure copper, except Zn atoms substitute some Cu atoms randomly and statistically, i. e. at every atomic position, the probability of the occupation of Cu and Zn is proportional to the composition of the alloy. In this sense the alloy can be considered as composed of statistical atoms Cu_xZn_{1-x}. X-ray analysis shows that the arrangement of atoms in the alloy is of the cubic face-centred close packing type. Density of the alloy $d = 8.51$ g cm⁻³. Calculate the radius of the statistical atoms in the alloy.

Given: $A_r(\text{Cu}) = 63.5$, $A_r(\text{Zn}) = 65.4$.

SOLUTION

1.1 i)



ii) a) $\Delta G^0 = 69 \text{ kJ mol}^{-1}$

b) $\Delta G^0 = -824 \text{ kJ mol}^{-1}$

c) $\Delta G^0 = -755 \text{ kJ mol}^{-1}$

iii) Calculation (dilute HCl solution can be considered as an ideal solution)

$$\Delta_r G = \Delta_r G^0 + 2 RT \ln [\text{H}^+][\text{Cl}^-] = -22.3 \text{ kJ mol}^{-1} < 0$$

Spontaneous: to the right

1.2 i) Formula: $\ln \frac{k_c(T_2)}{k_c(T_1)} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$E_a = 34.2 \text{ kJ mol}^{-1}$$

ii) overall reaction order = 0

when $b p(\text{O}_2) \gg 1$

$$r = k_c \theta = \frac{k_c b p(\text{O}_2)}{1 + b p(\text{O}_2)}; \quad r = k_c \quad \text{zero order}$$

1.3 i) (C) $E > 0$ ii) Net cell reaction: $\text{Cu(1)} = \text{Cu(2)}$ Thermodynamic reason for choosing 3 (C) is $\Delta_r G < 0$, $\Delta_r G = -nFE$ and $E > 0$

1.4 $r = 1.30 \times 10^{-10}$

formula: $a = 2\sqrt{2r}$

$$d = \frac{4(63.5 \times 0.75 + 65.4 \times 0.25) \times 10^{-3}}{a^3 N_A} = 8.51 \times 10^{-3} \text{ kg m}^{-3}$$

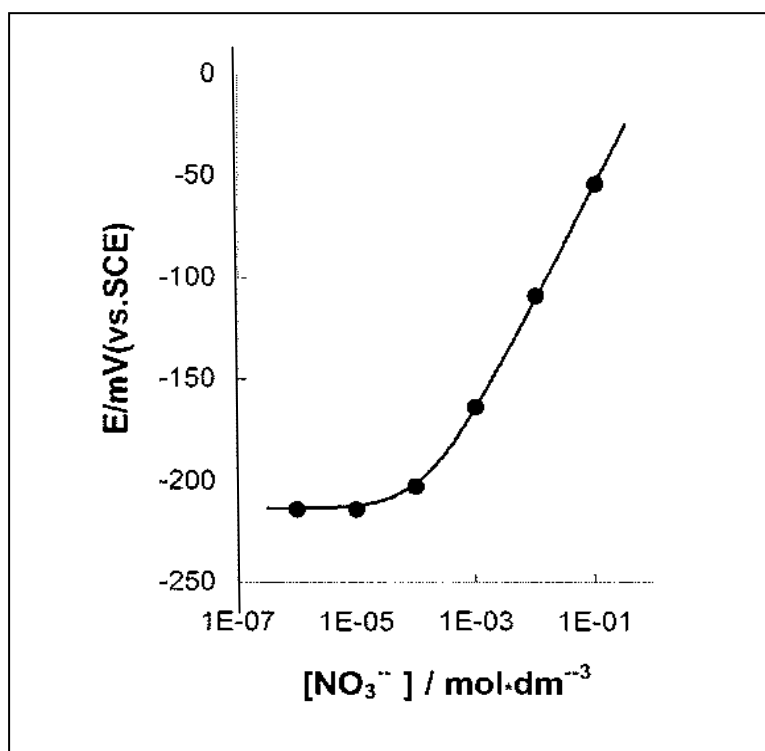
$$r^3 = 2.209 \times 10^{-30} \text{ m}^3$$

$$r = 1.30 \times 10^{-10} \text{ m}$$

PROBLEM 2

To control the quality of milk serum, a dairy by-product, the concentration of NO_3^- ion in serum is monitored by means of an ion selective electrode. Generally there is about 15 mg NO_3^- ion per litre in serum, measured on the basis of nitrogen mass.

2.1 For a nitrate ion selective electrode a calibration curve as shown below was obtained using a series of standard nitrate solutions containing $0.5 \text{ mol dm}^{-3} \text{ K}_2\text{SO}_4$, $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ and $2.6 \times 10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$ ion as the background. Decide whether it is feasible to measure concentration NO_3^- in serum under the above conditions.



2.2 Given are selective coefficients of Cl^- , SO_4^{2-} and ClO_4^- versus NO_3^- as follow

$$K_{\text{NO}_3, \text{Cl}^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{Cl}^-}} = 4.9 \times 10^{-2} \quad K_{\text{NO}_3, \text{SO}_4^{2-}} = \frac{c_{\text{NO}_3^-}}{c_{\text{SO}_4^{2-}}^{1/2}} = 4.1 \times 10^{-3}$$

$$K_{\text{NO}_3, \text{ClO}_4^-} = \frac{c_{\text{NO}_3^-}}{c_{\text{ClO}_4^-}} = 1.0 \times 10^{-3}$$

where the units of the concentrations are in mol dm⁻³ which is the best to reduce the interference of Cl⁻ to NO₃⁻ determination, so as to control the error in the NO₃⁻ concentration within 1 %, when there are 1.40×10⁻³ mol dm⁻³ NO₃⁻ and 1.60×10⁻² mol dm⁻³ Cl⁻ in serum:

- (a) AgNO₃ (b) Ag₂SO₄ (c) AgClO₄

Calculate the amount of the salt that should be added to 1 dm³ of the sample solution to be measured.

- 2.3** The NO₃⁻ ion concentration was determined by this method at 298 K. For 25.00 cm³ sample solution the electronic potential, *E*, is measured to be -160 mV. After adding 1.00 cm³ 1.00×10⁻³ mol dm⁻³ NO₃⁻ standard solution to the above solution, *E* changes to -130 mV. Find the *p*NO₃ of the serum.
- 2.4** The selective coefficient of CH₃COO⁻ versus NO₃⁻ $K(\text{NO}_3^-/\text{CH}_3\text{COO}^-) = 2.7 \times 10^{-3}$. If AgCH₃COO instead of Ag₂SO₄ is added to the sample solution of question 2.2, find the upper limit of the *pH* value below which the same requirement in question 2.2 can be met.

$$K_{\text{sp}}(\text{AgCl}) = 3.2 \times 10^{-10} \quad K_{\text{sp}}(\text{Ag}_2\text{SO}_4) = 8.0 \times 10^{-5}$$

$$K_{\text{sp}}(\text{AgCH}_3\text{COO}) = 8.0 \times 10^{-3} \quad K_{\text{a}}(\text{CH}_3\text{COOH}) = 2.2 \times 10^{-5}$$

$$A_{\text{r}}(\text{N}) = 14.00$$

SOLUTION

2.1 Yes

2.2 B

$$(1.4 \times 10^{-3} \times 0.01) / [\text{Cl}^-] = 4.9 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{Cl}^-] = 2.9 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{Excess } [\text{Cl}^-] = 1.6 \times 10^{-2} - 2.9 \times 10^{-3} \cong 1.6 \times 10^{-2} \text{ mol dm}^{-3}$$

To reduce the interference of Cl⁻ at least 1.6×10⁻² mol Ag⁺ ion or 8.0×10⁻³ mol Ag₂SO₄ has to be added to 1 dm³ sample solution.

2.3 $\Delta E = E_2 - E_1 = 0.059 \log \{(c_X V_X + c_S V_S)(c_X [V_X + V_S])\}$

$$0.03 = 0.059 \log [(25.00 V_x + 0.10) / (26.00 \times c_x)]$$

$$c_x = 1.7 \times 10^{-3} \text{ mol dm}^{-3}$$

$$p\text{NO}_3 = 2.77$$

2.4 $pH = 4.4$

$$(1.4 \times 10^{-3} \times x) \div 1.6 \times 10^{-2} = 2.7 \times 10^{-3}$$

$$x = 3.1 \% > 1 \%$$

$$(1.4 \times 10^{-3} \times 0.01) \div [\text{CH}_3\text{COO}^-] = 2.7 \times 10^{-3}$$

$$[\text{CH}_3\text{COO}^-] = 5.2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$1.6 \times 10^{-2} - 5.2 \times 10^{-3} = 1.08 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\{[\text{H}^+] \times 5.2 \times 10^{-3}\} \div (1.08 \times 10^{-2}) = 2.2 \times 10^{-5}$$

$$[\text{H}^+] = 4.3 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = 4.4$$

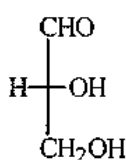
PROBLEM 3

1,3-Dihydroxyacetone can be converted to glyceraldehyde. On standing this glyceraldehyde changes spontaneously into a six member cyclic dimer $C_6H_{12}O_6$. The infrared spectrum of the dimer shows no absorption peak between $1600 - 1800\text{ cm}^{-1}$ and the dipole moment of the dimer is determined to be zero.

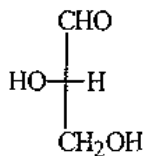
- 3.1 Write the Fischer projection structural formula(e) for the resulting glyceraldehyde and indicate configuration using D(+) and/or L(-).
- 3.2 Write the structural formula for the reaction intermediate of the conversion of 1,3-dihydroxyacetone to glyceraldehyde.
- 3.3 Write the structural formula for the dimer.
- 3.4 Using Haworth projection formula represent the possible stereoisomers which fit the dipole moment data.
- 3.5 Denote each chiral carbon atom in the above formulae with *R* or *S*.

SOLUTION

3.1

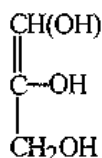


D(+)

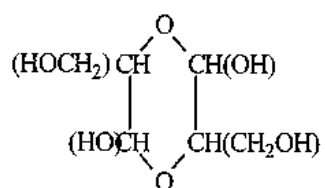


L(-)

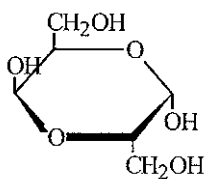
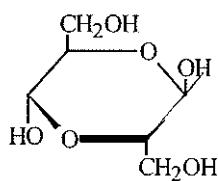
3.2



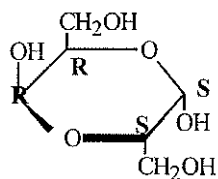
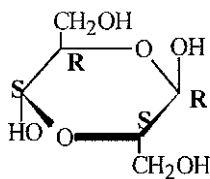
3.3



3.4



3.5



PROBLEM 4

Poly[(R)-3-hydroxyalkanoic acids], PHAs, are synthesized by a variety of bacteria and function as intracellular carbon and energy storage materials. These polymers are also biodegradable in environments, such as soil, anaerobic sewage and sea water. The inherent biologically mediated environmental degradability, useful physical properties, slow hydrolytic degradation and other favourable properties make bacterial polyesters exciting materials for both disposable biodegradable plastics (good for a clean environment) and special medical products.

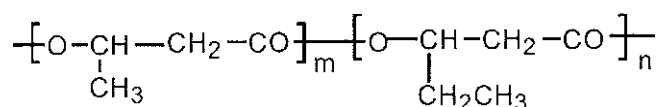
4.1 PHB, Poly(3-hydroxybutanoic acid), produced by bacteria contains only (R)-HB repeating units, while that synthesized by polymer chemists may contain only (R)-HB or only (S)-HB or both (R)-and (S)-HB in an alternating manner or both but in random distributions. Sketch chain structures of the atactic PHB, syndiotactic PHB and isotactic PHBs and denote each chiral carbon with (R) or (S). Five monomeric units are enough for each chain.

{Note: In "PHB", P means "poly" or "polymer of, HB represents the monomeric units contained in poly(3-hydroxybutanoic acid) molecules.)

4.2 Suggest two types of monomers that could be used for polymer chemists to synthesize a PHB, regardless of the stereochemistry of the products.

4.3 Poly[(R)-3-hydroxybutanoic acid] can be synthesized by feeding the bacteria (such as *Alcaligenes Eutrophus*) with sodium acetate in a nitrogen-free media. It is believed that the key steps for the conversion of acetate to PHB are the activation of acetate molecules by coenzyme A and the subsequent formation of the coenzyme A activated acetoacetate, which is then reduced by a reductase to form coenzyme A activated monomer 3-hydroxybutyrate. Polymerization of the monomer is achieved by a polymerase which would build the polymer molecules with unique stereospecificity. Sketch these steps with structural formulae. For coenzyme A the conventional abbreviation, -S-CoA (-CoA is as good), should be used in the sketch.

4.4 If sodium propanoate is used (as the sole carbon source) in the feeding media instead of sodium acetate, the principal product will be a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid with the following generalized structure:

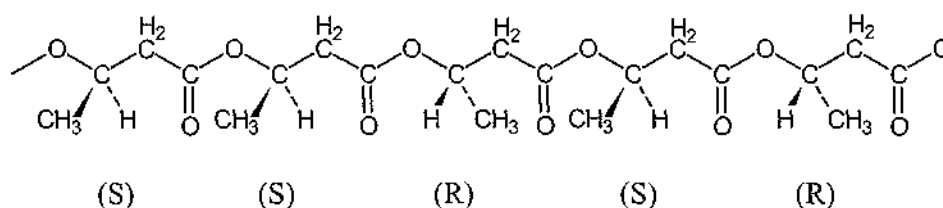


Rationalize the result.

(Note: Two different monomers are needed for the formation of the copolymer. The letters *m* and *n* in the structural formula are numbers of the units and have nothing to do with the answer, in other words, you may leave them out in your answer.)

SOLUTION

4.1

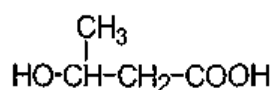


Other arrangements with (*R*) and (*S*) randomly distributed along the chain are correct, e.g. *RSRRS*, *SRSSR*, *RRSRS*, etc.

Syndiotactic PHB: This polymer has (*R*) and (*S*) units positioned along the chain in an alternating manner: *RSRSR* (or *SRSRS*).

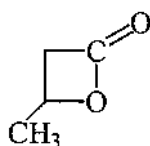
Isotactic PHB: All the chiral centres have the same configuration. There are 2 types of the isotactic PHBs: *SSSSS* and *RRRRR*.

4.2 Monomer 1:

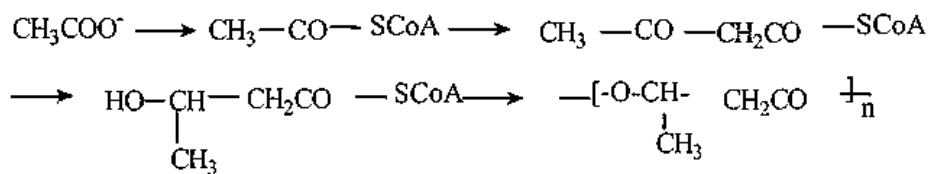


3-hydroxybutanoic acid

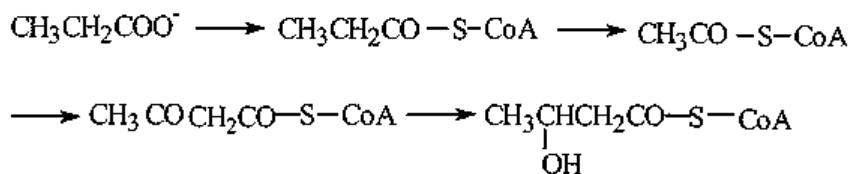
Monomer 2:



4.3

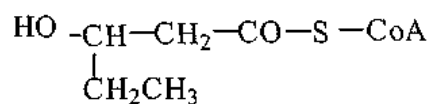


4.4

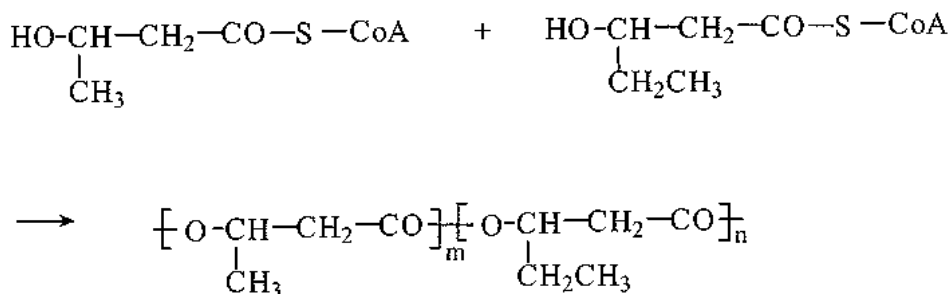


(Coenzyme A activated monomer 3-hydroxypentanoic acid)

This monomer may also be written in the following way:



Polymerization of these two monomers will result in the desired copolymer:



PROBLEM 5

The action of nitric oxide upon human body is dual. The nitric oxide generated in nerve cells will damage the cells, while the nitric oxide generated in endothelial cells of blood vessels can relax the vessels and control blood pressure.

5.1 Indicate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of NO molecule using one of symbols π , σ , π^* or σ^* , and indicate the electron(s) residing in the corresponding orbital using symbols \uparrow and/or \downarrow .

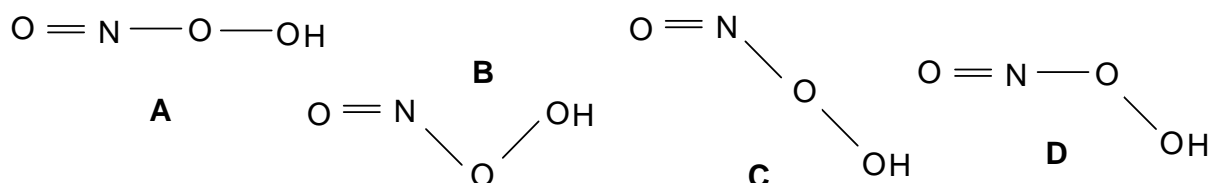
5.2 The relaxation of blood vessels is caused by a series of changes which are mediated by the coordination of NO molecule to iron ion, the latter being a component of an enzyme containing heme. It was known that the coordinated NO behaves as CO molecule (isoelectronic), which one of the following species really exists in the iron complex?

- a) NO b) NO⁺ c) NO⁻

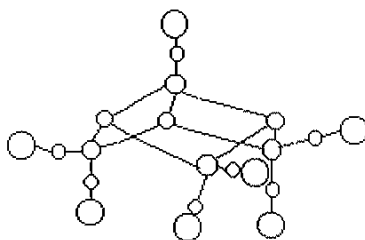
5.3 The cell damage is caused by free radical OH, which is one of the product of reaction between O₂⁻ and NO:



in which an intermediate with composition of HOONO is evolved. HOONO is a weak acid. Choose the structural formula with correct bond angles for the intermediate.



5.4 For preservation of meat, sodium nitrite is usually added and as a result NO is, then, formed. Consequently, NO reacts with the sulphur and iron atoms from decomposition of proteins, forming [Fe₄S₃(NO)₇]⁻. The complex anion is bacteriostatic and antiseptic. X-ray crystallography shows that the complex anion has a structure as shown below:



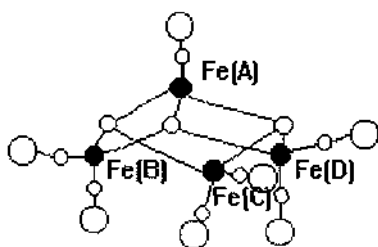
- i) Blacken all the circles corresponding to iron atoms and add symbols Fe(A), Fe(B), Fe(C) and Fe(D) beside the circles in the sequence of top → left → right.
- ii) The configuration of 3d electron shell of the iron atoms has been studied with modern structural analysis. Knowing that the mean oxidation number of the four iron atoms is -0.5 , give their configurations of 3d shell, respectively. Assume that each iron atom adopt sp hybridization.

5.5 $[\text{Fe}_4\text{S}_3(\text{NO})_7]^-$ anion can be reduced and a new complex $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ is formed which contains a cyclic structure unit of Fe_2S_2 .

- i) Write the structural formula for the anion $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$.
- ii) Give the oxidation state of each iron atom with Arabic numerals.
- iii) $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$ can be converted into $[\text{Fe}_2(\text{SCH}_3)_2(\text{NO})_4]^n$, a carcinogen. Which of the following three species is added to $[\text{Fe}_2\text{S}_2(\text{NO})_4]^{2-}$: CH_3^+ , $\bullet\text{CH}_3$ or CH_3^- ? Assign the value of n.

SOLUTION

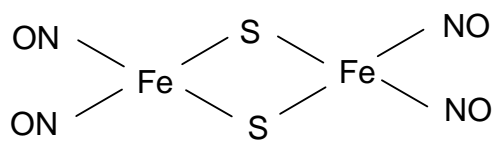
1. The HOMO of NO molecule is π^* , its electron arrangement \uparrow ;
The LUMO of NO molecule is π^* .
2. (b)
3. B
- 4.



Fe(A) has $3d^7$ configuration;

Fe(B), Fe(C) , and F(D) have $3d^9$ configuration.

5. i)



ii) Fe(-1) Fe(-1)

iii) The species added to S atom is CH_3^+ ; $n = 0$.

PROBLEM 6

A surfactant molecule can generally be modelled as Fig. 1 where a circle presents the polar head (PH), i.e. the hydrophilic part of the molecule, and a rectangle represents the non-polar tail (NT), i. e. the hydrophobic part of the molecule.

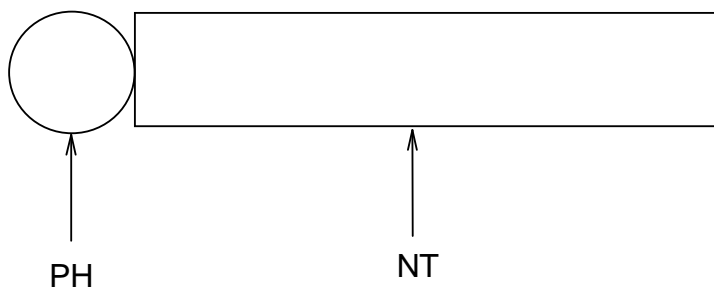


Fig. 1

6.1 AOT is a surfactant. Its systematic name (IUPAC name) is sulfobutanedioic acid 1,4-bis-(2-ethylhexyl) ester sodium salt (formula $C_{20}H_{37}NaO_7S$).

- i) Write the structural formula for AOT and fill its PH and NT in the circle and rectangle on your answer sheet.
- ii) Choose the type of surfactant AOT among the following.
 - a) Non-ionic; b) Anionic; c) Cationic; d) Others.

6.2 Mixing an aqueous solution of 50 mmol AOT with isooctane (volume ratio 1 : 1), a micellar extraction system will be formed in the isooctane phase (organic phase).

- i) Using the model as shown in Fig. 1, draw a micelle with 10 AOT molecules under the given condition.
- ii) What species are in the inner cavity of this micelle? Write their chemical formulas.

6.3 There is an aqueous solution containing the proteins as listed below:

Protein	Molecular mass (M_r) $\times 10^4$	Isoelectric point (PI)
A	1.45	11.1
B	1.37	7.8
C	6.45	4.9
D	6.80	4.9
E	2.40	4.7
F	2.38	0.5

The separation of proteins can be performed by mixing the AOT micellar extraction system with the solution. Adjusting the *pH* value of the solution to 4.5, only three of the above listed six proteins can be extracted into the micelles. Which proteins will be extracted?

- 6.4 The three proteins entered into the micelles will be separated from each other by the following procedure shown as in Fig. 2. Each extracted protein can be sequentially transported into a respective water phase.

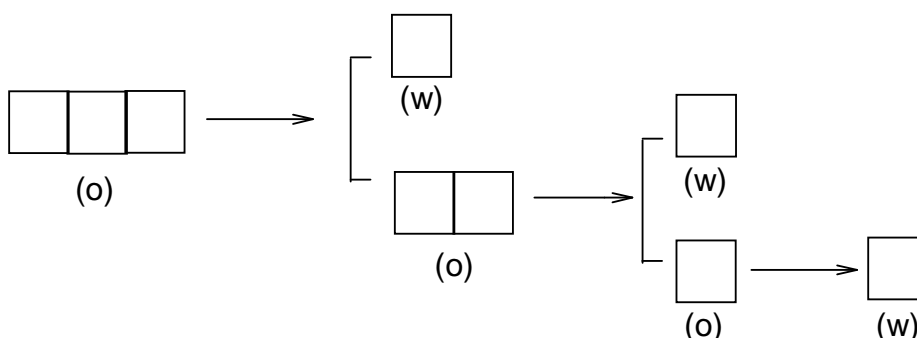


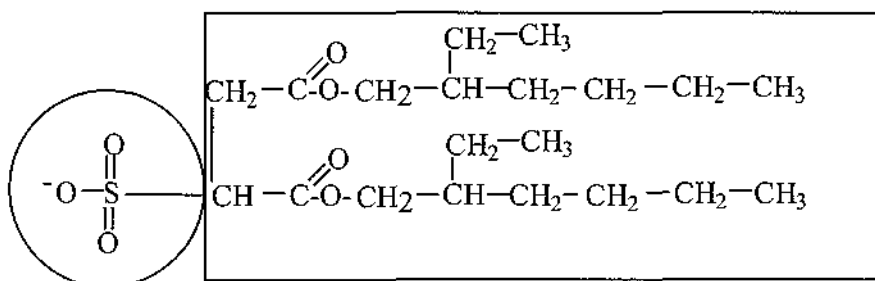
Fig. 2

Note: (w) represents water phase; (o) represents organic phase

Fill the three extracted proteins in the left boxes first and then separate them by the procedure given, and give the separation conditions above each arrow as well.

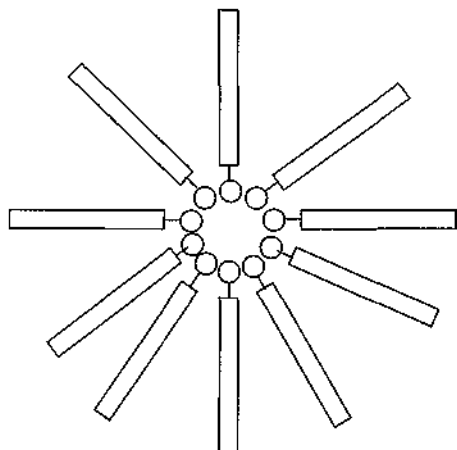
SOLUTION

6.1 i)



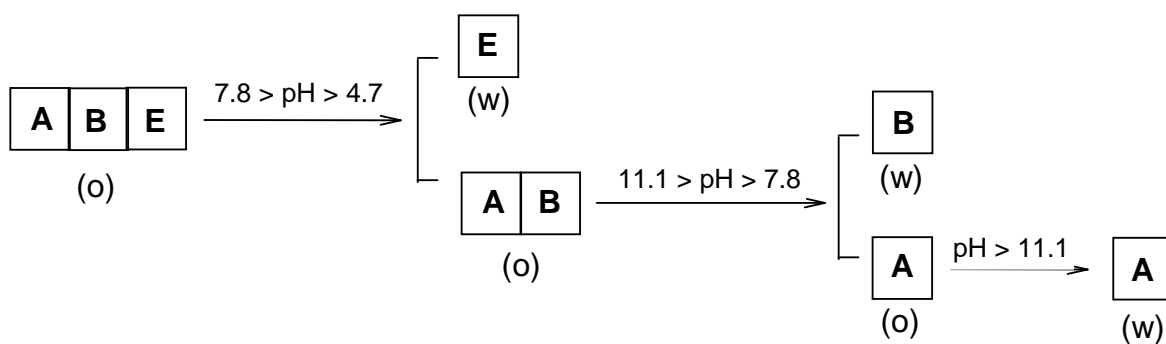
ii) (b)

6.2 i)



6.3 A, B, and E.

6.4



PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Identification of Unknown Solutions**

You are supplied with five different solutions contained in five test tubes labelled as A, B, C, D and E, respectively. The solution in each test tube contains one of the following compounds:



Identify these solutions.

Reagents

H_2SO_4 (conc.)	H_2SO_4 (6 mol dm ⁻³)
HNO_3 (conc.)	HNO_3 (6 mol dm ⁻³)
HCl (conc.)	HCl (6 mol dm ⁻³)
$\text{Ba}(\text{OH})_2$ (satd.)	NaOH (6 mol dm ⁻³)
BaCl_2 (0.5 mol dm ⁻³)	$\text{Ba}(\text{NO}_3)_2$ (0.5 mol dm ⁻³)

NOTES:

- (1) You can only select the provided reagents and use a procedure as simple as possible to complete your task. You are getting a mark not only according to the correct identification, but also to the number of steps you have taken.
- (2) You have to carry out the whole analysis by using the provided amount of these unknown solutions. Supplement of them will be available, but it will reduce the mark you obtain.

PROBLEM 2 (Practical)**Preparation of cis-Copper-bis-Glycinate Hydrate [Cu(gly)₂·xH₂O]**

Copper(II) amino acidate coordination compounds are monomeric units for synthesizing important biopolymers such as metalloenzymes like ceruloplasmin, on which every living organism depends. In laboratory cis-copper-bis-glycinate hydrate can be produced by the reaction of cupric hydroxide with glycine at a temperature of ca. 70 °C.

Reagents:

CuSO₄ · 5 H₂O(s)

NH₃ (aq) (3 mol dm⁻³)

glycine(s)

95% ethanol,

acetone

NaOH (2 mol dm⁻³)

BaCl₂ (0.5 mol dm⁻³)

1. Preparation of Cu(OH)₂

Procedure:

- (1) Dissolve your pre-weighted sample of CuSO₄ · 5 H₂O (6.0 g) in 40 cm³ of water with a 250 cm³ beaker as a container.
- (2) Add slowly 3 mol dm⁻³ ammonia solution to the CuSO₄ solution, gently stirring, until the precipitate is completely dissolved and the solution is turning blue-violet.
- (3) Add 2 mol dm⁻³ NaOH solution to the above solution until no more precipitate formed.
- (4) Filter the precipitate over a Büchner funnel under reduced pressure. Wash the precipitate with water until no SO₄²⁻ ion is detected in the filtrate.
- (5) Collect Cu(OH)₂ for the preparation of Cu(gly)₂ · x H₂O.

Write the equations for the main chemical reactions having taken place in the above procedure.

2. Preparation of cis-Copper-bis-Glycinate Hydrate

Procedure:

- (1) Dissolve a pre-weighted sample of glycine (3.6 g) in 130 cm³ of water and then warm the solution in a hot water bath (70 °C). Add the Cu(OH)₂ to the solution, stir gently until the precipitate is dissolved. Perform a hot filtration and add 10 cm³ of 95 % ethanol.
- (2) Cool the solution and when needle-like crystals appear, place it in the ice water bath for 10 min.
- (3) Filter the crystals over a Büchner funnel under reduced pressure, wash once with 10 cm³ of ethanol-water mixing solvent and then twice with 10 cm³ acetone, squeeze the crystals as dry as possible on the funnel.
- (4) Collect the crystals to a watch glass and dry it (consult your supervisor).
- (5) Half an hour later weigh the product. Write the mass of product and the percentage of yield on your student's report. Give the expressions for calculation to show how you calculate.

SOLUTION

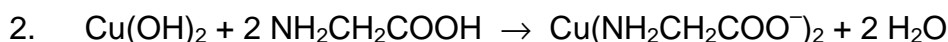
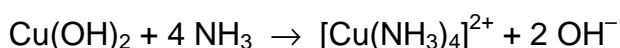
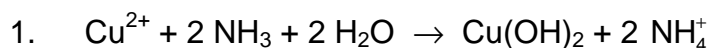
The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield in g.
- The yield obtained as a percentage of the theoretical yield.

Tasks:

Write down the balanced chemical equations used in the preparation:

Solution of the tasks:



PROBLEM 3 (Practical)**Determination of Copper(II) Content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$**

The Cu(II) content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$ crystals prepared yourself can be determined by iodometry with starch solution as indicator. Based on the data obtained one can calculate

the moles of hydrate in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$.

Reagents:

Standard KIO_3 (see the label on the bottle to get the accurate concentration)

H_2SO_4 (1.0 mol dm^{-3}) as indicator.

KI (0.6 mol dm^{-3})

KSCN (2 mol dm^{-3})

Starch (0.5 %)

$\text{Na}_2\text{S}_2\text{O}_3$ (to be standardized)

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution

Procedure

- (1) Transfer 25.00 cm^3 of standard KIO_3 solution to an Erlenmeyer flask.
- (2) Add 5 cm^3 of water, 10 cm^3 of KI solution and 5 cm^3 of H_2SO_4 (1.0 mol dm^{-3}) to the flask.
- (3) Titrate immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution.
- (4) Add 2 cm^3 starch solution when the colour of the titrand turns pale yellow.
- (5) Continue titrating until the blue colour of the solution disappears.
- (6) Proceed with step (1) – (5) twice parallel.

2. Determination of Cu(II) content in $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$

- (1) Weigh $1.0 - 1.2 \text{ g}$ (precision of $\pm 0.0002 \text{ g}$) of $\text{Cu}(\text{gly})_2 \cdot x \text{H}_2\text{O}$ with a dry 100 cm^3 beaker as the container.
- (2) Dissolve it with 40 cm^3 of water and 8 cm^3 of H_2SO_4 (1.0 mol dm^{-3}).
- (3) Transfer the above solution quantitatively to a 100 cm^3 volumetric flask and dilute to the mark.

- (4) Transfer 25.00 cm³ of the Cu(II) solution to an Erlenmeyer flask, add 50 cm³ of water and 10 cm³ of KI solution to the flask.
- (5) Titrate immediately with standardized Na₂S₂O₃ solution.
- (6) Add 2 cm³ of starch solution and 3 cm³ of KSCN solution to the flask when the colour of the titrand turns from brown to pale yellow.
- (7) Titrate continuously until the blue colour of the solution disappears.
- (8) Proceed with steps (4) – (7) twice parallel.

SOLUTION

The following values were required to be written on the Answer Sheet :

Part 1

- Volumes of Na₂S₂O₃ solution
- Calculation of the concentration of Na₂S₂O₃ solution.

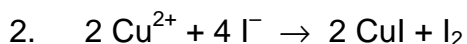
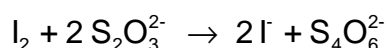
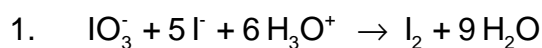
Part 2

- Mass of the product.
- Volumes of Na₂S₂O₃ solution
- Mass % of Cu(II) in Cu(gly⁻)₂ · x H₂O. Calculation.
- The value of x in the formula of the product. Calculation.

Other Tasks:

1. Write two equations for chemical reactions taking place during the standardization of Na₂S₂O₃ solution.
2. Write the equation for the reaction between Cu²⁺ and I⁻.

Solutions of the tasks:



28th



International Chemistry Olympiad

**7 theoretical problems
2 practical problems**

THE TWENTY-EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD 14--23 JULY 1996, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

The stereoregular polymerization of unsaturated hydrocarbons is usually considered as one of the most important for the industrial organic chemistry. The salts of big nonlinear cations carrying a sufficiently high charge to attack the electron density distributed along the π -bonds of the olefin molecules are usually used as the catalysts in these processes. Chloroaluminate anions (like AlCl_4^-) possessing a highly delocalized negative charge are used usually as the anions. The necessity to develop new catalysts of this kind urged the chemists to study the interaction in the system A - B, where A = Te(cryst.) and B = $(\text{TeCl}_4 + 4 \text{AlCl}_3)$. The second component B was considered as an analog of Te(IV) chloroaluminate $\text{Te}[\text{AlCl}_4]_4$ which, however, cannot be isolated as an individual compound. It was found out that the interaction of the components A and B can lead to the formation of three new compounds (**I**, **II** and **III**) in the systems containing initially 77.8, 87.5 and 91.7 mol. % of the component A, respectively. It was also noticed that while in the case of compounds **II** and **III** no side products were formed, the formation of **I** was accompanied by the evolution of 1 mole of volatile TeCl_4 per two moles of **I**.

The compounds **I** and **II** attracted a particular interest of investigators. They both have pinkish-purple color and both dissociate into three ions as the conductivity studies in melted NaAlCl_4 showed. The cryoscopic measurements in NaAlCl_4 melt enabled to determine the molecular weights of these compounds being equal to $1126 \pm 43 \text{ g mol}^{-1}$ and $867 \pm 48 \text{ g mol}^{-1}$ for **I** and **II**, respectively. In the IR spectra of both compounds there is only one band observed which can be attributed to a vibration mode of a bond formed by Te atom. This band lies at 133 cm^{-1} and is therefore so low in energy that this bond undoubtedly is a kind of Te - Te interaction. The ^{27}Al NMR data for the complexes **I** and **II** show that in each compound there is only one type of tetrahedrally coordinated

aluminum. However, the observed chemical shifts of aluminium for the compounds **I** and **II** are different, thus manifesting that Al atoms are different in them.

- 1.1 Determine Te : Al : Cl minimal atomic ratio for the complexes **I**, **II** and **III**.
- 1.2 Write the molecular-formulae of the compounds **I** and **II**.
- 1.3 Write the formulae of the anions and cations in compounds **I** and **II**.
- 1.4 Draw stereochemical formulae of cations and anions in the structures of **I** and **II** assuming that the cations in **I** and **II** are examples of inorganic aromatic systems.
- 1.5 Which compound has a higher thermal stability, **I** or **II**, taking into account that AlCl_3 is extremely volatile compound.
- 1.6 If one of the compounds **I** or **II** can be transformed into the other by heating, write the corresponding reaction equation.

SOLUTION

- 1.1 Te : Al : Cl ratios:

Compound I 2 : 2 : 7

Compound II 2 : 1 : 4

Compound III 3 : 1 : 4

solution:

The determination of the Te : Al : Cl ratios can be made using the data on the content of Te(cryst.) thus:

77.8 % of Te(cryst.) corresponds to $\text{Te}(\text{cryst.}) + 2 \text{TeCl}_4 + 8 \text{AlCl}_3$ and the minimum atomic ratio for the composition from which the excess of TeCl_4 is not subtracted is Te : Al : Cl = 9 : 8 : 32, where the contents of Al and Cl are even and can be divided by 4, while that of Te exceeding the analogous even number by 1. Subtracting one mole of TeCl_4 from the obtained ratio and dividing by 2 we obtain $4 \text{Te} + 4 \text{Al} + 14 \text{Cl}$ and the ratio is Te : Al : Cl = 2 : 2 : 7, which can be then verified by comparison with the molecular weight given 87.5 % of Te(cryst.) corresponds to $7 \text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4 \text{AlCl}_3 = 8 \text{Te} + 4 \text{Al} + 16 \text{Cl}$ and the ratio is Te : Al : Cl = 2 : 1 : 4. 91.7 % of Te(cryst.) corresponds to $11 \text{Te}(\text{cryst.}) + \text{TeCl}_4 + 4 \text{AlCl}_3 = 12 \text{Te} + 4 \text{Al} + 16 \text{Cl}$ and the ratio is Te : Al : Cl = 3 : 1 : 4.

- 1.2 The molecular formulae of compounds **I** and **II**:

Compound I: $\text{Te}_4\text{Al}_4\text{Cl}_{14}$

Compound II: $\text{Te}_4\text{Al}_2\text{Cl}_8$

Molecular formulae can be deduced from the data on molar weights. Both correspond to double simplest formula.

For compound I: 2 ($\text{Te}_2\text{Al}_2\text{Cl}_7$) gives calculated $M_r = 1114.7$ while experimental value is 1126 ± 43 .

For compound II: 2 (Te_2AlCl_4) gives calculated $M_r = 848$ while experimental value is 867 ± 48 .

1.3 Cations and anions in compounds I and II:

Compound I: $[\text{Te}_4]^{2+} [\text{Al}_2\text{Cl}_7]^-$

Compound II: $[\text{Te}_4]^{2+} [\text{AlCl}_4]^-$

The compositions of the ions included in the structures of **I** and **II** can be determined by taking into consideration that both **I** and **II** are tri-ionic electrolytes, and the fact that all the tellurium atoms should be equivalent according to IR and are bonded only to each other. The Al atoms are in both compounds tetrahedrally coordinated and equivalent. At least in one case this can be AlCl_4^- anion which seems probable for **II**, which therefore can be formulated as $[\text{Te}_4]^{2+}[\text{AlCl}_4]_2^-$. As according to similar colouration the cations are likely to be the same in both cases, the structure of **I** should contain $[\text{Te}_4]^{2+}$ cations and $[\text{Al}_2\text{Cl}_7]^-$ anions, which seems also to be in a good agreement with NMR data, assigning to Al atoms in **I** with a different tetrahedral geometry than that in **II**.

1.4 The geometry of the cation:

$[\text{Te}_4]^{2+}$ is a plane square due to proclaimed aromaticity.

The plane square configuration appears to be more favourable because the cation is mentioned to be aromatic, which means planar and possessing equal bond lengths for the sides of the corresponding aromatic ring.

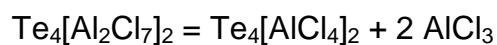
The geometry of anions:

AlCl_4^- is a single tetrahedron;

Al_2Cl_7^- - there are two tetrahedra sharing a common vertex (a chlorine atoms).

1.5 The thermal stability of **II** should be higher than that of **I**. They both are ionic compounds with high melting points, but compound **I** can be transformed into **II** by the elimination of AlCl_3 , which is a volatile solid and can be relatively easily removed on heating.

1.6 The reaction equation:



PROBLEM 2

The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the least mass of an element which can be determined by a given method with a given accuracy.

As an example we shall consider the method used for the determination of microscopic amounts of bismuth. In 1927 German chemist Berg suggested to precipitate bismuth as a practically insoluble salt: 8-hydroxyquinolinium tetraiodobismuthate $[\text{C}_9\text{H}_6(\text{OH})\text{NH}][\text{BiI}_4]$ ($M_r = 862.7$).

2.1 a) Draw the structural formulae of the cation and anion of this salt.

b) What is the oxidation state of Bi atom in this compound?

2.2 Evaluate the smallest mass of bismuth (in *mg*), which can be determined reliably by Berg method, if the smallest mass of precipitate which can be reliably measured is 50.0 mg.

For the determination of trace amounts of bismuth R. Belcher and co-workers from Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount ($\approx 2 \text{ cm}^3$) of cold acidified solution containing trace amounts of Bi^{3+} 50 mg of potassium hexathiocyanatochromate(III) ($\text{K}_3[\text{Cr}(\text{SCN})_6]$) is added in the cold, that leads to practically quantitative precipitation of bismuth.

2.3 Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 cm^3 of 10 % solution of sodium hydrogen carbonate. Upon this treatment the initial precipitate transforms into the precipitate of oxobismuth(III) carbonate $(\text{BiO})_2\text{CO}_3$ with liberation of hexathiocyanatochromate(III) ions into solution.

2.4 Write a balanced net ionic equation of this reaction.

Step 3: To the slightly acidified filtrate transferred to a separatory funnel 0.5 cm^3 of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidizes the ligand of the complex ion to ICN and sulphate ion.

2.5 Write a balanced net ionic equation of this reaction.

Step 4: Upon 5 minutes 4 cm³ of 2 M H₂SO₄ solution are added to the mixture. The acidification leads to the reaction of coproportionation with the evolution of molecular iodine.

2.6 Write a balanced net ionic equation of the reaction occurred on acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. Aqueous layer is transferred to a flask, to which 1 cm³ of bromine water is added, and the mixture is mixed for 5 minutes.

2.7 Write the balanced net ionic equations of the reactions occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidized into IO₃⁻.

Step 6: To eliminate an excess of molecular bromine 3 cm³ of 90 % methanoic (formic) acid is added to the mixture.

2.8 Write a balanced net ionic equation of this reaction.

Step 7: To the slightly acidic solution an excess (1.5 g) of potassium iodide is added.

2.9 Write the balanced net ionic equations of the reactions occurred upon the addition of KI, taking into consideration that iodide reacts with BrCN in a similar manner as with ICN to form molecular iodine.

Step 8: The resulting solution is titrated by a standard 0.00200 M Na₂S₂O₃ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

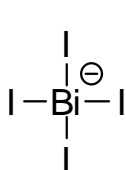
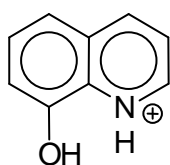
2.10 a) How many moles of thiosulphate are equivalent to 1 mol of bismuth in the initial sample?

b) What is the least mass of bismuth which can be determined by this method (assume that reliable determination requires no less than 1 cm³ of standard 0.00200 M Na₂S₂O₃ solution)?

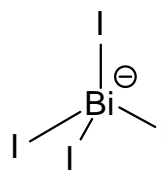
2.11 By how many times the multiplicative method just described is more sensitive than Berg's gravimetric method?

SOLUTION

2.1 a)



or



Cation

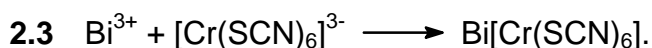
Anion

b)

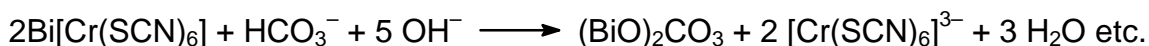
The oxidation number of bismuth in 8-hydroxyquinolinium tetraiodobismuthate: **III**

2.2 The smallest mass of bismuth determined reliably by Berg method, 12.1 mg.

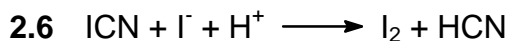
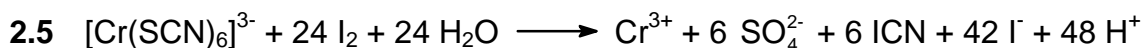
Molar mass of the precipitate is 862.7 g, which contains 209.0 g of bismuth. Thus, 0.0500 g of the precipitate correspond to 1.21×10^{-2} g = 12.1 mg of bismuth.



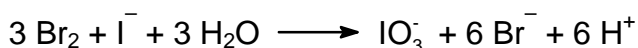
or



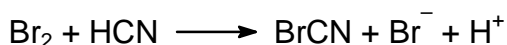
(variations are possible)



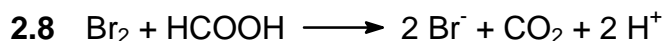
2.7 a)



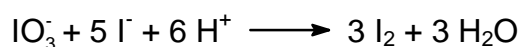
b)



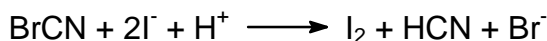
Comment. From reaction 2.5 it is evident that considerably more of ions I^- are formed than of ICN molecules. Therefore, after the completion of reaction 2. 6 an excess of I^- ions will be left.



2.9 a)



b)



2.10 a)

228 moles of thiosulphate correspond to 1 mole of bismuth.

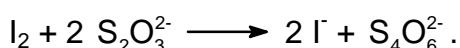
b)

The least mass of bismuth, $1.83 \cdot 10^{-3}$ mg

Solution:

a)

Titration of iodine by thiosulphate involves the reaction:



Assume that the initial solution contained 1 mole of Bi. In the reaction 5 each mole of Bi leads to the formation of 42 moles of iodide (for convenience divide all coefficients of reaction 4 by 2), of which 6 moles of iodide-ion was consumed in reaction 2.6. Thus, 36 moles of iodide was consumed in reaction 2.7a) to give 36 moles of IO_3^- , which in reaction 2.9a) gave $36 \times 3 = 108$ moles of I_2 , which take $108 \times 2 = 216$ moles of thiosulphate for titration. However, that is not all. Indeed, 6 moles of HCN are generated per mole of Bi^{3+} according to reactions 2.5 and 2.6. The oxidation of HCN by bromine in reaction 2.7b) gives 6 moles of BrCN, which in its turn in reaction 2.9b) gives 6 moles of iodine taking 12 more moles of thiosulphate. Thus, total amount of thiosulphate is $216 + 12 = 228$.

b)

1.00 cm^3 of 0.00200 M thiosulphate solution contains 2.00×10^{-6} mole of $\text{Na}_2\text{S}_2\text{O}_3$, which corresponds to $209.0 \times 2.00 \times 10^{-6} / 228 = 1.83 \times 10^{-6} \text{ g} = 1.83 \times 10^{-3} \text{ mg} = 1.83 \text{ } \mu\text{g}$.

2.11 $\frac{\text{Detection limit of gravimetric method}}{\text{Detection limit of multiplied method}} = 6600$

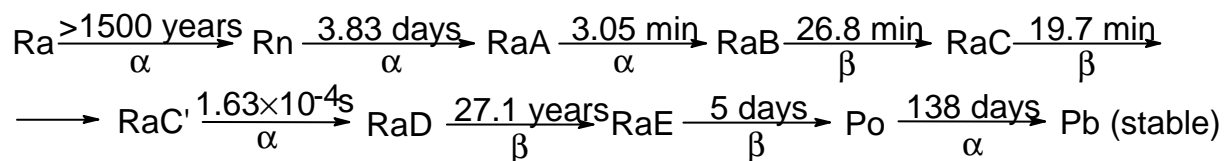
The multiplicative method is more sensitive than the gravimetric method by $12.1 \text{ mg} / 1.83 \times 10^{-3} \text{ mg} = 6600$ times.

PROBLEM 3

In 1908 Rutherford together with H. Geiger measured the rate of emission of α -particles (x) by radium (in the nature this element is represented by a single nuclide ${}^{226}_{88}\text{Ra}$) and found that 1.00 g of radium emits $x = 3.42 \times 10^{10}$ α -particles per second.

In 1911 Rutherford and American physical chemist B. Boltwood measured the rate of formation of helium from radium. This experiment permits to obtain the most accurate value of Avogadro's number available at that time, given that the value of molar volume of ideal gas was well established. To achieve this goal a sample of radium salt purified from decay products and containing $m = 192$ mg of Ra was put into a device and the volume of the evolved helium was measured. After 83 days ($t = 83.0$ days) of the experiment 6.58 mm^3 of He was collected ($V_{\text{He}} = 6.58 \text{ mm}^3$ corrected to 0° C and 1 atm).

To understand the results of this experiment we shall need the kinetic scheme of radioactive decay of Ra which is given below (half-lives are over the arrows, the type of decay is below the arrows).



(RaA -RaE are intermediate products of radon decay).

3.1 Write the first six radioactive decays using a modern notation showing atomic and mass numbers of all nuclei involved.

As a rough first approximation half-lives of all radium decay products, except those of RaD and Po, may be assumed to be negligible compared to the time of measurement t . Using this approximation perform the following calculations.

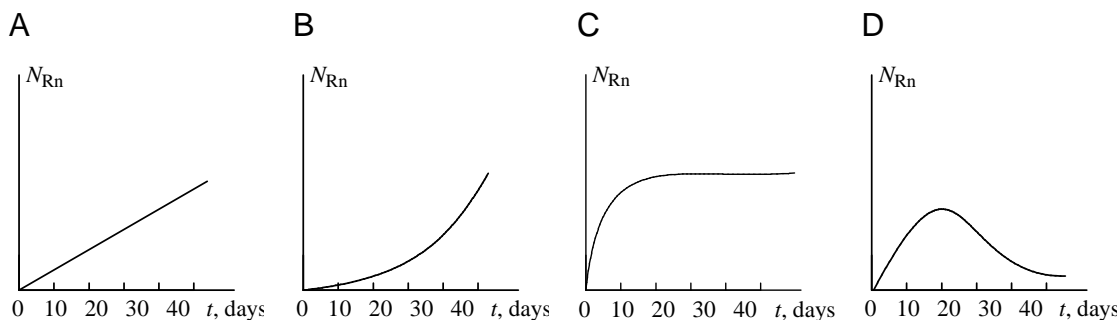
3.2 a) How many helium atoms were formed from each decayed radium atom after 83 days?

b) How many helium atoms were formed in total during the experiment?

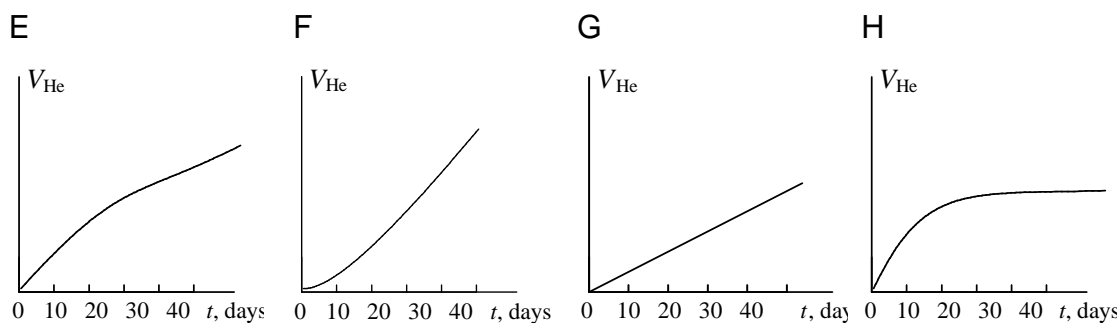
3.3 Calculate an approximate value of Avogadro's number from the above data.

For a more accurate computation of Avogadro's number the half-life of radon $T_{1/2}(\text{Rn}) = 3.83$ days cannot be neglected as it is comparable with the duration of experiment t and not all of radon atoms decayed to the end of experiment.

3.4 Choose which of the plots given below displays the time dependence of the number N_{Rn} of radon atoms in the course of the experiment.



3.5 Choose which of the plots given below shows the time dependence of the volume of helium in the course of the experiment.



3.6 Choose the relation between the decay rate k of any given nuclide and its half-life $T_{1/2}$.

3.7 a) Using a short kinetic scheme



(where k_1 and k_2 are the rate constants of the corresponding reactions) and the plot which you have selected in question 4, write a relation between the number of radon atoms at the end of experiment N'_{Rn} and the number of radium atoms N_{Ra} .

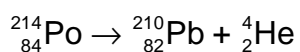
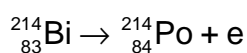
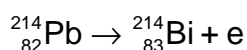
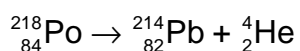
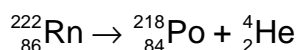
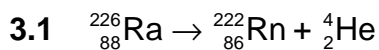
b) Calculate N'_{Rn} using the rate of radium decay given above ($x = 3.42 \times 10^{10}$ α -particles per gram of radium per second).

3.8 How many helium atoms could be formed from radon atoms remaining at the end of experiment N'_{Rn} , if all these atoms had decayed to RaD?

3.9 Using the solutions of the above questions calculate a better approximation to:

- the number of helium atoms formed;
- the Avogadro's number.

SOLUTION



3.2 a) The correct answer: 4

b) Number of helium atoms (rough 1.9×10^{17} estimate)

$$N_{\text{He}} = 4 \times m \times t = 1.9 \times 10^{17}$$

3.3 The first estimate of Avogadro's number: $6.4 \times 10^{23} \text{ mol}^{-1}$

Solution: The Avogadro's number N_A is the number of particles in one mole.

$N_A = N_{\text{He}} / \nu_{\text{He}}$, where N_{He} is number of helium atoms, and ν_{He} is the number of moles of helium formed within time t . If we assume that all radon atoms formed from radium atoms decayed during the time of experiment (this assumption follows from the assumption that radon half-life can be neglected in comparison with 83 days, that introduces an error of about 5 %), then we obtain that during time t the number of helium atom emitted is $N_{\text{He}} = 4xmt$, and

$$N_A = \frac{4 \times m \times t}{\nu_{\text{He}}} = \frac{4 \times 3.42 \times 10^{10} \times 0.192 \times (83 \times 24 \times 3600)}{6.58 \times 10^{-6} / 22.4} = 6.4 \times 10^{23} \text{ mol}^{-1}.$$

3.4 Correct answer: **C**.

The number of radon atoms reaches a quasi-stationary state which is sometimes called as the radioactive equilibrium.

3.5 Correct answer: **F**.

In the beginning helium is formed only from α -particles emitted by radium, but to the end of the experiment α -particles are emitted both by radium and by decay products, the amount of which is four times that of radium.

3.6 Underline the correct answer:

$k = 1 / T_{1/2}$	<u>$k = \ln 2 / T_{1/2}$</u>	$k = \ln 2 \cdot T_{1/2}$	$k = \pi / T_{1/2}$
-------------------	---	---------------------------	---------------------

3.7 a) Underline the correct answer:

<u>$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2$</u>	$N'_{\text{Rn}} = k_2 \cdot N_{\text{Ra}} / k_1$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 2k_2$	$N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / 3k_2$
--	--	---	---

The number of radon atoms reaches a quasi-stationary state, at which the rate of formation is equal to the rate of decay $k_2 N'_{\text{Rn}} = k_1 N_{\text{Ra}}$, whence $N'_{\text{Rn}} = k_1 \cdot N_{\text{Ra}} / k_2$

b) $N'_{\text{Rn}} = 3.14 \times 10^{15}$

The rate of radium decay is $k_1 N_{\text{Ra}} = xm$, whence

$$N'_{\text{Rn}} = \frac{xm}{\ln 2} = \frac{3.42 \times 10^{10} \times 0.192}{0.693} = 3.14 \times 10^{15}$$

$$T_{1/2(\text{Rn})} \quad 3.83 \times 24 \times 3600$$

3.8 Underline the correct answer:

$4N'_{\text{Rn}}$	$2N'_{\text{Rn}}$	$5N'_{\text{Rn}}$	N'_{Rn}	<u>$3N'_{\text{Rn}}$</u>
-------------------	-------------------	-------------------	------------------	-------------------------------------

3.9 a) A more accurate estimate of the number of helium atoms: 1.79×10^{17}

$$N_{\text{He}} = 4 xmt - 3 N'_{\text{Rn}} = 1.9 \times 10^{17} - 3 \times 3.14 \times 10^{15} = 1.79 \times 10^{17}$$

 b) A more accurate estimate of Avogadro's number (mol^{-1}): 6.09×10^{23}

$$N_A = \frac{N_{\text{He}}}{n(\text{He})} = \frac{1.79 \times 10^{17}}{\frac{6.58 \times 10^{-6}}{22.4}} = 6.09 \times 10^{23}$$

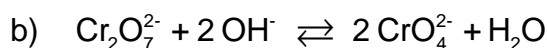
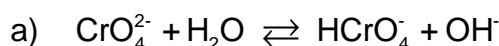
PROBLEM 4

The precipitation is widely used in classical methods of the quantitative and qualitative analysis for the separation of ions. The possibility of separation is determined by the equilibrium concentrations of all species in a solution to be analyzed.

Potassium dichromate is one of the most widely used precipitating reagents. The following equilibria are established in aqueous solutions of Cr(VI).



4.1 Calculate the equilibrium constants



The ionic product of water $K_W = 1.0 \times 10^{-14}$.

4.2 In what direction shall the equilibrium state 1b shift upon the addition of the following reagents to the aqueous solution of potassium dichromate?

- KOH
- HCl
- BaCl₂
- H₂O

The solubility product of BaCrO₄ is 1.2×10^{-10} . BaCr₂O₇ is well soluble in water.

4.3 Calculate the pH value of the following solutions

- 0.010 M K₂CrO₄
- 0.010 M K₂Cr₂O₇
- 0.010 M K₂Cr₂O₇ + 0.100 M CH₃COOH

Dissociation constant of acetic acid $K_a = 1.8 \times 10^{-5}$.

4.4 Calculate the equilibrium concentrations of the following ions in the solution of 0.010 M K₂Cr₂O₇ + 0.100 M CH₃COOH

- CrO₄²⁻
- Cr₂O₇²⁻

Pb²⁺ and Ag⁺ form poorly soluble compounds with chromate and dichromate ions.

The solubility products of these compounds are indicated below.



To the aqueous solution of the mixture of 1.0×10^{-3} M $\text{Pb}(\text{NO}_3)_2$ and 2.0×10^{-4} M AgNO_3 an equal volume of 0.020 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.200 M CH_3COOH was added.

- 4.5 a) Shall Pb^{2+} be precipitated?
 b) Shall Ag^+ be precipitated?
 c) Shall a quantitative separation of Pb^{2+} and Ag^+ ions be thus achieved?

The quantitative precipitation is achieved if the residual concentration of the ion being precipitated is not higher than 1×10^{-6} M.

SOLUTION

4.1

a)

Equilibrium constant = 3.2×10^{-8}

$$\frac{[\text{HCrO}_4^-][\text{OH}^-]}{[\text{CrO}_4^{2-}]} = \frac{[\text{HCrO}_4^-][\text{OH}^-][\text{H}^+]}{[\text{CrO}_4^{2-}][\text{H}^+]} = \frac{K_w}{K_1}$$

$$\frac{1.0 \times 10^{-14}}{3.16 \times 10^{-7}} = 3.2 \times 10^{-8}$$

b) Equilibrium constant $> 4.4 \times 10^{13}$

$$\frac{K_1^2}{K_2 K_w^2} = \frac{\left(\frac{[\text{CrO}_4^{2-}][\text{H}^+]}{[\text{HCrO}_4^-]} \right)^2}{\frac{[\text{HCrO}_4^-]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \cdot \left([\text{H}^+][\text{OH}^-] \right)^2} = \frac{10^{-2 \times 6.50}}{10^{1.36} \times 10^{-2 \times 14.00}} = 10^{13.64} = 4.4 \times 10^{13}$$

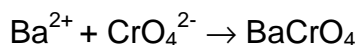
4.2 Place a checkmark at the correct answer

The equilibrium will	shift to left	shift to right	not shift
a)		<input checked="" type="checkbox"/>	
b)	<input checked="" type="checkbox"/>		
c)		<input checked="" type="checkbox"/>	
d)		<input checked="" type="checkbox"/>	

Calculations:

In case a) and b) the answer is self-evident.

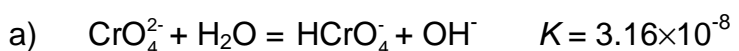
- c) BaCl_2 shifts the equilibrium to the right due to the binding of chromate ion into a poorly soluble compound



- d) This answer may appear as strange, as water is among the products specified in the right part of the equilibrium equation. However, this is too formal. Actually in dilute aqueous solutions the concentration of water may be regarded as fairly constant and the addition of water would not affect it. Nevertheless, the addition of water to dichromate solution leads to the dilution, which in its turn shifts the dichromate ion dissociation equilibrium to the right. Second, in the aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ the value of $\text{pH} < 7$ due to the processes described in the problem statement (cf. also the solution to 3b). With the dilution of any aqueous solution pH is varying towards 7, that in this case means the increase of pH . This also shifts the equilibrium to the right.

- 4.3 a) $\text{pH} = 9.25$
 b) $\text{pH} = 4.20$
 c) $\text{pH} = 2.87$

Calculations:

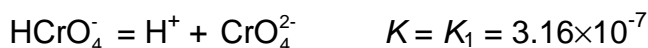


$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] \approx [\text{CrO}_4^{2-}],$$

$$[\text{HCrO}_4^-] \approx [\text{OH}^-]$$

$$[\text{OH}^-]^2/c_{\text{Cr}} = K, [\text{OH}^-] = \sqrt{K c_{\text{Cr}}} = \sqrt{3.16 \times 10^{-8} \times 0.01} = 1.78 \times 10^{-5}$$

$$[\text{H}^+] = 5.65 \cdot 10^{-10}, \quad \text{pH} = 9.25$$



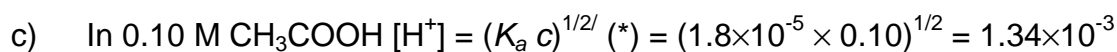
$$[\text{H}^+] \approx [\text{CrO}_4^{2-}] \Rightarrow [\text{H}^+] = \sqrt{K_1[\text{HCrO}_4^-]}$$

$$[\text{HCrO}_4^-] = ?$$

$$c_{\text{Cr}} = 2.0 \cdot 10^{-2} \text{ M (**)} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}] \approx [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}]$$

$$[\text{HCrO}_4^-] = x; \quad K_2 = [\text{Cr}_2\text{O}_7^{2-}] / [\text{HCrO}_4^-]^2 = (c_{\text{Cr}} - x) / 2x^2; \quad 2 K_2 x^2 + x - c_{\text{Cr}} = 0$$

$$\text{hence } [\text{H}^+] = (3.16 \times 10^{-7} \times 1.27 \times 10^{-2})^{1/2} = 6.33 \times 10^{-5}; \quad \text{pH} = 4.20$$



$$\text{pH} = 2.87$$

4.4 Equilibrium concentrations

a)	3.0×10^{-6}
b)	3.7×10^{-3}

Calculations:

The different methods can be used.

Method 1.

a)

$$[\text{HCrO}_4^-] = 1.3 \times 10^{-2} \text{ (*)}$$

$$[\text{CrO}_4^{2-}] = K_1[\text{HCrO}_4^-] / [\text{H}^+] = 3.16 \times 10^{-7} \times 1.3 \times 10^{-2} / 1.34 \times 10^{-3} = 3.0 \times 10^{-6}$$

b)

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2 [\text{Cr}_2\text{O}_7^{2-}]$$

$$[\text{Cr}_2\text{O}_7^{2-}] = \frac{1}{2}(c_{\text{Cr}} - [\text{CrO}_4^{2-}] - [\text{HCrO}_4^-]) = \frac{1}{2}(2.0 \times 10^{-2} - 3.0 \times 10^{-6} - 1.3 \times 10^{-2}) = 3.7 \times 10^{-3}$$

or otherwise

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-]^2 = 22.9 \times (1.3 \times 10^{-2})^2 = 3.9 \times 10^{-3}$$

Method 2

a)

$$[\text{CrO}_4^{2-}] = x; [\text{HCrO}_4^-] = x[\text{H}^+] / K_1$$

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = x^2 K_2 [\text{H}^+]^2 / K_1^2$$

$$c_{\text{Cr}} = [\text{CrO}_4^{2-}] + [\text{HCrO}_4^-] + 2[\text{Cr}_2\text{O}_7^{2-}] = 2K_2 [\text{H}^+]^2 / K_1^2 x^2 + (1 + [\text{H}^+] / K_1)x$$

$$K_1 = 3.16 \times 10^{-7}; K_2 = 22.9; [\text{H}^+] = 1.34 \times 10^{-3}$$

$$8.24 \times 10^8 x^2 + 4.24 \times 10^3 x - 2.0 \times 10^{-2} = 0$$

$$x = 3.0 \times 10^{-6}$$

b)

$$[\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-] = K_2 [\text{H}^+]^2 / K_1^2 [\text{CrO}_4^{2-}]^2 = 4.12 \times 10^8 \times (3.0 \times 10^{-6})^2 = 3.7 \times 10^{-3}$$

PROBLEM 5

Potentiometric and spectrophotometric methods are widely used for the determination of equilibrium concentrations and equilibrium constants in solution. Both methods are frequently used in combination to achieve simultaneous determination of several species.

Solution I contains a mixture of $\text{FeCl}_2(\text{aq})$ and $\text{FeCl}_3(\text{aq})$, and solution II contains a mixture of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$. The concentrations of iron-containing species satisfy the relations $[\text{Fe}^{2+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{4-}]_{\text{II}}$ and $[\text{Fe}^{3+}]_{\text{I}} = [\text{Fe}(\text{CN})_6^{3-}]_{\text{II}}$. The potential of platinum electrode immersed into the solution I is 0.652 V, while the potential of platinum electrode immersed into solution II is 0.242 V. The transmittance of the solution II measured relative to the solution I at 420 nm is 10.7 % (optical pathlength $l = 5.02$ mm). The complexes $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, and $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ do not absorb light at 420 nm.

Molar absorption at this wavelength $\varepsilon([\text{Fe}(\text{CN})_6^{3-}]) = 1100 \text{ M}^{-1} \text{ cm}^{-1}$.

Standard redox potential for $\text{Fe}(\text{H}_2\text{O})_6^{3+} / \text{Fe}(\text{H}_2\text{O})_6^{2+}$ is 0.771 V.

The factor before the logarithm in the Nernst equation is 0.0590.

5.1 Write Nernst equations for redox systems of

- solution I,
- solution II.

5.2 What are the units of the pre-logarithm factor 0.0590 in the Nernst equation?

5.3 Calculate the ratio of the stability constants $\beta[\text{Fe}(\text{CN})_6^{3-}] / \beta[\text{Fe}(\text{CN})_6^{4-}]$.

5.4 What is the absolute range of variation for the following physical values

- transmittance T ;
- absorbance A .

5.5 Sketch the graphs of concentration dependences satisfying the Lambert-Beer law for

- absorbance A ;
- transmittance T ;
- molar absorption ε .

5.6 Calculate the concentrations of

- Fe^{2+} in solution I;
- Fe^{3+} in solution II.

5.7 Mixing solutions I and II gives intense blue colour. What species is characterized by this colour? Write the reaction equation.

SOLUTION

5.1 Nernst equations:

$$\text{a) } E_1 = E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$\text{b) } E_1 = E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) + 0.0590 \log \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]}$$

5.2 The units of pre-logarithm factor: V

5.3 The ratio of stability constants

$$\beta_1\{\text{Fe}(\text{CN})_6^{3-}\} / \beta_2\{\text{Fe}(\text{CN})_6^{4-}\} = 8.90 \times 10^6$$

Calculations:

$$\begin{aligned} E_{II} &= E^\circ(\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}) + 0.0590 \log[\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}] = \\ &= E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) + 0.0590 \log(\beta_1 / \beta_2) + 0.0590 \log([\text{CN}^-]^6 / [\text{CN}^-]^6) + \\ &\quad + 0.0590 \log[\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}] = 0.242 \end{aligned}$$

(where β_1 and β_2 are stability constants for $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively.)

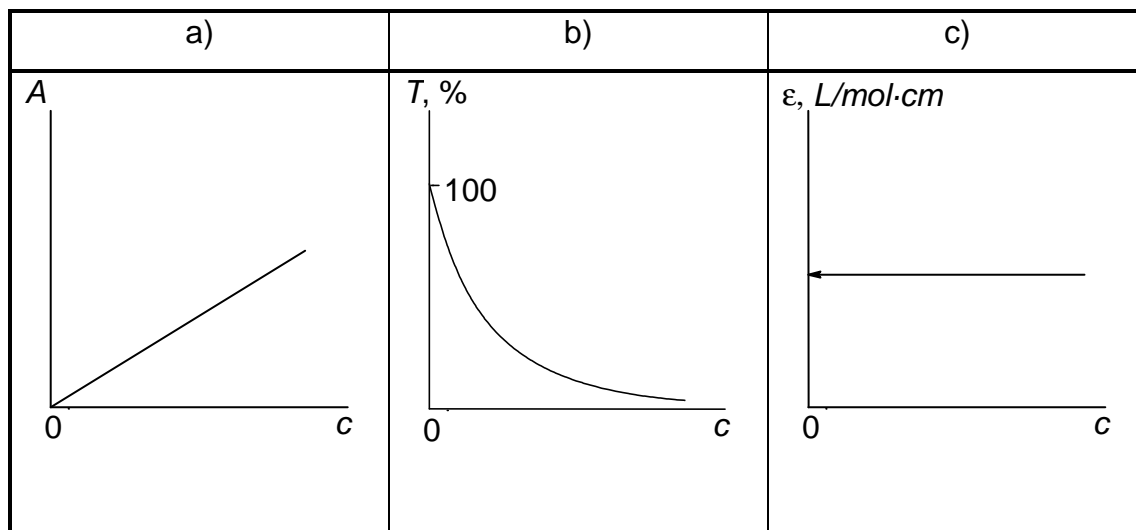
$[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}] = [\text{Fe}^{3+}] / [\text{Fe}^{2+}]$, therefore

$$\Delta E = E_{II} - E_1 = 0.0590 \cdot \log(\beta_1 / \beta_2), \text{ and } \beta_2 / \beta_1 = 8.90 \times 10^6.$$

5.4 The ranges of variation:

- a) from 0 to 100
- b) from 0 to ∞

5.5



5.6 a) Using Bouguer-Lambert-Beer law

$$A = \varepsilon / c = \varepsilon / c[\text{Fe}(\text{CN})_6^{3-}] = 0.971;$$

$$c[\text{Fe}(\text{CN})_6^{3-}] = 0.971 / (1100 \times 0.502) = 1.76 \times 10^{-3} \text{ M} = c[\text{Fe}^{3+}]$$

b) using Nernst's equation

$$\begin{aligned} E &= E^\circ(\text{Fe}^{3+} / \text{Fe}^{2+}) + 0.0590 \log [\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = \\ &= 0.771 + 0.0590 \log [\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = 0.652 \text{ V.} \end{aligned}$$

hence,

$$[\text{Fe}^{3+}]_i / [\text{Fe}^{2+}]_i = 9.62 \times 10^{-3};$$

$$[\text{Fe}^{2+}]_i = 1.76 \times 10^{-3} / 9.62 \times 10^{-3} = 0.183 \text{ M.}$$

PROBLEM 6

Two isomeric hydrocarbons **A** and **B** contain 85.7 mass % of carbon.

6.1 Write a general formula which satisfies this condition.

The hydrocarbons **A** and **B** possess the following properties. The reaction of each of the compounds with ozone with subsequent treatment of the product with zinc dust in the presence of acid gives a single organic product **C**. The oxidation of compound **C** gives a single product, the carboxylic acid **D**. According to spectral data all hydrogen atoms in this acid except the one in carboxylic group are contained in methyl groups. The density of vapours of **D** corrected to normal conditions (0 °C, 1 atm) is 9.1 g dm⁻³.

Compound **A** is more reactive than compound **B** in the reaction with cold neutral potassium permanganate. A single compound **F** is formed from **A**, and a 1 : 1 mixture of isomers **G1** and **G2** is formed from **B**.

6.2 Draw the structural formulae of the compound **D** both in aqueous solution and in vapour phase.

6.3 Write the formula of compound **C**.

6.4 Draw the structures of isomers **A** and **B**.

6.5 a) Write the reactions of the transformation of **A** or **B** into **C** and **D**.
b) Write the reactions of the transformation of **A** and **B** into **F**, **G1** and **G2**.

6.6 Compounds **G1** and **G2** readily react with acetone in the presence of acids and form compounds **H1** and **H2**. Draw the structures of **H1** and **H2**.

6.7 Compounds **A** and **B** react with bromine. One of the products of these reactions is non-polar (dipole moment of this molecule is practically equal to zero) and optically inactive. Draw the stereochemical formula of this product, and write the reaction of its formation. Determine the absolute configuration of chiral atoms in this molecule (if any) and mark them according to *R,S* nomenclature by *R* or *S* letters.

Alkenes react with peroxyacids with the addition of oxygen to double bond to form a three-member oxygen-containing ring. This epoxidation reaction is highly stereospecific to retain the relative positions of substituents at the bond to which the oxygen atom is attached.

The epoxidation of compound **A** by peroxyacetic acid yields a single compound **K**. Under the same conditions **B** gives a mixture of isomers **L1** and **L2** (the ratio is 1:1).

6.8 Is the compound **K** optically active? Draw the stereochemical formula of **K**. Are the individual compounds **L1** and **L2** optically active? Draw the stereochemical formulae of **L1** and **L2**.

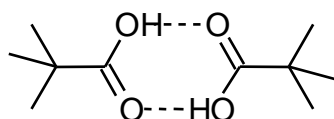
SOLUTION

6.1 The general formula: C_nH_{2n}

6.2 Compound **D**:

In aqueous solution: $(CH_3)_3CCOOH$

In vapours:

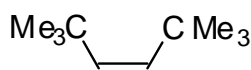


Dimeric structure in vapour phase is guessed using the value of vapour density.

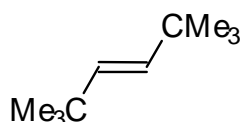
The relative molar weight in vapour phase is $9.1 \times 22.4 = 204$ which is close to double value of the molar weight of $(CH_3)_3CCOOH$. Possibly, as other simple fat acids, this acid is also dimerized in vapours.

6.3 Compound **C**: $(CH_3)_3CCHO$

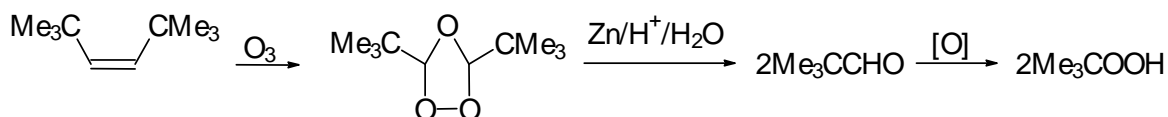
6.4 **A**:

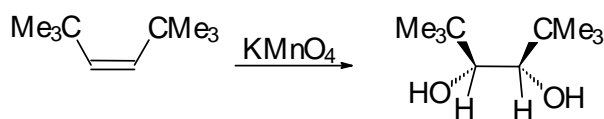
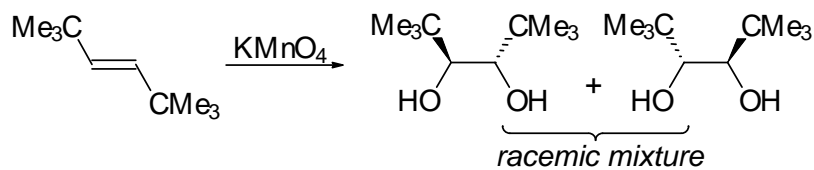


B:

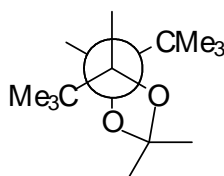


6.5

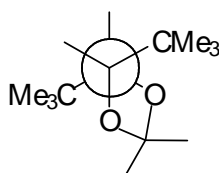


A \longrightarrow F

 B \longrightarrow G1 + G2


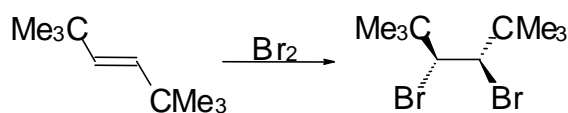
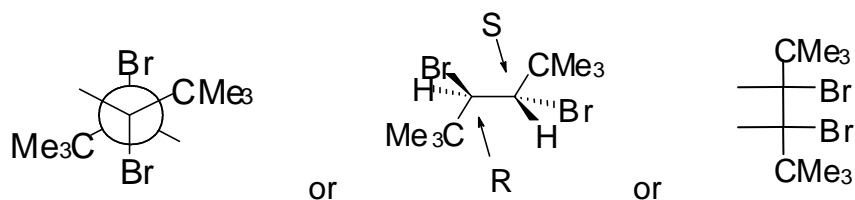
6.6 H1:



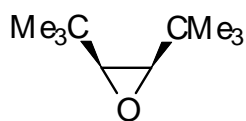
H2:



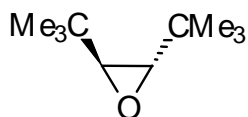
6.7 Non-polar bromination product (either of three types of structures may be given)



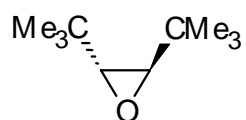
6.8 K:

 NO; The molecule is not optically active.

L1:

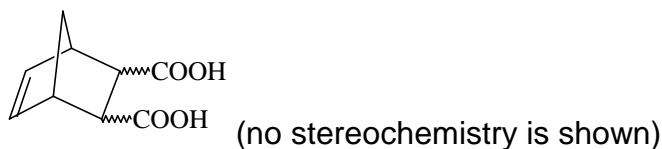
 YES; The molecule is optically active.

L2:

 YES; The molecule is optically active.

PROBLEM 7

Stereochemistry of organic compounds can sometimes be determined by studying their chemical behavior. The stereochemical configuration of one of the isomers of 5-norbornene-2,3-dicarboxylic acids (compound **X**)



was established by the following experiments.

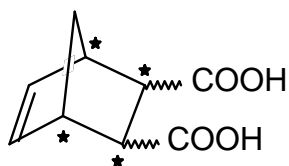
On heating this substance decomposes producing water and a new compound **Y**. Compound **Y** slowly dissolves in excess of aqueous NaOH with the formation of product **X₁** same to that is formed in the reaction of **X** with NaOH. The resulting solution of **X₁** is treated by I₂ to give compounds containing iodine. Acidification of the solution leads to a mixture of two isomeric compounds, **A** and **B** in the 3 : 1 ratio. The titration of 0.3913 g of compound **A** by 0.1000 M aqueous solution of NaOH in the presence of phenolphthalein takes 12.70 cm³ of alkali. The same amount of 0.1000 M solution of NaOH is required for the titration of 0.3913 g of compound **B**. On heating compound **A** slowly transforms into compound **C**, which contains no iodine and is able to react with water. Under the same conditions compound **B** does not undergo this transformation, but on heating with hydrochloric acid slowly transforms into **A**.

All reactions must be written as balance equations. No mechanisms are required.

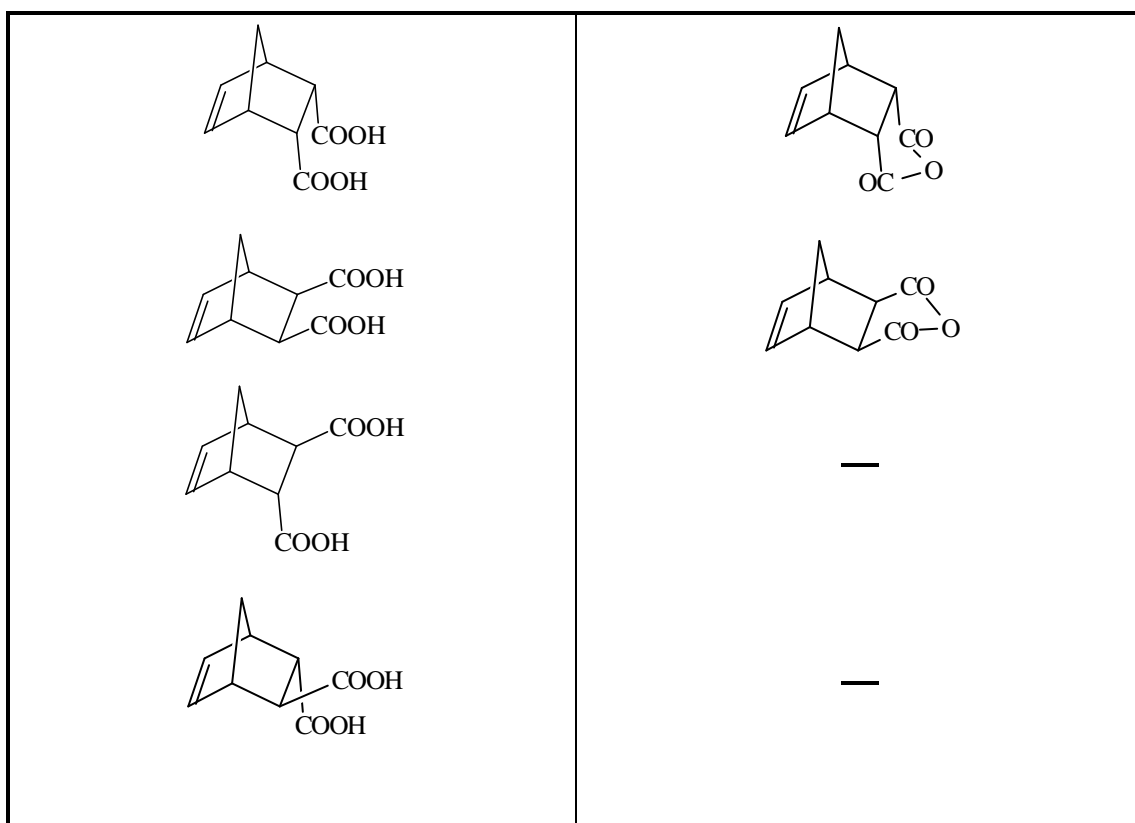
- 7.1 Mark by asterisks (*) the asymmetric carbon atoms in the structure of 5-norbornene-2,3-dicarboxylic acids.
- 7.2 Draw the stereochemical formulas of all stereoisomers of compound **X**, and the structures of products of their dehydration in those cases when it is possible.
- 7.3 Write the reactions of NaOH with a stereoisomer of **X** and a stereoisomer of **Y**.
- 7.4 Calculate the molar mass of compound **A**. Write the reactions leading from **X₁** to **A**.
- 7.5 Write the reaction of the formation of **C** from **A** and the reaction of **C** with water.
- 7.6 Draw the stereochemical formula of compound **X** which satisfies all of the data given in the problem.
- 7.7 Write the reactions leading from **B** to **A**.
- 7.8 Are the compounds **A** and **B** diastereomers?

SOLUTION

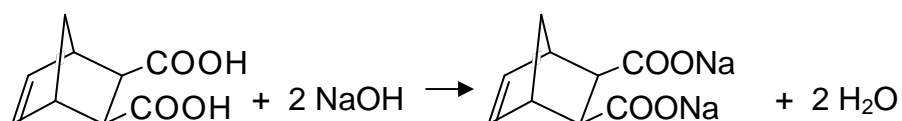
7.1



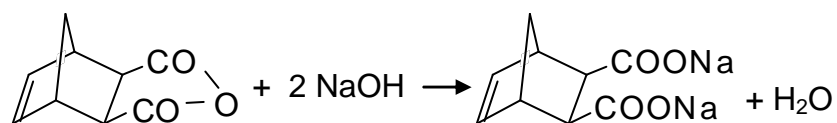
7.2 Fill in left column with the structures of stereoisomers of **X**, and the right column with the corresponding structures of dehydration products (when such structure does not exist write a minus).



7.3 The reaction of a stereoisomer of **X** with NaOH:

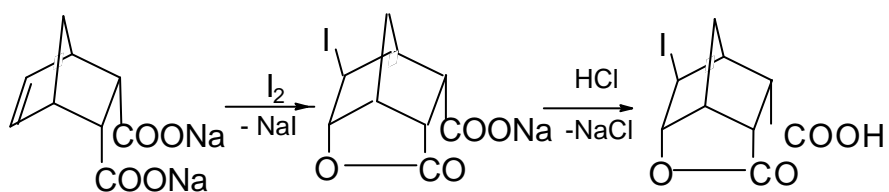


The reaction of a stereoisomer of **Y** with alkali:

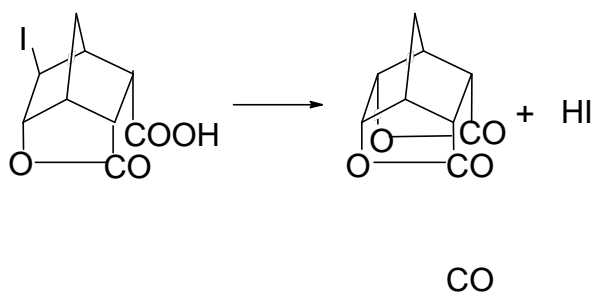


7.4 The molar mass of **A**: 308 g mol^{-1}

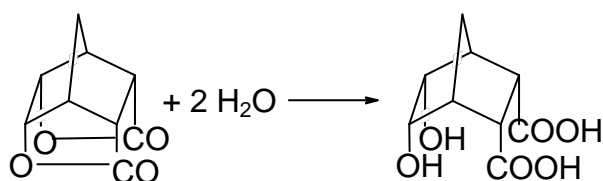
The reactions leading from **X₁** to **A**



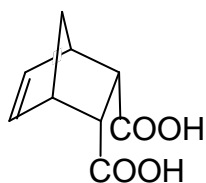
7.5 The transformation of **A** to **C**:



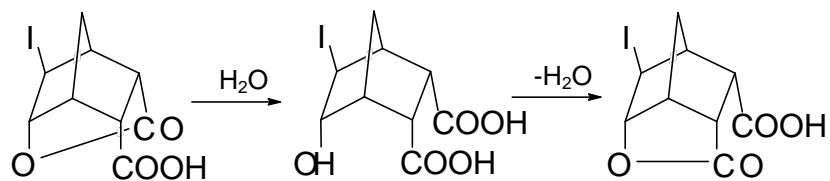
The reaction of **C** with water:



7.6 The structure of compound **X**:



7.7 The transformation of **B** to **A**:



7.8 No, **A** and **B** are not diastereomers.

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Iodometric Determination of the Concentration of Copper(II) and Iron(III) in a Sample of Technological Solution****Reagents**

- $\text{K}_2\text{Cr}_2\text{O}_7$, 0.008333 M
- KI, 20 % by mass.
- HCl, 1 M
- H_2SO_4 , 1 M
- $\text{Na}_4\text{P}_2\text{O}_7$, 5 % by mass.
- Starch, 1 % by mass.
- $\text{Na}_2\text{S}_2\text{O}_3$ (should be standardized)
- The solution to be analyzed in 100 cm³ volumetric flask.

Procedure

1. Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution
 - (1) 10 cm³ of 1 M solution of H_2SO_4 and 2 cm³ of 20 % KI solution are placed into an Erlenmeyer flask (the solution remains colourless).
 - (2) 10.00 cm³ of $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added.
 - (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
 - (4) 100 cm³ of water is added to the flask.
 - (5) The mixture is titrated immediately with $\text{Na}_2\text{S}_2\text{O}_3$ solution until the colour of mixture changes to pale yellow. Then 10 drops of starch solution are added. The titration continues until blue colour disappears completely.
 - (6) It is recommended to repeat the titration (steps 1 through 5) two more times.

Do the following and fill in the answer sheet form

- 1.1 Write the reactions involved in the procedure of standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution
- 1.2 Calculate the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and write your calculations.

2. The determination of copper

- (1) The solution to be analyzed in a 100 cm³ volumetric flask is diluted with water to the mark and stirred
- (2) A 10.00 cm³ aliquot of the solution is placed into an Erlenmeyer flask.
- (3) 20 cm³ of 5 % solution of Na₄P₂O₇, 7 cm³ of 1 M solution of HCl, and 10 cm³ of 20 % solution of KI are added. A precipitate may form upon the addition of Na₄P₂O₇.
- (4) The Erlenmeyer flask is covered with a watch glass and left in a dark place for 3 - 5 min.
- (5) The mixture is titrated immediately with Na₂S₂O₃ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.
- (6) It is recommended to repeat the titration (steps 2 through 5) two more times.

Do the following and fill in the answer sheet form

- 1.3 Write the reactions involved in the procedure of determination of Cu²⁺ ion.
- 1.4 Calculate the mass of copper in the solution under analysis, and write your calculations.

3. The determination of total amount of copper and iron

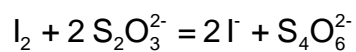
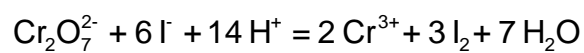
- (1) A 10.00 cm³ aliquot of the solution prepared in the item 2(1) is placed into an Erlenmeyer flask.
- (2) 2 cm³ of 1 M HCl solution and 10 cm³ of 20 % KI solution are added.
- (3) The Erlenmeyer flask is covered with a watch glass and kept in a dark place for 3 to 5 min.
- (4) The mixture is titrated immediately with Na₂S₂O₃ solution until the colour of suspension changes to pale yellow. Then, 10 drops of starch solution are added. The titration continues until the colour of suspension becomes clear white.
- (5) It is recommended to repeat the titration (steps 1 through 4) two more times.

Do the following and fill in the answer sheet form

- 1.5 Write the reactions involved in the procedure of determination of Fe³⁺ ion.
 - 1.6 Calculate the mass of iron in the solution under analysis, and write your calculations.
-

SOLUTION**1.1**

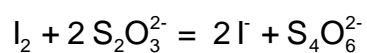
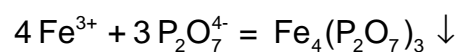
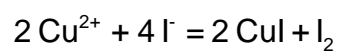
Equations:



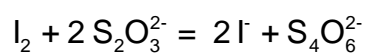
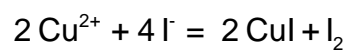
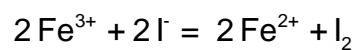
i

1.3

Equations:

**1.5**

Equations:



PROBLEM 2 (Practical)

Qualitative Determination of Paracetamol in a Sample of Unknown Drug

Introduction

Three organic compounds are most widely used as pain relieving drugs: acetylsalicylic acid (ortho-acetoxybenzoic acid), phenacetine (*para*-ethoxyacetanilide), and paracetamol (*para*-hydroxyacetanilide). Paracetamol is now the most popular, being the base of a large number of well known patented pharmaceuticals (panadol, solpadeine, coldrex, calpol, efferalgan etc.), as it is now considered as the safest and highly efficient drug.

You were given a sample of unknown drug which claims to contain paracetamol. Your task is to prove or disprove this claim experimentally. To do this you shall have to prepare an authentic sample of *para*-hydroxyacetanilide, and run a thin layer chromatography test.

Reagents

- *Para*-aminophenol, 3.10 g in a weighing beaker
- Acetic anhydride, 4.00 cm³ in an Erlenmeyer flask
- Ethanol
- Eluent (heptane : ethyl acetate : ethanol = 41 : 47 : 12 by volume)
- Sample of unknown drug in a test tube, 1 % solution in ethanol
- Water (use tap water for all purposes)

Procedure

Preparation of *para*-hydroxyacetanilide

A 50 cm³ round bottom flask is equipped with reflux condenser and installed on a laboratory stand over a hot plate. Note that the space between the top of hot plate and the bottom of flask be about 1-1.5 cm. Use two clamps to properly support the flask and condenser. Remove the hot plate. Do not switch on the hot plate until you finish with adding reagents and reassembling the apparatus. With reflux condenser temporarily removed, 3.10 g of *para*-aminophenol is placed to the flask using a funnel (use a glass rod

to push it through the funnel, if necessary). Water (10 cm³) is then added through the same funnel. The condenser is mounted back, and acetic anhydride (4.00 cm³) is carefully poured to the reaction mixture through the condenser (*attention!* acetic anhydride has a strong irritating smell. In case of spill immediately wash hands with water and ask the supervisor to help with the disposal of spilled compound). Carefully stir the contents by slightly relieving clamps and waving the flask 2 - 3 times. Be careful as the mixture and the flask gets very hot due to the reaction heat. Place back the hot plate and switch it on. The reaction mixture is heated for 15 minutes beginning from the time when you switch on the hot plate. Then, the heater is switched off and removed from the apparatus. The mixture is allowed to cool first by immersing the flask into a bath with cold tap water. You may do this immediately after you remove the plate as the flask is made of highly durable glass. After approximately five minutes unattach the condenser and pour the contents into an empty 100 cm³ pyrex glass beaker. Put the beaker into a metal dish filled with ice and water. Accurately rub the walls of beaker with spatula and observe the crystallization of crude product as small white crystals.

Assemble a suction filtration device: put the frit filter onto a rubber ring and a heavy-wall flask. Connect the flask to a suction vacuum pump and turn on water in the pump by turning tap. (*Attention!* Never turn off the water tap if your device is under vacuum. First always disconnect the flask from vacuum pump by carefully pulling off the rubber tubing from the inlet.)

The crystalline precipitate is quantitatively moved onto a filter by spatula. Remaining solid can be washed with small portions of ice cold water (as small as possible, as the compound possesses an essential solubility in water, and the losses of dissolved compound must not outweigh the losses due to incomplete transfer of product to the filter). The product in the filter is carefully washed with 2 - 3 portions of 2 - 3 cm³ of cold water by a) connecting the vacuum suction flask to the atmosphere; b) addition of water and careful mixing it with the precipitate using a spatula; c) reapplying vacuum; d) pressing the precipitate with flat tip of a glass rod to squeeze out as much water as possible.

Several crystals of material are used for chromatography test (see below). All other precipitate is moved to a sheet of filtering paper in a Petri dish, and spread out over the filter in a thin layer, and allowed to dry on a shelf to exclude accidental spill. For rapid drying it is critical to spread it as thin as possible, to break all large pieces, and to stir it

and spread again every 3-5 minutes to expose all wet crystals to air. It is established after a numerous repetition of this procedure, that after 30 min the product contains no more than 5 % of water. Such wetness is considered as insignificant for evaluating the results of the preparation.

Chromatography test

(If for some reason you have failed to obtain *para*-hydroxyacetanilide, you can obtain a sample for chromatography from your supervisor.)

While still wet several crystals of the material obtained by you are dissolved in a tube in 1 - 2 cm³ of ethanol. The unknown drug is already dissolved in ethanol and given to you as 1 % solution. These solutions are used for thin layer chromatography, as follows:

Prepare a sheet of chromatography plate covered with silica. Using a sharp pencil draw a start line and marks for sample spots. A small spot of each solution is placed on a chromatography plate using a capillary. The spots are allowed to dry for 1-2 minutes.

The plate is immersed into a beaker containing the eluent and allowed to be eluted. Use forceps to move the plate in and out of the beaker. After the elution, remove the plate from the flask, mark the front of eluent, and allow it to dry under the hood for 5 minutes. Examine the chromatogram under UV light in a special cabinet. Outline the dark spots (if there are any) with a sharp pencil.

Weighting of sample

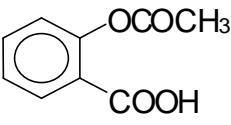
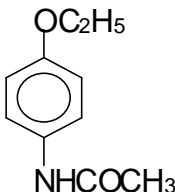
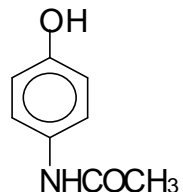
After you complete the chromatography, your product usually is almost dry and is ready for weighting. Ask you supervisor to weight an empty weighing beaker. Put the dry product into a weighted beaker and give it to the supervisor for weighting. Weights are written in your answer sheet by the supervisor. Calculate the weight of the product.

Do the following and fill in the answer sheet form

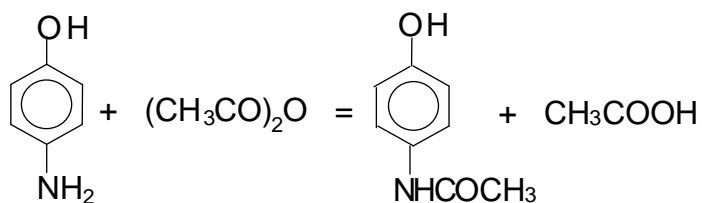
- 2.1 Draw the structures of three main pain relieving drugs mentioned above.
- 2.2 Draw the reaction equation involved in the preparation of *para*-hydroxyacetanilide. Calculate the stoichiometric amounts of reagents needed for the reaction. How much acetic anhydride is taken in excess over the stoichiometry? The density of acetic anhydride is 1.08 g cm⁻³.
- 2.3 Calculate the yield of product obtained by you.
- 2.4 Calculate and compare the values of R_f of unknown drug and your product.
- 2.5 Is it likely that paracetamol is contained in the sample of drug?

SOLUTION

2.1

Acetylsalicylic acid	Phenacetine	Paracetamol
		

2.2



2.5 Yes, the sample is likely to contain paracetamol.

29th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

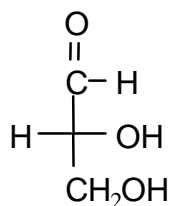
THE TWENTY-NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 13--22 JULY 1997, MONTREAL, CANADA

THEORETICAL PROBLEMS

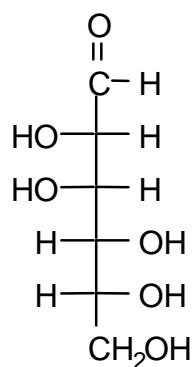
PROBLEM 1

Compound **X** is a trisaccharide which occurs principally in cottonseed meal. Compound **X** does not react with Benedict's or Fehling's solutions nor does it mutarotate. Acid-catalyzed hydrolysis gives three different D-hexoses, **A**, **B**, and **C**. Compounds **A** and **B**, as well as compound **1** (see below), all give the same osazone upon reaction with excess acidic phenylhydrazine. Compound **C** reacts with nitric acid to give an optically inactive compound **D**. The Kiliani-Fischer approach is used to establish the configurational relationship between D-glyceraldehyde and **C**. The intermediate aldotetrose which leads to **C** does not give a meso compound when oxidized by nitric acid. When **A** is treated with nitric acid, the dicarboxylic acid (aldaric acid) produced is optically active. Both **A** and **B** react with 5 moles of HIO_4 ; one mole of **A** gives 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) while one mole of **B** gives 3 moles of methanoic (formic) acid and 2 moles of methanal (formaldehyde) and one mole of carbon dioxide. Both **A** and **B** are related to the same aldotetrose which is the diastereoisomer of the one to which **C** is related. Methylation of **X** followed by hydrolysis gives a 2,3,4-tri-O-methyl-D-hexose (**E**) (derived from **A**), a 1,3,4,6-tetra-O-methyl-D-hexose (**F**) (derived from **B**), and a 2,3,4,6-tetra-O-methyl-D-hexose (**G**) (derived from **C**).

- 1.1 On the answer sheet, draw Fischer projection formulas of **A**, **B**, **C**, and **D**.
- 1.2 On the answer sheet, complete the appropriate Haworth projection formulas to clearly show the ring size and absolute stereochemistry of **E**, **F**, and **G**. Either of the anomeric forms are acceptable as an answer.
- 1.3 On the answer sheet, underline the correct representation of the connectivity sequence of the three monosaccharides present in trisaccharide **X**.



D-Glyceraldehyde

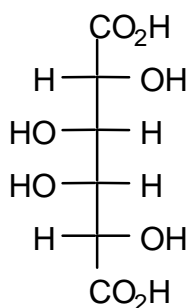


Compound 1

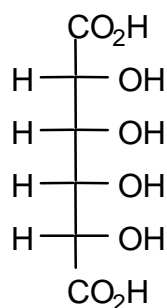
SOLUTION

1.1

Compound **X** is a trisaccharide which does not react with Benedict's solution nor does it mutarotate. This shows that **X** is a non-reducing sugar and therefore only acetal or ketal linkages exist at all of the anomeric carbons. Of the three monosaccharides, **A** and **B** give the same osazone and therefore have identical stereochemistry at C-3, C-4, and C-5 (and C-6). **A** and **B** are also different from compound **1** (i.e. D-mannose) yet give the same osazone, and thus one of them must be the C-2 epimer of D-mannose (i.e. D-glucose) and the other must be the corresponding keto sugar at C-2 (i.e. D-fructose). (This deduction is confirmed later in the oxidative cleavage reactions.) Compound **C**, after reaction with nitric acid, gives an optically inactive aldaric acid **D**. The two possible aldaric acids which could be **D** are thus:

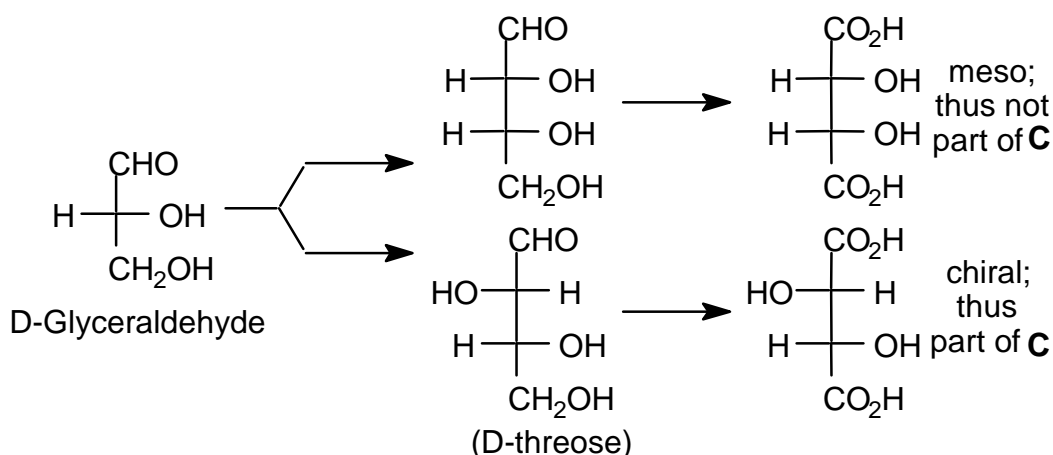


AA1 (=D)



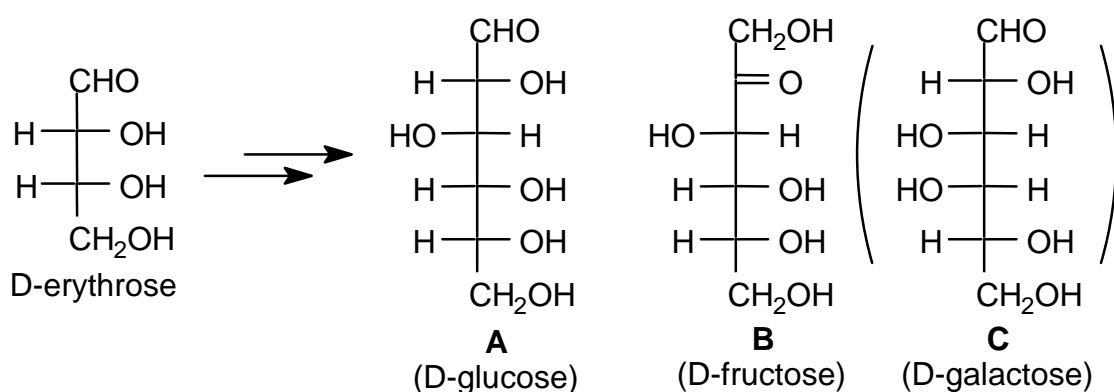
AA2

The aldotetrose which is the precursor of **C** (and thus also of **D**) does not give a meso compound after reaction with nitric acid and therefore must be the D-threose:



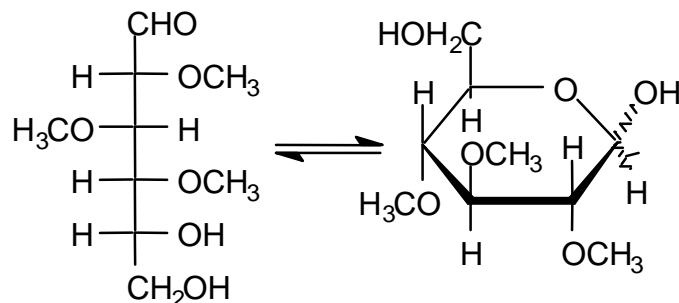
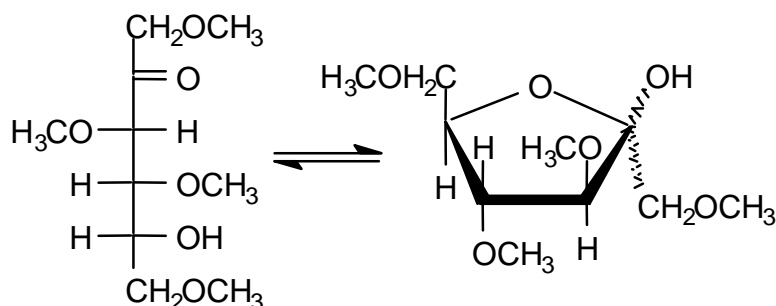
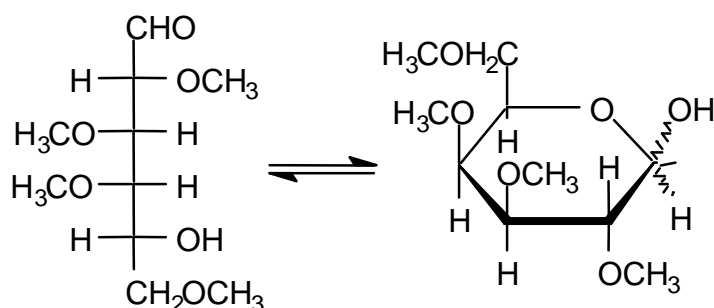
It follows from this that the aldaric acid **D** produced from **C** above is **AA1** and thus that **C** must be D-galactose. Compound **A** reacts with 5 moles of HI to give 5 moles of methanoic (formic) acid and one mole of methanal (formaldehyde) suggesting that it is an aldohexose while **B** reacts with 5 moles of HI to give 4 moles of methanoic (formic) acid, one mole of methanal (formaldehyde) and one mole of CO₂ suggesting that it is a ketohexose.

Compounds **A** and **B** are related to the same tetrose which is not the same as that of **C** (i.e. are related to D-erythrose). The tetrose which is related to **A** and **B** must therefore have the following structure and accordingly **A** is D-glucose and **B** is D-fructose.



Methylation of **X** followed by hydrolysis yields **E**, **F** and **G** below:

1.2

**E** derived from **A****F** derived from **B****G** derived from **C**

1.3

During methylation, only hydroxyl groups not involved in acetal/ketal formation (either intra- or intermolecular) will be etherified. From the methylation data, only **E** has two free hydroxyl groups with which to link to the other carbohydrates. Thus **A** must be the central carbohydrate.

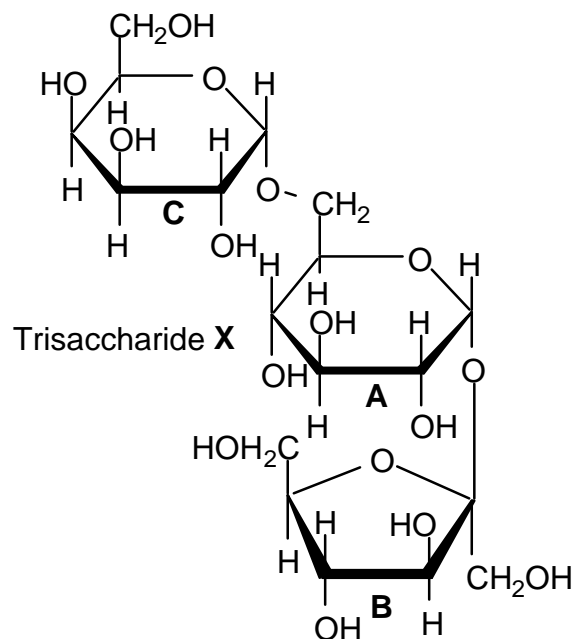
These results indicate that the sequence of monosaccharides in **X** is **C-A-B** (or **B-A-C**).

If: **A5** represents the furanose (5-membered ring) form of carbohydrate **A**.

A6 represents the pyranose (6-membered ring) form of carbohydrate **A**.

B5 represents the furanose (5-membered ring) form of carbohydrate **B**, etc. then the trisaccharide **X** would be represented as: **C6-A6-B5**

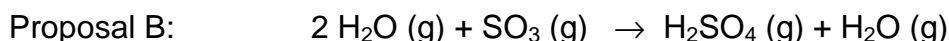
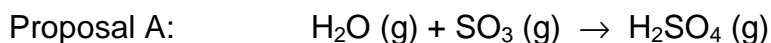
One of the 4 possible variations in the structure of **X** is given below.



Note: The nature of the anomeric linkages was not specified in the problem. The linkage arrangement of **A** to **B** and **C** may also be reversed (i.e. a 1,1' linkage between **C** and **A** and a 1,6 linkage between **A** and **B**).

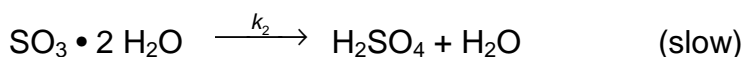
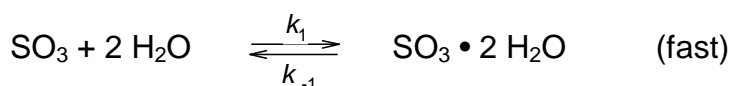
PROBLEM 2

Professor Molina of the Massachusetts Institute of Technology won the 1995 Nobel Prize in Chemistry for his work on atmospheric chemistry. One reaction that he has studied in detail is the acid rain reaction which produces H_2SO_4 in the atmosphere. He has proposed two possible stoichiometric reactions:



2.1 Using simple collision theory, what reaction orders would be expected for Proposal A and for Proposal B?

Proposal B is thought to proceed by the following two-step process:



($\text{SO}_3 \cdot 2 \text{H}_2\text{O}$ is a complex which is stabilized by hydrogen bonds and $k_2 \ll k_1$ or k_{-1})

2.2 By applying the principle of stationary (steady) states, derive the appropriate rate law and hence the reaction order of the two-step mechanism for Proposal B.

2.3 Recent quantum chemical calculations have shown that the overall reaction activation energies for the two proposals are:

$$E_A = + 80 \text{ kJ mol}^{-1} \text{ for Proposal A} \quad E_B = - 20 \text{ kJ mol}^{-1} \text{ for Proposal B}$$

State the relationship between the rate constant and the temperature (Arrhenius relationship) for each proposal and predict the temperature dependence of the rate constants for each proposal.

2.4 The formation of H_2SO_4 is faster in the upper atmosphere ($T = 175 \text{ K}$) than at the earth's surface ($T = 300 \text{ K}$). Which proposed pathway must dominate in the upper atmosphere given the activation energies in part (iii) and your understanding of the Arrhenius equation?

SOLUTION

2.1 Proposal A:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{H}_2\text{O}][\text{SO}_3]$$

Summing the exponents gives a second order process

Proposal B:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k[\text{SO}_3][\text{H}_2\text{O}]^2$$

Summing the exponents gives a third order process

2.2 The steady state approximation gives:

The rate law here will be similar to that found for an enzymatic process which proceeds through a rapid reversible binding step followed by a slower reaction process.

$$\frac{d[\text{SO}_3 \cdot 2\text{H}_2\text{O}]}{dt} = k_1[\text{SO}_3][\text{H}_2\text{O}]^2 - k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] - k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = 0$$

Thus:
$$k_{-1}[\text{SO}_3 \cdot 2\text{H}_2\text{O}] + k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = k_1[\text{SO}_3][\text{H}_2\text{O}]^2$$

and therefore:
$$[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1[\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

Also:
$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}]$$
 and substituting from above yields

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = k_2[\text{SO}_3 \cdot 2\text{H}_2\text{O}] = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1} + k_2}$$

However, since $k_2 \ll k_{-1}$ the above reduces to:

$$\frac{d[\text{H}_2\text{SO}_4]}{dt} = \frac{k_1 k_2 [\text{SO}_3][\text{H}_2\text{O}]^2}{k_{-1}} = K_{\text{eq}} k_2 [\text{SO}_3][\text{H}_2\text{O}]^2 = k[\text{SO}_3][\text{H}_2\text{O}]^2$$

which is also third order

2.3 Knowing the Arrhenius relationship: $k = A e^{-E/RT}$

For proposal A: $k = A e^{-E_A/RT} = A e^{-83.6/RT}$ which increases with increasing T.

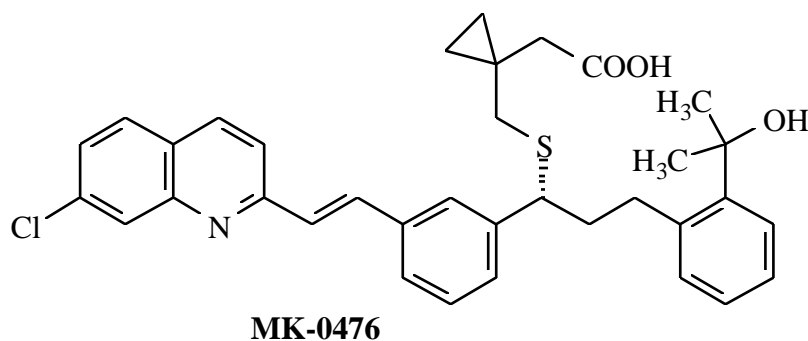
For proposal B only the slow step is critical in determining the dependence of the rate constant on the temperature. The complexation step is very stable which explains the negative activation energy.

For proposal B: $k = A e^{-E_B/RT} = A e^{+83.60/RT}$ which decreases with increasing T

2.4 Assuming that the pre-exponential factors are comparable in magnitude as is usually the case, the reaction will be faster at the lower temperatures found in the upper atmosphere due to the temperature dependence deduced above, and thus Proposal B must be operating. The rationale for Proposal B which involves the relative sizes of the rate constants is nonsense and was included to balance the choices. The rationale for Proposal A involving collision probabilities appears plausible but is not a factor — it is the massive negative activation energy which controls the situation.

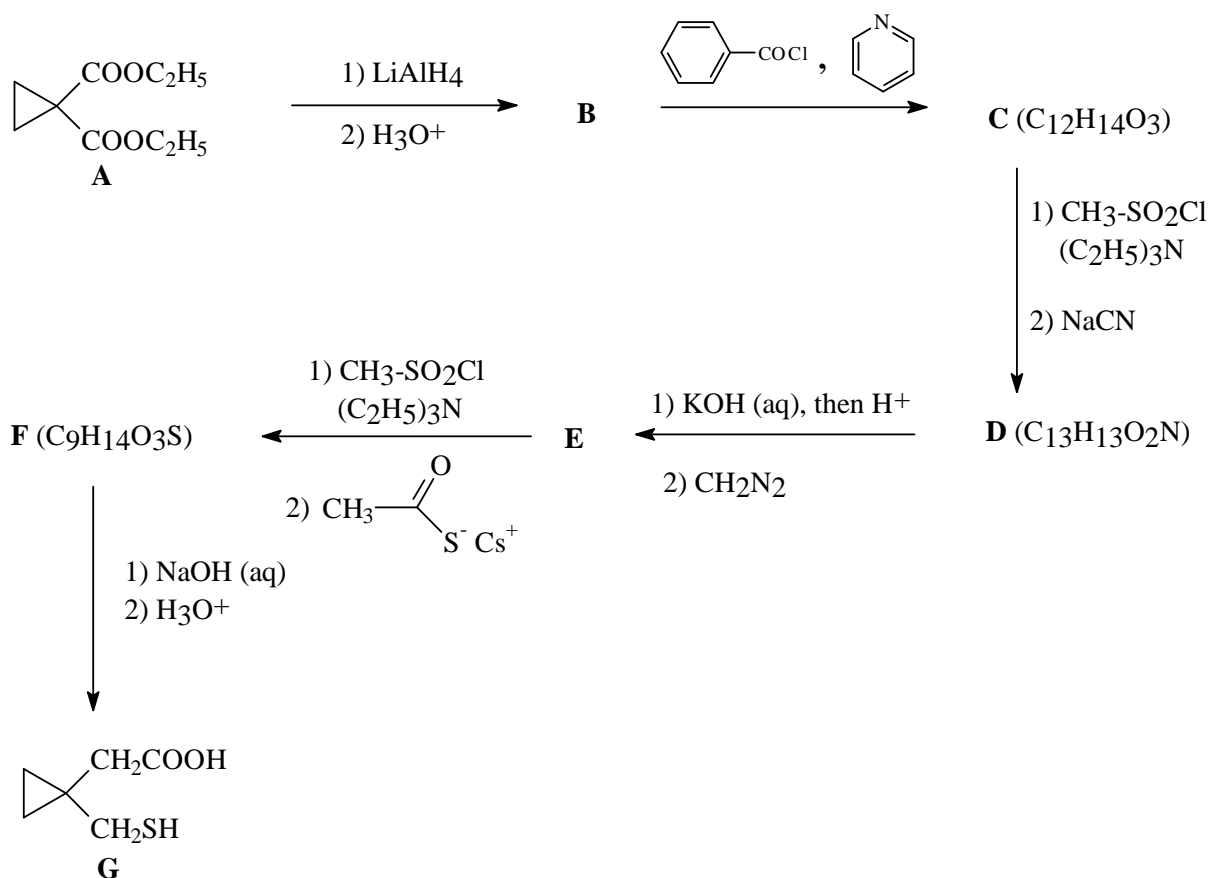
PROBLEM 3

Chemists at Merck Frosst Canada in Montréal have developed a promising drug which is useful against asthma. The structure of MK-0476 is shown below.

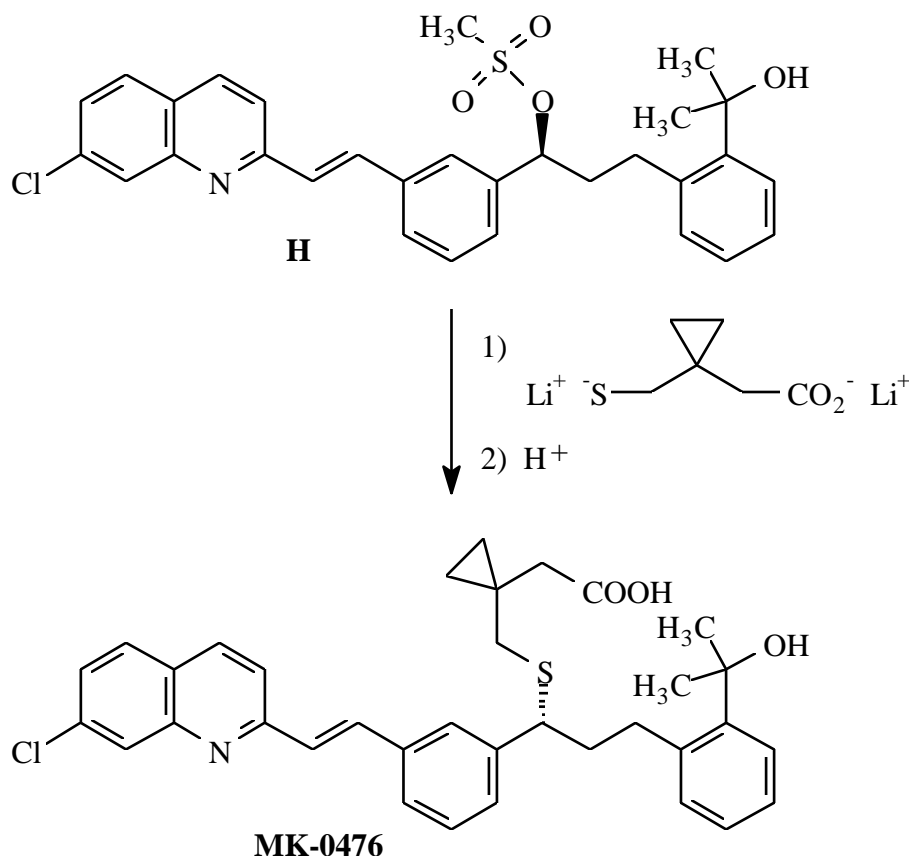


During their investigation, they devised a simple and efficient synthesis, depicted below, for the thiolated portion of MK-0476 starting from diethyl ester **A**.

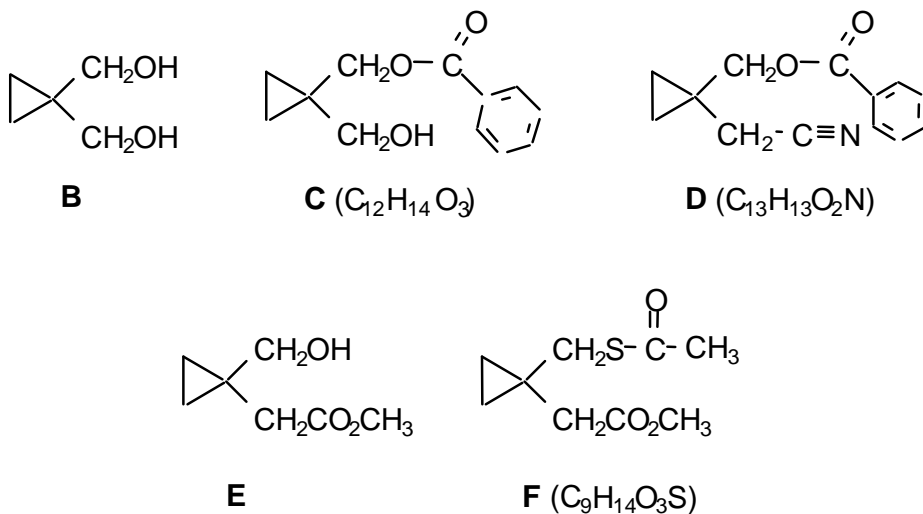
3.1 Give the structures of the intermediate products **B - F** prepared during this synthesis.



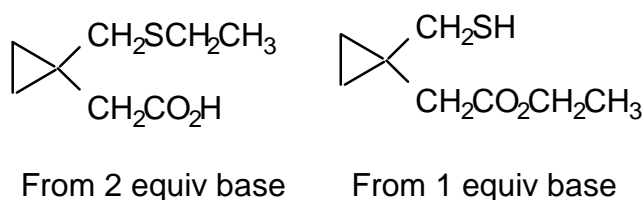
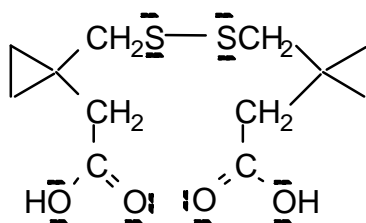
In one of the last steps of the synthesis on MK-0476, the dilithium salt of the above thiol acid (**G**) was coupled with the side chain of the rest of the molecule as shown below.



- 3.2** Based on the observed stereochemistry of the above reaction, what is the mechanistic designation of this coupling process?
- 3.3** If the process proceeds by your proposed mechanism, what change would occur to the overall rate of the reaction if the concentration of both the thiolate salt and the substrate **H** were simultaneously tripled?
- 3.4** For the nucleophilic substitution reaction, model studies were carried out using bromoethane as the substrate to perfect the above coupling. Draw only the structure of the major product of the reaction of one molar equivalent of bromoethane with:
- G** plus two molar equivalents of base
 - G** plus one molar equivalent of base
- 3.5** A side reaction of **G** is its oxidative dimerization.
Draw the structure of the dimeric product, showing all non-bonded electrons.

SOLUTION**3.1****3.2** S_N2 Bimolecular Nucleophilic Substitution**3.3** Rate = k[substrate] [nucleophile]

The overall rate is directly dependent on the concentration of both the substrate and the nucleophile. Thus tripling the concentration of both of the reactants will result in a 9-fold increase in the overall reaction rate.

3.4**3.5**

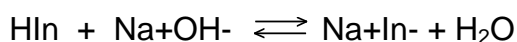
oxidative coupled product

PROBLEM 4

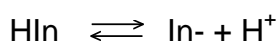
Graph paper is provided for your optional use in this question.

If you choose to use it, print your name and identification code in the upper right corner of the graph paper.

HIn is a weakly acidic indicator.



also written as

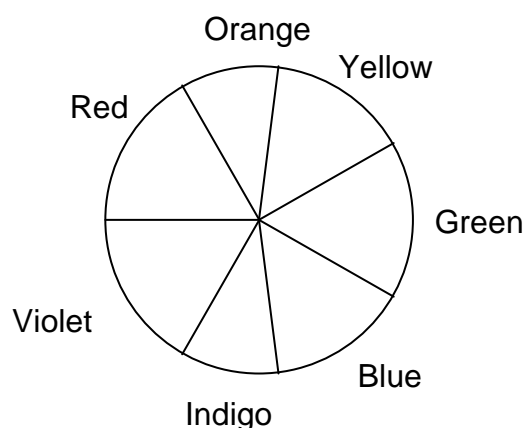


At normal temperatures, the acid dissociation constant for this indicator is $K_a = 2.93 \times 10^{-5}$.

The absorbance data (1.00 cm cells) for 5.00×10^{-4} M (mol dm^{-3}) solutions of this indicator in strongly acidic and strongly alkaline solutions are given in the following table.

Absorbance Data (A)

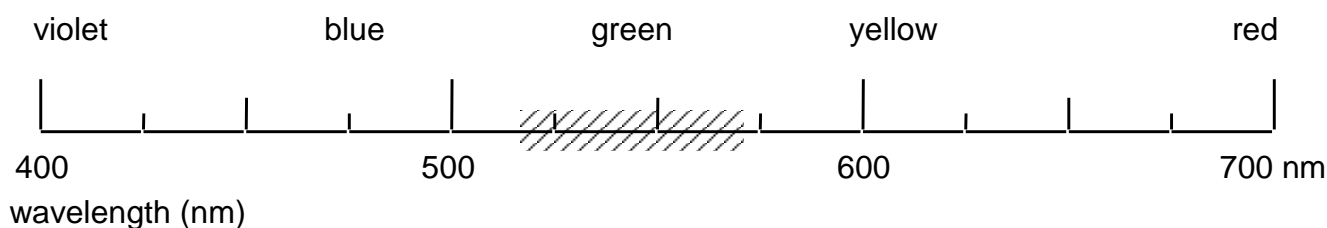
λ , nm	$pH = 1.00$	$pH = 13.00$
400	0.401	0.067
470	0.447	0.050
485	0.453	0.052
490	0.452	0.054
505	0.443	0.073
535	0.390	0.170
555	0.342	0.342
570	0.303	0.515
585	0.263	0.648
615	0.195	0.816
625	0.176	0.823
635	0.170	0.816
650	0.137	0.763
680	0.097	0.588



4.1 Predict the observed colour of the a) acidic and b) basic forms of the indicator.

Using a “50 nm wide bar”, shade the appropriate area of the wavelength scale on the answer sheet which would correspond to the colour of the indicator at the *pH* values given in the table.

For example, if observed colour is green, your answer would appear as:



4.2 A filter is located between the light source and the sample. What colour filter would be most suitable for the photometric analysis of the indicator in a strongly acidic medium?

4.3 What wavelength range would be most suitable for the photometric analysis of the indicator in a strongly basic medium?

4.4 What would be the absorbance of a 1.00×10^{-4} M (mol dm⁻³) solution of the indicator in alkaline form if measured at 545 nm in a 2.50 cm cell?

4.5 Solutions of the indicator were prepared in a strongly acidic solution (HCl, *pH* = 1) and in a strongly basic solution (NaOH, *pH* = 13). Perfectly linear relationships between absorbance and concentration were observed in both media at 490 nm and 625 nm, respectively.

The molar absorptivities at the two wavelengths are:

	$\lambda = 490$ nm	$\lambda = 625$ nm
HIn (HCl)	9.04×10^2 M ⁻¹ cm ⁻¹	3.52×10^2 M ⁻¹ cm ⁻¹
In ⁻ (NaOH)	1.08×10^2 M ⁻¹ cm ⁻¹	1.65×10^3 M ⁻¹ cm ⁻¹

(M = mol dm⁻³)

Calculate the absorbance (1.00 cm cell) at the two wavelengths for an aqueous 1.80×10^{-3} M (mol dm⁻³) solution of the indicator HIn.

SOLUTION

4.1 The observed colour will be the complementary colour to that of the absorption maximum.

a) Acidic conditions ($pH\ 1$):

The sample absorbs at 490 ± 25 (blue-green) and thus will transmit the complementary colour and will appear to be yellow-orange ($625 \pm 25\text{ nm}$).

b) Basic conditions ($pH\ 13$):

The sample absorbs at 625 ± 25 (yellow-orange) and thus will transmit the complementary colour and will appear to be blue-green ($490 \pm 25\text{ nm}$).

4.2 The filter should transmit the colour that the sample will absorb most efficiently. The acidic sample absorbs most strongly in the blue range ($490 \pm 25\text{ nm}$) and thus a similar colour filter would be most suitable for the photometric analysis of the sample.

4.3 The wavelength range to be used for maximum sensitivity should correspond to that at which the sample absorbs most strongly. The maximum absorbance for the basic form of the indicator in solution occurs at $625 \pm 25\text{ nm}$ and this is the most suitable wavelength for the analysis.

4.4 From a graph of A versus wavelength, the absorbance of a $5.00 \times 10^{-4}\text{ M}$ basic solution at 545 nm is 0.256 . From the plot, it is clear that this region of the graph is linear and thus the above value can also be interpolated from the data table.

$$A = \varepsilon l c \quad (\text{Beer's Law})$$

where l = length of cell, c = concentration of analyte, ε = molar absorptivity.

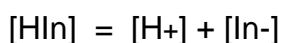
$$\text{Therefore } \varepsilon = \frac{A}{lc} = \frac{0.256}{1.0 \times 5.00 \times 10^{-4}} = 5.12 \times 10^2\text{ M}^{-1}\text{ cm}^{-1}$$

$$lc = 1.0 \times 5.00 \times 10^{-4}$$

Absorbance of a $1.00 \times 10^{-4}\text{ M}$ basic solution of the indicator using a 2.50 cm cell is:

$$A = 5.12 \times 10^2 \times 2.50 \times 1.0 \times 10^{-4} = 0.128$$

4.5 The dissociation reaction of the indicator is:



accordingly,

$$[\text{H}^+] = [\text{In}^-] \quad (1)$$

and

$$[\text{HIn}] + [\text{In}^-] = 1.80 \times 10^{-3} \text{ M} \quad (2)$$

$$K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} \quad (3)$$

Substitute (1) and (2) into (3)

$$K_a = \frac{[\text{In}^-]^2}{1.8 \times 10^{-3} - [\text{In}^-]} = 2.93 \times 10^{-5}$$

Rearrangement yields the quadratic expression

$$[\text{In}^-]^2 + 2.93 \times 10^{-5} [\text{In}^-] - 5.27 \times 10^{-8} = 0$$

which results in

$$[\text{In}^-] = 2.15 \times 10^{-4} \text{ M}$$

$$[\text{HIn}] = 1.80 \times 10^{-3} \text{ M} - 2.15 \times 10^{-4} \text{ M} = 1.58 \times 10^{-3} \text{ M}$$

The absorbance at the two wavelengths are then:

$$A_{490} = (9.04 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.08 \times 10^2 \times 1 \times 2.15 \times 10^{-4}) = 1.45$$

$$A_{625} = (3.52 \times 10^2 \times 1 \times 1.58 \times 10^{-3}) + (1.65 \times 10^3 \times 1 \times 2.15 \times 10^{-4}) = 0.911$$

PROBLEM 5

Iron metal melts at 1811 K. Between room temperature and its melting point, iron metal can exist in different allotropic or crystalline forms. From room temperature to 1185 K, the crystal structure of iron metal exists as a body-centred cubic (bcc) lattice known as α -iron. From 1185 K to 1667 K, the structure becomes face-centred cubic (fcc) and is called γ -iron. Above 1667 K, and up to its melting point, iron reverts to a bcc structure similar to that of α -iron. The latter phase is called δ -iron.

Given that the density of pure iron metal is 7.874 g cm^{-3} at 293 K:

5.1 Calculate the atomic radius of iron (expressed in cm).

5.2 Calculate its density (expressed in g cm^{-3}) at 1250 K.

Notes: Ignore the small effects due to the thermal expansion of the metal.

Clearly define any symbols which you use, e.g. r = atomic radius of Fe.

Steel is an alloy of iron and carbon in which some of the interstitial spaces ("holes") of the crystal lattice (iron) are occupied by small atoms (carbon). Its carbon content typically ranges from 0.1 % to 4.0 %. In a blast-furnace, the melting of iron is facilitated when it contains 4.3 % of carbon by mass. If this mixture is cooled too rapidly the carbon atoms remain dispersed within the α -iron phase. This new solid, called martensite, is extremely hard and brittle. Although it is slightly distorted, the size of the unit cell of this solid (martensite) is the same as that of α -iron (bcc).

Assuming that the carbon atoms are evenly distributed in the iron structure:

5.3 Calculate the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

5.4 Calculate the density (expressed in g cm^{-3}) of this material.

Molar masses and constants:

$$M(\text{Fe}) = 55.847 \text{ g mol}^{-1}$$

$$M(\text{C}) = 12.011 \text{ g mol}^{-1}$$

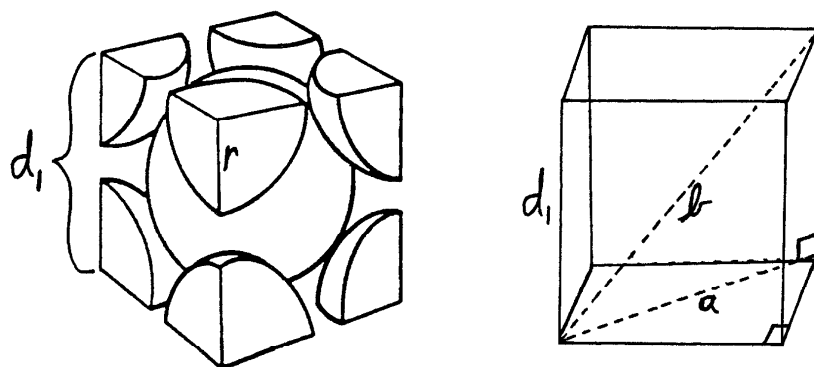
$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

SOLUTION**5.1 Calculation of the atomic radius of iron (expressed in cm).****5.2 Calculation of its density (expressed in g cm^{-3}) at 1250 K.**Expected steps of the calculation:

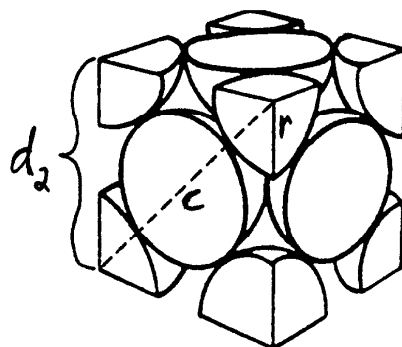
1. Define the length a , b , c , d_1 , d_2 , and r and volume V_1 and V_2 parameters for both bcc and fcc structures of iron (*cf.* Details below).
2. Calculate the volume V_1 of the unit cell of α -iron from its density ρ_{bcc} at 293 K, the molar weight $M(\text{Fe})$ of iron, and Avogadro's number N_A .
3. Calculate the length d_1 of the edge of the bcc unit cell from its volume V_1 .
4. Calculate the atomic radius r of iron from the length "d₁".
5. Calculate the length d_2 of the edge of the fcc unit cell at 1250 K from the atomic radius r of iron.
6. Calculate the volume V_2 of the fcc unit cell of γ -iron from the length d_2 of its edge.
7. Calculate the mass m of the number of iron atoms in a unit cell of γ -iron from the molar weight $M(\text{Fe})$ of iron and Avogadro's number N_A .
8. Calculate the density ρ_{fcc} of γ -iron from the values of "m" and "V₂".

An alternative route to ρ_{fcc} of γ -iron, involving the percent space filling ratios of both the bcc and fcc unit cells, can replace the aforementioned steps 5 through 8. In this route, these steps are labeled from 5' through 8' as listed below:

- 5'. Calculate the percent space filling ratio of the bcc unit cell.
- 6'. Calculate the percent space filling ratio of the fcc unit cell.
- 7'. Calculate the $\rho_{\text{fcc}}/\rho_{\text{bcc}}$ density ratio from the fcc/bcc space filling ratios.
- 8'. Calculate the density ρ_{fcc} of γ -iron from the value found in step 7'.



Body centered cubic structure (bcc)



Face-centered cubic structure (fcc)

Calculations in details

At 293 K, α -iron has a bcc crystal structure.

Each unit cell possesses 2 atoms and one of them is in the center of the cell.

At 1250 K, γ -iron has a fcc crystal structure.

Each unit cell possesses 4 atoms and each side has one-half an atom at its center.

r = atomic radius of iron.

a = length of the diagonal on one side of the bcc unit cell.

b = length of the diagonal passing through the center of the bcc unit cell.

c = length of the diagonal on one side of the fcc unit cell.

d_1 = length of the edge of the bcc unit cell of α -iron.

d_2 = length of the edge of the fcc unit cell of γ -iron.

V_1 = Volume of the bcc unit cell of α -iron.

V_2 = Volume of the fcc unit cell of γ -iron.

V_a = Volume of one atom.

V_{a1} = Volume occupied by 2 atoms in one bcc unit cell.

V_{a2} = Volume occupied by 4 atoms in one fcc unit cell.

R_1 = Percent space filling ratio in a bcc unit cell.

R_2 = Percent space filling ratio in a fcc unit cell.

$$V_a = \left(\frac{4}{3}\right) \pi r^3$$

$$V_{a1} = 2 V_a$$

$$V_{a2} = 4 V_a$$

$$b = 4 r;$$

$$a^2 = 2 d_1^2;$$

$$b^2 = d_1^2 + a^2 = 3 d_1^2$$

$$d_1 = (b^2/3)^{1/2} = (16 r^2/3)^{1/2};$$

$$V_1 = d_1^3 = [(16 r^2/3)^{1/2}]^3$$

$$c = 4 r; \quad c^2 = 2 d_2^2$$

$$d_2 = (c^2/2)^{1/2} = (16 r^2/2)^{1/2};$$

$$V_2 = d_2^3 = [(16 r^2/2)^{1/2}]^3$$

2. 1.000 cm³ of iron weights 7.874 g at 293 K (ρ_{bcc}).

1 mole of iron weights 55.847 g (M_{Fe}).

Thus, 0.1410 mol (7.874 g / 55.847 g mol⁻¹) of iron occupy a volume of 1.000 cm³ or
1 mole of iron will occupy a volume of 7.093 cm³

1 mole corresponds to 6.02214×10²³ atoms

$$V_1 = (7.093 \text{ cm}^3 \text{ mol}^{-1}) \times (2 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$$

$$V_1 = 2.356 \times 10^{-23} \text{ cm}^3 \text{ per unit cell}$$

$$3. \quad d_1 = (V_1)^{1/3} = (2.356 \times 10^{-23} \text{ cm}^3)^{1/3}$$

$$d_1 = 2.867 \times 10^{-8} \text{ cm}$$

$$4. \quad \text{For a bcc structure, the value of } d_1 \text{ can be expressed as: } d_1 = [(16 r^2)/3]^{1/2}$$

so the value of "r" will be: $r = (3 d_1^2/16)^{1/2}$

$$r = [3 (2.867 \times 10^{-8} \text{ cm})^2/16]^{1/2}$$

$$r = 1.241 \times 10^{-8} \text{ cm}$$

$$5. \quad \text{At 1250 K, in the fcc structure, the value of "d}_2\text{" is given by: } d_2 = (16 r^2/2)^{1/2}$$

$$d_2 = [16 (1.241 \times 10^{-8} \text{ cm})^2/2]^{1/2}$$

$$d_2 = 3.511 \times 10^{-8} \text{ cm}$$

$$6. \quad V_2 = d_2^3 = (3.511 \times 10^{-8} \text{ cm})^3$$

$$V_2 = 4.327 \times 10^{-23} \text{ cm}^3$$

7. The mass "m" of the 4 iron atoms in the fcc unit cell will be:

$$m = (55.847 \text{ g mol}^{-1}) \times (4 \text{ atoms/unit cell}) / (6.02214 \times 10^{23} \text{ atoms mol}^{-1})$$

$$m = 3.709 \times 10^{-22} \text{ g per unit cell}$$

$$8. \quad \rho_{\text{fcc}} = m / V_2 = (3.709 \times 10^{-22} \text{ g}) / (4.327 \times 10^{-23} \text{ cm}^3)$$

$$\rho_{\text{fcc}} = 8.572 \text{ g/cm}^3$$

Alternative route to ρ_{fcc} of γ -iron:

$$5'. \quad R_1 = [(V_{a1}) / (V_1)] \times 100\% = [(2 V_a) / (V_1)] \times 100\%$$

$$R_1 = [(2 \times (4/3) \pi r^3) / [(16 r^2/3)^{1/2}]^3] \times 100\%$$

$$R_1 = [(8/3) \pi r^3] / [(16/3)^{3/2} r^3] \times 100\%$$

$$R_1 = [(8/3) \pi] / [(16/3)^{3/2}] \times 100\%$$

$$R_1 = [(8.378) / (12.32)] \times 100\%$$

$$R_1 = 68.02 \%$$

$$6'. \quad R_2 = [(V_{a2}) / (V_2)] \times 100\% = [(4 V_a) / (V_2)] \times 100\%$$

$$R_2 = [(4 \times (4/3) \pi r^3) / [(16 r^2/2)^{1/2}]^3] \times 100\%$$

$$R_2 = [(16/3) \pi r^3] / [8^{3/2} r^3] \times 100\%$$

$$R_2 = [(16/3) \pi] / [8^{3/2}] \times 100\%$$

$$R_2 = [(16.76) / (22.63)] \times 100\%$$

$$R_2 = 74.05\%$$

$$7'. \quad \rho_{\text{fcc}} / \rho_{\text{bcc}} = (74.05\%) / (68.02\%)$$

$$\rho_{\text{fcc}} / \rho_{\text{bcc}} = 1.089$$

$$8'. \quad \rho_{\text{fcc}} = 1.089 \times \rho_{\text{bcc}}$$

$$\rho_{\text{fcc}} = 1.089 \times 7.874 \text{ g cm}^{-3}$$

$$\rho_{\text{fcc}} = 8.572 \text{ g cm}^{-3}$$

5.3 Calculation of the average number of carbon atoms per unit cell of α -iron in martensite containing 4.3 % C by mass.

5.4 Calculation of the density (expressed in g cm^{-3}) of this material.

Expected Steps of the Calculation:

1. From the percent composition of martensite (by mass), calculate the relative amounts of moles of carbon and iron.
2. Bring the C/Fe molar ratio to one (1) unit cell (Note: 2 Fe atoms per unit cell).
3. Find the smallest whole number of C atoms for the smallest whole number of unit cell (facultative).
4. Calculate the mass of iron per unit cell.
5. Calculate the mass of carbon per unit cell.
6. Calculate the total mass of carbon and iron in one unit cell.
7. Calculate the density of martensite [$\rho(\text{martensite at 4.3 \%C})$] from the total mass of C and Fe and volume (V_1) of α -iron bcc unit cell.

Details:

1. In 100.0 g of martensite at 4.3 % C: $(4.3 \text{ g C}) / (12.011 \text{ g mol}^{-1}) = 0.36 \text{ mol C}$
 $(95.7 \text{ g Fe}) / (55.847 \text{ g mol}^{-1}) = 1.71 \text{ mol Fe}$

So we have 1 carbon atom for 4.8 iron atoms or

0.21 carbon atoms per iron atom.

2. Martensite has a "bcc" crystal structure (2 iron atoms per unit cell).

$[(1 \text{ C atom}) / (4.8 \text{ Fe atoms})] \times (2 \text{ Fe atoms} / \text{unit cell})$

or: 0.42 carbon atoms per unit cell

3. 5 carbon atoms $[(0.42 \text{ C atom} / 0.42) \times 5]$ in 12 unit cells $[(1 \text{ unit cell}/0.42) \times 5]$.
5 carbon atoms dispersed in 12 unit cells
4. $[(55.847 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})] \times (2 \text{ atoms/unit cell of } \alpha\text{-iron})$
 $1.8547 \times 10^{-22} \text{ g Fe per unit cell of } \alpha\text{-iron}$
5. $(12.011 \text{ g/mol}) / (6.02214 \times 10^{23} \text{ atoms/mol})$
 $1.9945 \times 10^{-23} \text{ g C per atom}$
6. $[1.8547 \times 10^{-22} \text{ g Fe} + (0.42 \text{ C at.} \times 1.9945 \times 10^{-23} \text{ g / C at.})]$ per unit cell
 $1.938 \times 10^{-22} \text{ g C and Fe per unit cell}$
7. Each unit cell of α -iron occupies a volume, $V_1 = 2.356 \times 10^{-23} \text{ cm}^3$
(cf. Question i)
 $\rho(\text{martensite at 4.3 \% C}) = (1.938 \times 10^{-22} \text{ g C and Fe}) / (2.356 \times 10^{-23} \text{ cm}^3)$
 $\rho(\text{martensite at 4.3 \% C}) = 8.228 \text{ g cm}^{-3}$
-
-

PROBLEM 6

6.1 Much of the world's supply of platinum group metals is derived from the residues recovered from the electrolytic refining of copper and nickel. A flow chart for the recovery of platinum and palladium is shown on the following page.

- i) Clearly draw the shape (geometry) of both the PtCl_6^{2-} and the PdCl_4^{2-} anions.
- ii) Clearly draw all possible stereoisomeric structures of monomeric $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. Label the structures that you have drawn with their correct stereochemical descriptors.
- iii) What is the role of the FeSO_4 in the second step of the flow chart? Write a balanced equation for the reaction of FeSO_4 in this step.
- iv) Write a complete balanced equation for the ignition of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in air to give Pd metal. In this reaction, what is being oxidized and what is being reduced?

6.2 Reaction of a main group chloride (24.71 g) with ammonia (10.90 g) gave a mixture of products consisting of NH_4Cl (25.68 g), a solid element **A** (2.57 g) and a yellow crystalline nitride of this element (7.37 g) according to the equation below.



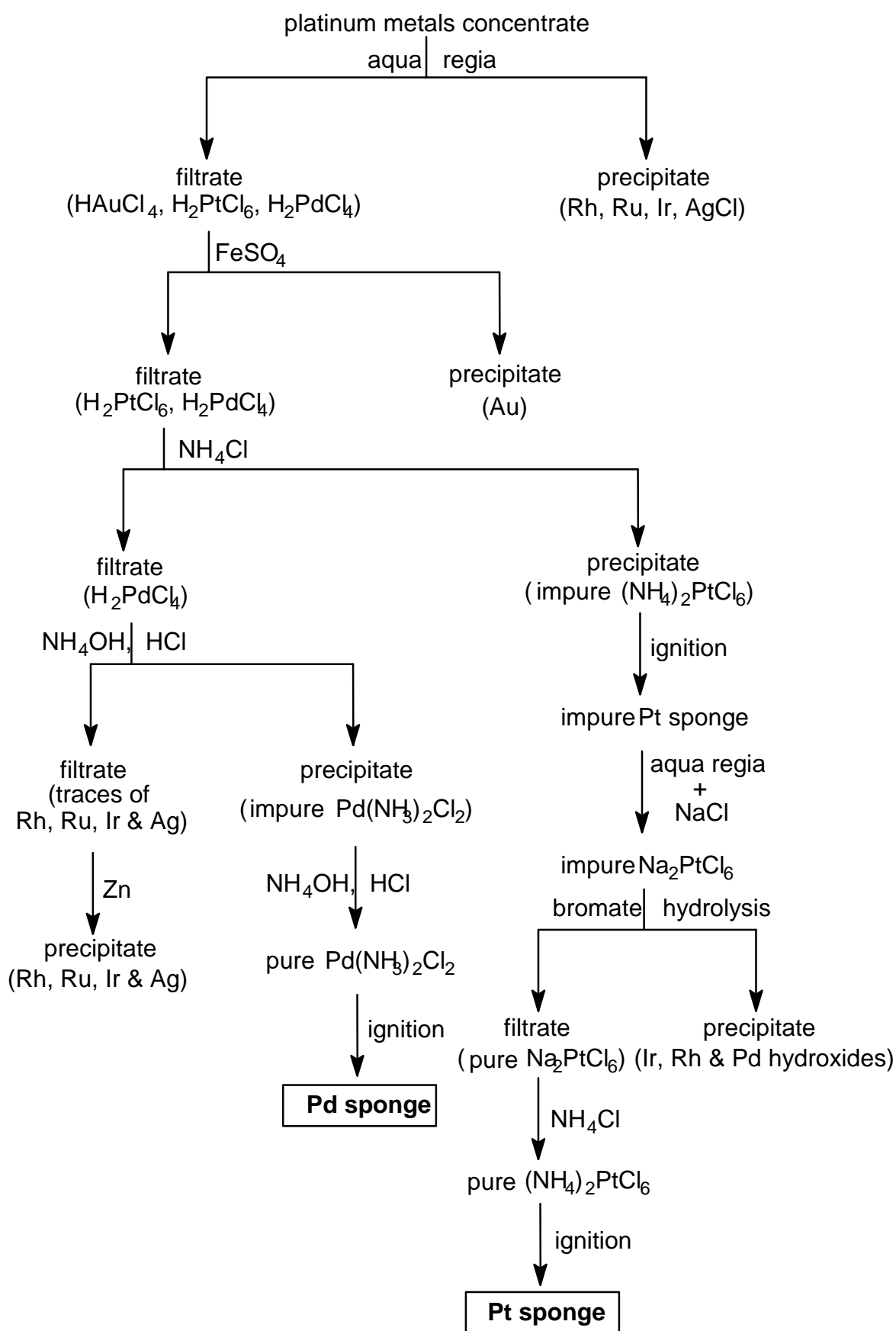
(where n, m, p, q, r, w, x, y and z are coefficients to be determined)

A sample of the nitride exploded violently when struck with a hammer, but it underwent controlled polymerization on heating to give a bronze-coloured, fibrous solid which exhibits metallic conductivity. Element **A** also undergoes polymerization to a high molecular weight linear polymer upon heating.

Molar masses:

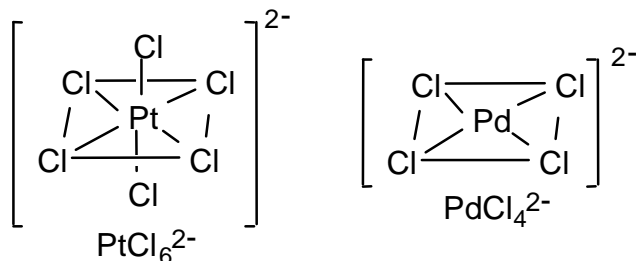
$$M(\text{Cl}) = 35.453 \text{ g mol}^{-1} \quad M(\text{N}) = 14.007 \text{ g mol}^{-1} \quad M(\text{H}) = 1.008 \text{ g mol}^{-1}$$

- i) Identify element **A**.
- ii) Write a complete balanced equation for the reaction of the chloride with ammonia.
- iii) Assuming conventional oxidation states, write the balanced redox half-reaction equations involved in this reaction.

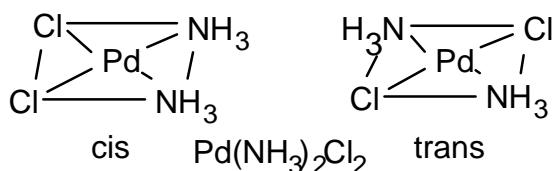
Method of Purification of Platinum and Palladium

SOLUTION**6.1**

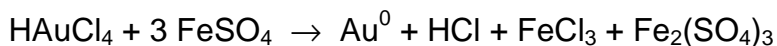
- i) The PtCl_6^{2-} anion consists of a Pt(IV) centred in a regular octahedron of Cl^- ions. The PdCl_4^{2-} anion consists of a Pd(II) centred in a square of Cl^- ions.



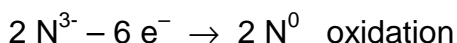
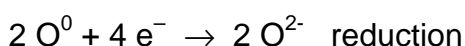
- ii) Like PdCl_4^{2-} , $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is also square planar. However, in this case there are two distinct ways in which the two different substituent groups (ligands) can be arranged. One places the two Cl^- on adjacent corners of the square (and axiomatically, the two NH_3 on the other two adjacent corners). This arrangement is called the *cis* isomer. The second arrangement has the pairs of the same ligand placed on diagonally opposite corners of the square. This arrangement is called the *trans* isomer. There are only these two stereoisomers possible for a monomeric form of the complex.



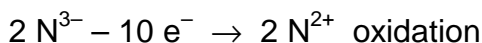
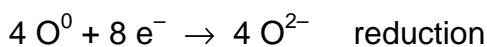
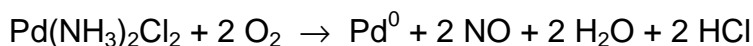
- iii) The FeSO_4 [i.e. Fe(II)] acts as a reducing agent. Under the conditions used in the process, the Fe(II) is a strong enough reducing agent to reduce Au(III) to Au(0), but not to reduce Pd(II) or Pt(IV).



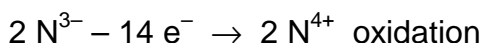
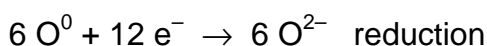
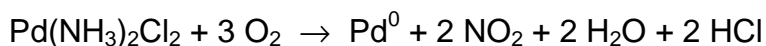
- iv) $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{O}_2 \rightarrow \text{Pd}^0 + \text{N}_2 + 2 \text{H}_2\text{O} + 2 \text{HCl}$



or



or



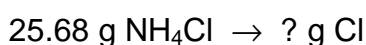
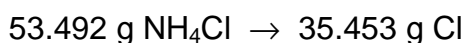
In this reaction the ammonia is oxidized to water and dinitrogen (or nitrogen oxides) and the Pd(II) and dioxygen are being reduced.

Part of the oxidation is due to the Pd(II) acquiring two electrons to go to Pd(0), and part by dioxygen which is reduced to water. In the presence of noble metal catalysts, NH_3 can also be oxidized to $(\text{NO})_x$. Thus other nitrogen species are also in principle possible in the above ignition.

6.2

i) A = sulphur

All Cl is located in the NH_4Cl , and thus the weight of Cl is found by:



$$? = 25.68 \times 35.453 / 53.492 = 17.02 \text{ g Cl}$$

Total amount of A in the reaction is $24.71 \text{ g Cl} - 17.02 \text{ g Cl} = 7.69 \text{ g A}$ There is 2.57 g free A and $(7.69 - 2.57) = 5.12 \text{ g A}$ in the nitride.

The amount of N bound in nitride is therefore

$$7.37 \text{ g nitride} - 5.12 \text{ g A bound in nitride} = 2.25 \text{ g N bound in nitride}$$

The amount of nitrogen bound in NH_4Cl is $25.68 - 17.02 = 8.66 \text{ g}$

The rule of multiple proportions is applied:

Proportions of 1 : 1

Chloride:



? g A binds \rightarrow 35.453 g Cl

? = $35.453 \times 7.69/17.02 = 16.02$ g

A could be oxygen, but it is a main group element and it is a gas and thus it can be excluded.

Nitride:

5.12 g A binds \rightarrow 2.25 g N

? g A binds \rightarrow 14.007 g N

? = $14.007 \times 5.12/2.25 = 31.87^*$ g

A could be sulphur, fits the physical description and $M_r(\text{S}) = 32.064$

(*Phosphorus, $M_r(\text{P}) = 30.97$, is also possible, but the highest degree of "polymerization" known is 4, in the P_4 molecule and thus P must also be excluded.)

Proportions of 1 : 2

Chloride:

7.69 g A binds \rightarrow 17.02 g Cl

? g A binds $\rightarrow 2 \times 35.453$ g Cl

? = $2 \times 35.453 \times 7.69 / 17.02 = 32.03$ g. Again A could be sulphur.

Nitride:

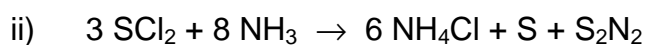
5.12 g A binds \rightarrow 2.25 g N

? g A binds $\rightarrow 2 \times 14.007$ g N

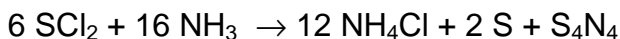
? = $2 \times 14.007 \times 5.12 / 2.25 = 63.75$ g

A could be Cu but it is a Group B element and thus can be excluded.

Therefore element A must be sulphur.



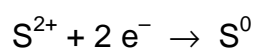
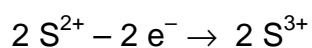
or



In fact the elemental S is in the form of S_8 and so the equation should be multiplied by a factor of 8. Although S_2N_2 roughly fits the description of colour and explosive instability, it is actually S_4N_4 that is produced in this reaction. Both of these ring compounds under carefully controlled heating polymerize to give the high molecular weight linear polymer $(\text{SN})_n$, which is one of the rare examples of a metal containing only lighter p-group elements. The tendency of these ring compounds to polymerize

is due to the relatively weak S-N bonds and the large amount of strain energy in the ring. The S-S bond is also quite weak and can be broken by heating. For this reason the S₈ ring also undergoes polymerization at high temperature. However, there is hardly any energy stored in the form of ring strain in this ring and so the polymerization is not highly exothermic or explosive. Other sulphur chlorides (S₂Cl₂ and SCl₄) do not fit the stoichiometry of the reaction.)

iii) A disproportionation reaction involving sulfur occurs:



PROBLEM 7

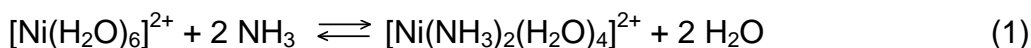
7.1 One mole of Cl₂ (g), which may be assumed to obey the ideal gas law, initially at 300 K and 1.01325×10⁷ Pa, is expanded against a constant external pressure of 1.01325×10⁵ Pa to a final pressure of 1.01325×10⁵ Pa. As a result of the expansion, the gas cooled to a temperature of 239 K (which is the normal boiling point of Cl₂), and 0.100 mol of Cl₂ condensed.

The enthalpy of vaporization of Cl₂ (l) is 20.42 kJ mol⁻¹ at the normal boiling point, the molar heat capacity of Cl₂ (g) at constant volume is $C_V = 28.66 \text{ J K}^{-1} \text{ mol}^{-1}$ and the density of Cl₂ (l) is 1.56 g cm⁻³ (at 239 K). Assume that the molar heat capacity at constant pressure for Cl₂ (g) is $C_p = C_V + R$.

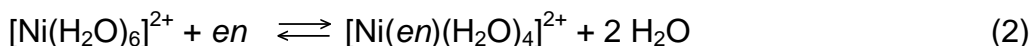
(1 atm = 1.01325×10⁵ Pa, $R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

- i) Either draw a complete molecular orbital energy diagram or write the complete electronic configuration of Cl₂. Predict the bond order of Cl₂ and thus whether this molecule will be diamagnetic, ferromagnetic, or paramagnetic.
- ii) For the changes described above, calculate the change in the internal energy (ΔE) and the change in the entropy (ΔS_{sys}) of the system.

7.2 For the following reactions occurring in dilute aqueous solution at 298 K:



$$\ln K_c = 11.60 \text{ and } \Delta H^0 = -33.5 \text{ kJ mol}^{-1}$$

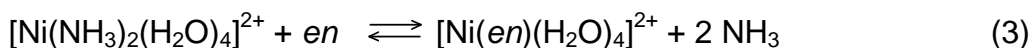


$$\ln K_c = 17.78 \text{ and } \Delta H^0 = -37.2 \text{ kJ mol}^{-1}$$

Note: en is ethylenediamine (a neutral bidentate ligand)

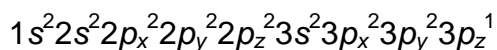
$$(R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1})$$

Calculate ΔG^0 , ΔS^0 , and K_c at 298 K for reaction [3] occurring in a dilute aqueous solution:



SOLUTION**7.1**

i) Electronic configuration of a Cl atom:



Significant atomic orbitals (AO) = 1(K) + 4(L) + 4(M) = 9 AO

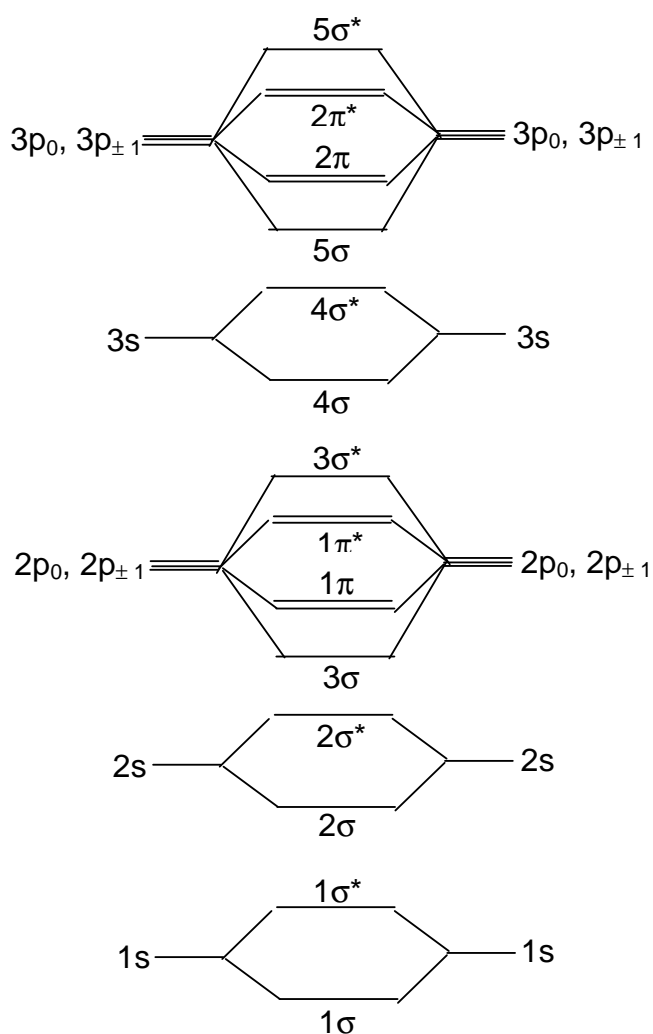
Number of electrons in these AOs: 17

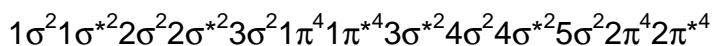
Number of molecular orbitals (MO) equals number of AOs:

Thus $2 \times [1(K) + 4(L) + 4(M)] = 18$ MOs are present in a Cl₂ molecule

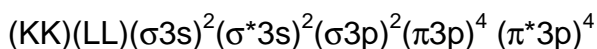
In the formation of Cl₂: $2 \times 17 = 34$ electrons to go into the 18 MOs.

MO description of Cl₂:

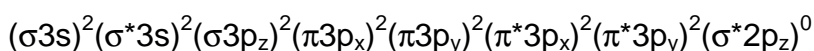
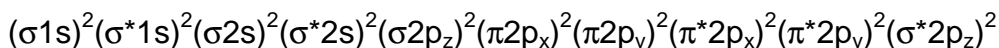




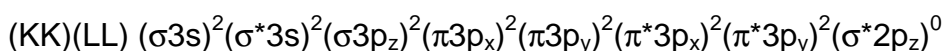
or



or



or



*assumption: - bond formation is along the z-axis

(equivalent formulae for x or y axes are accepted)

Bond order is given by $(n-n^*)/2$:

$$n = 18; \quad n^* = 16$$

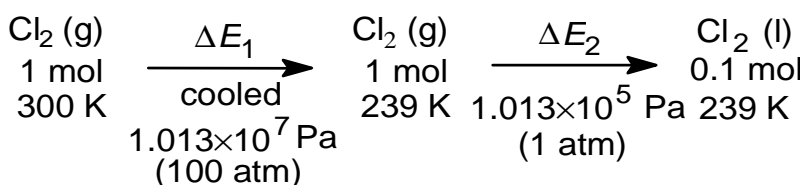
$$(18 - 16) / 2 = 1$$

(1 σ bond, no π bond)

The Cl_2 molecule has a bond order of 1.

The Cl_2 molecule is diamagnetic since there are no unpaired electrons.

ii) Summary of the changes involved:



The total process is an expansion plus an isobaric change of phase (gas to liquid) and since the internal energy (E) is a function of state, the total change in the internal energy is $\Delta E = \Delta E_1 + \Delta E_2$.

Process 1:

$$\Delta E_1 = \int n C_V dT = 1 \times 28.66 \times 239 - 300 = -1748.3 \text{ J}$$

- Note:
- ΔE for a perfect gas is a function only of T
 - C_V is constant
 - “-” sign means a loss of energy due to the work needed for expansion of 1 mole of gas

Process 2: For convenience, the data were manipulated in atm; equivalent procedure in Pa will require the appropriate conversion factor

From an energetic point of view, the liquid formation Process 2 can be split into two separate steps :

- the vaporization heat loss (decreased internal energy, -) from the system into surroundings (since the process takes place at constant pressure, the heat is equal to the change in the enthalpy)
- the work done by the surroundings in compressing the system to a smaller volume (increased internal energy, +).

Volume of gas which condensed is

$$V = n R T / P = (0.1 \times 0.0820584 \times 239) / 1 = 1.96 \text{ dm}^3$$

$$\text{Volume of liquid Cl}_2: (0.1 \times 2 \times 35.454) / 1.56 = 4.54 \text{ cm}^3$$

$$\Delta E_2 = \Delta H_2 - \int P_{\text{ext}} \Delta V(\text{phase change}) = \Delta H_2 - P_{\text{ext}}(V_l - V_g)$$

but V_l is approximately 0 and can be neglected

(ca. 4.5 cm³ liquid volume vs. ca. 17.6 dm³; ca. 0.03 % error)

$$\Delta E_2 = (0.1) (-\Delta H_{\text{vap}}) + P_{\text{ext}} V_g$$

$$= 0.1 \times (-20420) + (1 \times 1.96 \text{ L}) \times 101.325 \text{ J dm}^{-3} \text{ atm}^{-1} = -2042.0 + 198.5 = -1843.5$$

$$\Delta E = \Delta E_1 + \Delta E_2 = -1748.3 + (-1843.5) = -3591.8$$

Entropy S is a function of two variables of state. Since in Process 1 the known variables are T and P , expression of S is chosen as $S(T, P)$.

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 \text{ and}$$

$$\bar{C}_p = \bar{C}_v + R = 28.66 + 8.314 = 36.97 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \Delta S_1 &= n C_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} = 1.0 \times 36.97 \ln \frac{239}{300} - 8.314 \ln \frac{1}{100} = -8.40 + 38.29 = \\ &= 29.89 \text{ J K}^{-1} \end{aligned}$$

For the phase transition (constant temperature), by definition $\Delta S_2 = Q / T$

Since the pressure is constant in this case, $Q / T = Q_p / T = \Delta H / T$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{0.1 \times (-20420)}{239} = -8.54 \text{ J K}^{-1}$$

$$\Delta S_{\text{sys}} = 29.89 - 8.54 = 21.35 \text{ J K}^{-1}$$

7.2 Beware of round-off errors in the variations to the solution to this problem: One can get small differences due to conversion into and out of the \ln relationships. It is the approach which matters.

One reverses the signs of $\ln K_c$ and ΔH° for Reaction 1 when it is reversed.

Equilibrium constants are multiplied when equations are added, thus $\ln K$'s will add.

Reaction 3 = Reaction 2 - Reaction 1

Thus $\Delta S_3 = \Delta S_2 - \Delta S_1$ and $\Delta G_3 = \Delta G_2 - \Delta G_1$

$$\Delta G_1^0 = -RT \ln K_{c1} = -8.314 \times 298 \times 11.60 = -28740 \text{ J mol}^{-1} = -28.74 \text{ kJ mol}^{-1}$$

$$\Delta H_1^0 = -33.5 \text{ kJ mol}^{-1}$$

$$\Delta S_1^0 = (\Delta H_1^0 - \Delta G_1^0) / T$$

$$= (-33.5) - (-28.74) / 298 = -0.0161 \text{ kJ K}^{-1} \text{ mol}^{-1} = -16.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

Similarly:

$$\Delta G_2^0 = -44.05 \text{ kJ mol}^{-1}$$

$$\Delta H_2^0 = -37.2 \text{ kJ mol}^{-1}$$

$$\Delta S_2^0 = -22.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reaction 3 = Reaction 2 - Reaction 1, thus

$$\Delta H_3^0 = \Delta H_2^0 - \Delta H_1^0 = -3.7 \text{ kJ}$$

$$\Delta S_3^0 = \Delta S_2^0 - \Delta S_1^0 = 39.08 \text{ J K}^{-1}$$

$$\Delta G_3^0 = \Delta H_3^0 - T \Delta S_3^0 = -15.35 \text{ kJ mol}^{-1}$$

$$\text{Thus } K_{c3} = e^{\frac{15.35}{RT}} = 4.90 \times 10^2$$

Alternatively:

$$\Delta G_3^0 = \Delta G_2^0 - \Delta G_1^0 = -44.05 - (-28.74) = -15.31 \text{ kJ mol}^{-1} \text{ thus } K = 4.82 \times 10^2$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) / T = (-3700 - (-15311)) / 298 = 38.96 \text{ J K}^{-1}$$

PROBLEM 8

An electrolyte is prepared from H_2SO_4 , CuSO_4 and distilled water and its volume is 100.0 cm^3 . The concentrations of H^+ and Cu^{2+} in the electrolyte are $c(\text{H}^+) = 1.000 \text{ M}$ (mol dm^{-3}) and $c(\text{Cu}^{2+}) = 1.000 \times 10^{-2} \text{ M}$ (mol dm^{-3}), respectively. Two cubic platinum electrodes are immersed in the electrolyte. Both of the electrodes are single crystals with only one face (100) exposed to the electrolyte (the other five faces are blocked physically by an insulator which is stable in the electrolyte). The exposed surface area of each electrode is equal to 1.000 cm^2 . During an electrolysis a total charge of 2.0000 C is passed between the cathode and the anode. At the cathode, two simultaneous processes are occurring: deposition of an epitaxial (layer-by-layer) Cu layer and H_2 gas generation. At the anode, O_2 gas is generated. The H_2 gas is collected in a flask under the following conditions (assume ideal gas behaviour):

$T = 273.15 \text{ K}$ and $P(\text{H}_2) = 1.01325 \times 10^4 \text{ Pa}$; the volume of H_2 is equal to 2.0000 cm^3

- 8.1** Write equations of the processes taking place at the electrodes.
- 8.2** Calculate the number of moles of H_2 gas generated at the cathode and the number of moles of Cu deposited on the electrode.
- 8.3** Calculate the number of Cu monolayers formed on the Pt (100) cathode.

Note that the lattice constant of Pt is $a(\text{Pt}) = 3.9236 \times 10^{-8} \text{ cm}$.

Both Pt and Cu have the fcc (face centred cubic) crystallographic structure.

Molar masses and constants:

$$M(\text{H}) = 1.00795 \text{ g mol}^{-1}$$

$$M(\text{Cu}) = 63.546 \text{ g mol}^{-1}$$

$$e = 1.60218 \times 10^{-19} \text{ C}$$

$$F = 96485.3 \text{ C mol}^{-1}$$

$$R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0820584 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

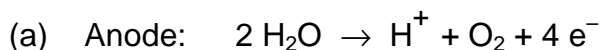
$$V_m = 22.4141 \text{ dm}^3$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

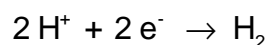
SOLUTION*Approach*

- Determine the number of H₂ moles generated by the electrolysis.
- Calculate the charge required for the H₂ production and the charge of the formation of the Cu deposit and thus the number of moles of Cu in the deposit.
- Calculate the surface concentration of atoms in the Pt (100) face thus the number of Pt atoms per 1 cm²; during an epitaxial growth the number of Cu atoms per 1 cm² equals the number of Pt atoms
- Determine the charge necessary to form one monolayer of Cu and subsequently the number of Cu monolayers on Pt (100)

*Calculations***8.1** Balanced electrode equations

(b) Cathode:

Two reactions occur simultaneously at the cathode:

**8.2** Determination of the charge necessary to generate 2.0000 cm³ of H₂ gas $(T = 273.15 \text{ K}, p = 10.1325 \text{ kPa})$ Two approaches to determination of the number of H₂ gas moles(a) *Determination of $n(\text{H}_2)$: $pV = n(\text{H}_2)RT$*

$$n(\text{H}_2) = \frac{10132.5 \times 2.0000 \times 10^{-6}}{8.314510 \times 273.15} = 8.9230 \times 10^{-6} \text{ mol}$$

$$n(\text{H}_2) = \frac{V(\text{H}_2)}{V_m}$$

$V_m = 22.4141 \text{ dm}^3 \text{ mol}^{-1}$ (V_m refers to the pressure of 1 atm or at $p(\text{H}_2) = 101.325 \text{ kPa}$ and because the pressure of H₂ is ten times smaller, one knows right away that the volume occupied under 1 atm would be 0.2000 cm^3)

$$n(\text{H}_2) = \frac{0.20000 \times 10^{-3}}{22.4141} = 8.9230 \times 10^{-6} \text{ mol}$$

Determination of the charge necessary to generate 8.9230×10^{-6} moles of H_2 gas

Two approaches to determination of the charge:

- (a) the number of H atoms, N_H , equals twice the number of H_2 molecules; if one multiplies N_H by e , then one gets the sought charge, Q_H

$$Q_H = 2 \times 8.9230 \times 10^{-6} \times N_A \times 1.60218 \times 10^{-19}$$

$$Q_H = 1.7219 \text{ C}$$

- (b) one may use the Faraday law

$$m_H = k_H Q_H$$

where k_H is the electrochemical equivalent of H thus the mass of H generated by 1 C; to use this formula one has to calculate k_H ; knowing that the charge of 1 F = 96485.3 C results in formation of 1 mole of H (1/2 mole of H_2), one may easily determine k_H

$$\frac{96485.3}{1.00795} = \frac{1.0000}{k_H}$$

$$k_H = 1.04467 \times 10^{-5} \text{ g C}^{-1}$$

Subsequently

$$Q_H = \frac{m_H}{k_H} = \frac{2 \times 8.9230 \times 10^{-6} \times 1.00795}{1.04467 \times 10^{-5}}$$

$$Q_H = 1.7219 \text{ C}$$

Determination of the Cu deposition charge

$$Q_{Cu} = 2.0000 - Q_H$$

$$Q_{Cu} = 2.0000 - 1.7219 = 0.2781 \text{ C}$$

The moles of Cu is thus $0.2781 / 2 F = 1.4412 \times 10^{-6}$

8.3 Determination of the charge of formation of 1 monolayer (ML) of the Cu deposit and the number of Cu monolayers on the Pt (100) substrate

Calculate the number of surface Pt atoms in the (100) face

Surface area of the fundamental unit:

$$A_u = a_{Pt}^2 = 1.5395 \times 10^{-15} \text{ cm}^2$$

Number of atoms per fundamental (100) unit: $n_u = 2$

Surface atom concentration:

$$s_{\text{Pt}(100)} = \frac{n_u}{A_u} = \frac{2}{1.5395 \times 10^{-15} \text{ cm}^2} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The number of Cu atoms per 1 cm^2 equals the number of Pt atoms - epitaxial growth

$$\sigma_{\text{Cu}(100)} = \sigma_{\text{Pt}(100)} = 1.2991 \times 10^{15} \text{ cm}^{-2}$$

The charge of formation of one monolayer (ML) of Cu equals:

$$q_{\text{ML}} = 2 \times e \times 1.2991 \times 10^{15}$$

$$q_{\text{ML}} = 4.1628 \times 10^{-4} \text{ C}$$

Determination of the number of Cu monolayers on the Pt (100) substrate

$$n_{\text{ML}} = \frac{0.2780 \text{ C}}{4.1628 \times 10^{-4} \text{ C}}$$

$$n_{\text{ML}} = 668 \text{ ML}$$

One can also calculate the number of Cu atoms (8.6802×10^{17}) formed from the number of moles produced and divide this by the number of atoms (1.2991×10^{15}) on the exposed Pt surface to also arrive at 668 monolayers.

PRACTICAL PROBLEMS**PROBLEM 1 (Practical)****Determination of Mg²⁺ and Ca²⁺ in Bottled Water**

- The K_{sp} for calcium oxalate is 2.3×10^{-9} and the K_{sp} for magnesium oxalate is 8.6×10^{-5} .
- In a solution buffered to maintain pH 10, Calmagite indicator is pink when bound to Mg^{2+} and blue in the absence of available magnesium ions. Calcium ions are not bound by Calmagite.
- EDTA binds to Mg^{2+} and Ca^{2+} even in the presence of Calmagite. The stoichiometry of the EDTA-metal complex formed with both Mg^{2+} and Ca^{2+} is 1:1.
- Molar masses: $M(Ca) = 40.08 \text{ g mol}^{-1}$ $M(Mg) = 24.31 \text{ g mol}^{-1}$

Chemicals Available

500 cm³ sample of "Bottled Water"

aqueous buffer (pH 10)

Calmagite indicator

aqueous saturated ammonium oxalate

aqueous ethylenediaminetetraacetic acid

aqueous standardized* Mg^{2+}

distilled water

*0.928 mg Mg^{2+} /cm³ solution, 0.0382 moles Mg^{2+} /dm³

ProcedureA. Precipitation of calcium ions

Precipitate the calcium ions in a 25.00 cm³ aliquot of the "Bottled Water" sample by accurately adding approximately 0.50 cm³ of saturated ammonium oxalate solution (from the common burettes in each lab room). Carefully swirl the solution to ensure uniform mixing. Allow at least 45 minutes for complete precipitation to occur.

B. Standardization of the EDTA solution

Using distilled water, dilute 5.00 cm³ of the standardized magnesium solution to a final volume of 100.0 cm³. Add 40 cm³ of distilled water, 5 cm³ of pH 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of diluted magnesium solution. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

C. Titration of Mg²⁺ and Ca²⁺

Add 40 cm³ of distilled water, 5 cm³ of pH 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of the "Bottled Water" sample. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

D. Titration of Mg²⁺

Add 40 cm³ of distilled water, 5 cm³ of pH 10 buffer solution, and some Calmagite indicator to 5.00 cm³ of the calcium-free "Bottled Water" sample prepared in part **A**. The presence of a small amount of calcium oxalate will not interfere with your titration. Titrate this sample with EDTA solution to a clear blue end point.

Repeat as necessary.

Calculations

Calculate the concentration of Mg²⁺ (in mg dm⁻³) in the "Bottled Water" sample.

Calculate the concentration of Ca²⁺ (in mg dm⁻³) in the "Bottled Water" sample.

PROBLEM 2 (Practical)

Organic qualitative analysis

You have six bottles containing six different organic compounds. From the list of eight compounds given below, identify the contents of each bottle using the reagents available.

Many of these compounds have strong odours. To prevent the laboratory from becoming too odorous, you must keep each bottle tightly capped when it is not in use. Dispose of any waste produced in the bottle labelled "ORGANIC WASTE" at your station. Also place used litmus paper in this bottle. Keep the waste bottle capped when not in use.

Chemicals Available

litmus paper, red and blue

aqueous ceric ammonium nitrate

aqueous chromic-sulfuric acid

aqueous 2,4-dinitrophenylhydrazine

aqueous 0.2% KMnO₄

acetone (2-propanone)

Possible Unknowns*

2-butanone

1-decene

2,3-diamino-2,3-dimethylbutane

hexane

3-methyl-1-butanol

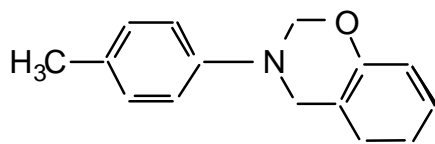
2-methyl-2-butanol

nonanal

propanoic acid

*Several of the unknowns are present as dilute aqueous solutions.

This will not interfere with the test results.

PROBLEM 3 (Practical)**Synthesis of the Substituted Dihydro-1,3-benzoxazine (C)****C**

Benzoxazines have long been recognized as useful biologically-active compounds. One such compound (**C**) will be prepared using the three-step synthesis described below. All of the product obtained in Step I should be used in Step II and similarly all of the product from Step II should be used in Step III. You will be evaluated on both the yield and purity of the final product.

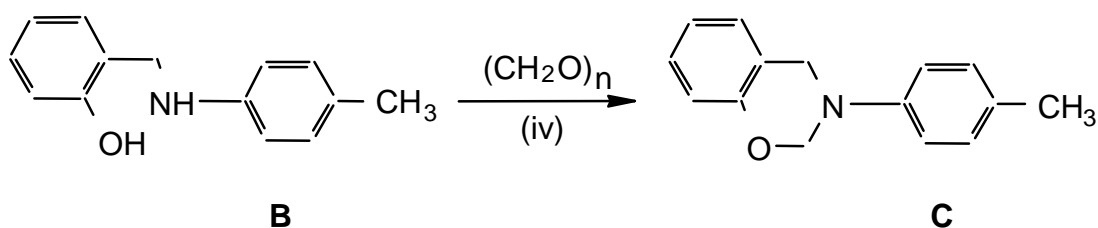
Chemicals available

5 cm³ reaction vial containing 2.5 cm³ of ethanolic 1-amino-4-methylbenzene (0.22 g),
 vial containing 0.25 g of 2-hydroxybenzaldehyde,
 vial containing 0.1 g of sodium borohydride,
 vial containing 0.042 g of paraformaldehyde,
 test tube containing dilute ethanolic KOH,
 (50 mg of KOH dissolved in 10 cm³ of ethanol),
 wash bottle containing dry ethanol,
 Ice is available in each laboratory room.

Molar masses:

$$\begin{array}{lll}
 M(\text{H}) = 1.008 \text{ g mol}^{-1} & M(\text{C}) = 12.011 \text{ g mol}^{-1} & M(\text{N}) = 14.007 \text{ g mol}^{-1} \\
 M(\text{O}) = 15.999 \text{ g mol}^{-1} & M(\text{Na}) = 22.990 \text{ g mol}^{-1} & M(\text{B}) = 10.811 \text{ g mol}^{-1}
 \end{array}$$

STEP III



1. Dissolve all of the paraformaldehyde (iv) in approximately 2.5 cm³ of ethanolic potassium hydroxide (v) in a 5 cm³ vial. Stir to dissolve all of the solid.
2. Add all of product **B** from Step II to the vial. Stir and gently reflux the mixture for 15 minutes. A clear solution should be obtained.
3. Concentrate the solution by carefully boiling off some of the ethanol leaving approximately 1 cm³ in the vial and allow the vial to cool. The crystals which form are the required product **C**.
4. Isolate the crude product **C** by vacuum (suction) filtration and air dry the crystals.
5. Recrystallize the crude product from ethanol. Air dry the crystals for 15 minutes.
6. Determine the melting point* and then mass of the final product.
7. Place all of your remaining product in the numbered vial labelled "PRODUCT C" and hand it in for evaluation.

* Note: A melting point is always recorded as a range -- from when the crystals first begin to melt until the last crystal has melted. The melting point apparatus should be allowed to cool to approximately 50 degrees before you use it. The supervisors will be rechecking both your reported melting point and mass for product C.

30th



International Chemistry Olympiad

**7 theoretical problems
2 practical problems**

THE THIRTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 5–14 JULY 1998, MELBOURNE, AUSTRALIA

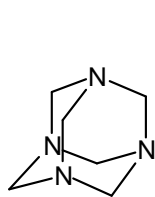
THEORETICAL PROBLEMS

PROBLEM 1

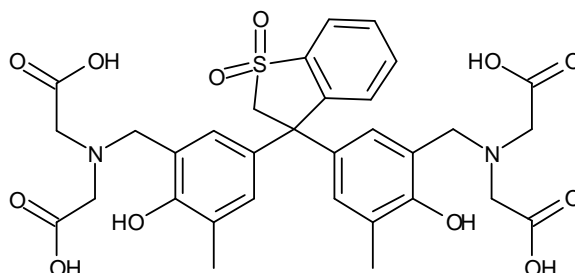
The following 8 steps describe the procedure for analysing a sample of alloy that contains both tin and lead.

1. A 0.4062 g sample of alloy was dissolved by heating it in a small beaker with a mixture of 11 M hydrochloric and 16 M nitric acid. The beaker was heated until the entire alloy dissolved. In this procedure, lead is oxidised to Pb(II) and tin becomes Sn(IV).
2. After 5 minutes of heating to expel oxides of nitrogen and chlorine, some acid remained. When the solution was cooled, a precipitate of some tin compounds and a lead compound appeared.
3. A 25.00 cm³ aliquot of 0.2000 M Na₂H₂EDTA solution was added. The precipitate dissolved and a clear, colourless solution was obtained.
4. This solution was quantitatively transferred to a 250.0 cm³ volumetric flask and made up to the mark with distilled water.
5. A 25.00 cm³ aliquot of this solution was treated with 15 cm³ of a 30 % w/v solution of hexamine (hexamethylenetetramine), some water and two drops of Xylenol Orange solution. The pH of each aliquot was 6.
6. The clear, yellow solution from Step 5 was titrated with standard 0.009970 M lead nitrate solution until the colour just changed from yellow to red. The titre at this endpoint was 24.05 cm³.
7. 2.0 g of solid NaF was added to the titration flask. The solution turned back to yellow.
8. The solution was titrated with more standard 0.009970 M lead nitrate solution until the colour changed to red again. The titre at this endpoint was 15.00 cm³.

Hexamine and Xylenol Orange have the structures shown below. The pK_b of hexamine is 9.5. Xylenol Orange is red below pH 4, yellow above pH 5.



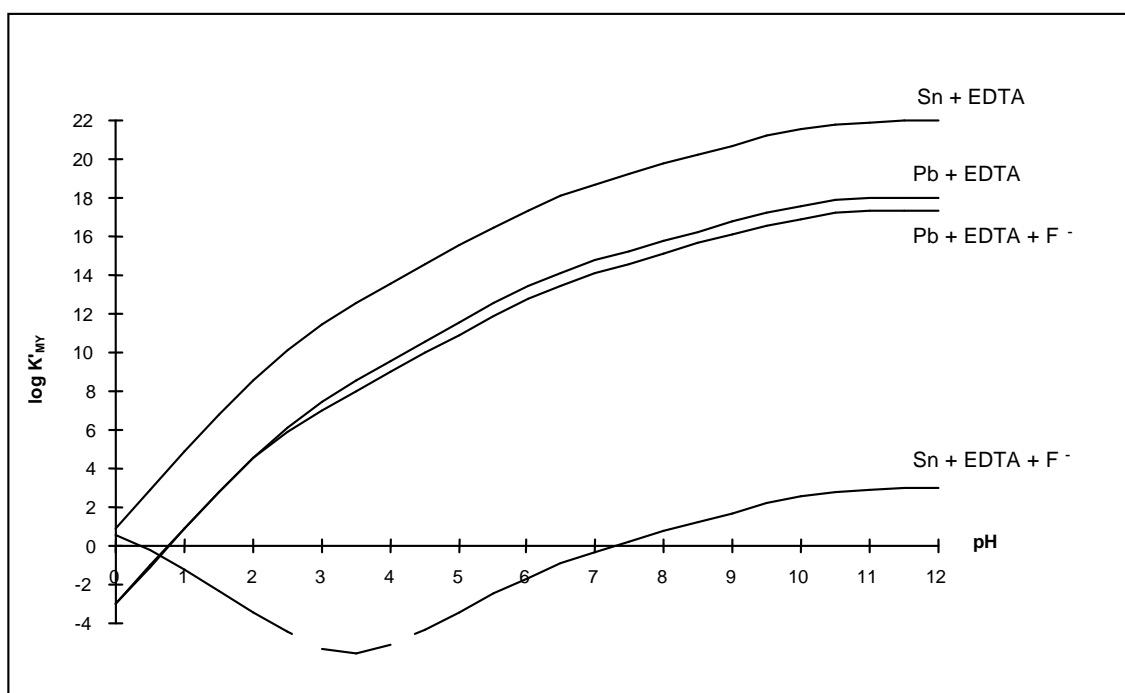
Hexamine



Xylenol Orange (XO)

K_{MY} is the conditional formation constant $= \alpha K_{MY}$.

K_{MY} for the formation of the EDTA complexes of Pb(II) and Sn(IV), in the presence and absence of fluoride, are shown in the following Figure.



- 1.1 What is the lead compound that precipitates in Step 2?
- 1.2 Write a balanced ionic equation that explains the disappearance of the precipitate in Step 3 (at pH 6).
- 1.3 What is the purpose of hexamine in Step 5 of the analysis?
- 1.4 What is the purpose of Xylenol Orange in the analysis?

- 1.5 Write balanced ionic equations for the reactions occurring during the titration and responsible for the colour change at the endpoint in Step 6 of the analysis
- 1.6 What is the purpose of NaF in Step 7 of the analysis?
- 1.7 Write a balanced ionic equation for the reaction that occurs in Step 7.
- 1.8 Write a balanced ionic equation that explains why the colour changed from red to yellow in Step 7 of the analysis.
- 1.9 Write a balanced ionic equation that explains why the lines on the graph below of $\log K_{MY}$ vs pH for Pb + EDTA and Pb + EDTA + F⁻ are coincident below pH 2.
- 1.10 Calculate the percentage by weight of Sn and Pb in the alloy.

SOLUTION

- 1.1 PbCl₂ or any hydroxo species etc.
- 1.2 $PbCl_2(s) + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+ + 2 Cl^-$ or similar
- 1.3 It forms a pH buffer.
- 1.4 It is a metallochromic indicator.
- 1.5 (i) The reaction that occurs during the titration:
 $Pb^{2+} + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+$
- (ii) At the endpoint, a slight excess of Pb²⁺ forms a red complex with the xylenol orange indicator:
 $Pb^{2+} + XO \text{ (yellow)} \rightarrow PbXO^{2+} \text{ (red)}$
- 1.6 The role of the NaF: It forms a complex with tin.
- 1.7 From the graph of $\log K_{MY}$ vs pH , it can be seen that the fluoride forms a stable complex with Sn⁴⁺ but not with Pb²⁺ at pH 6, displacing EDTA:
 $SnY + nF^- + 2 H^+ \rightarrow SnF_n^{(n-4)-} + H_2Y^{2-}$ where n is typically 4 - 6.
- 1.8 The released EDTA destroys the small amount of red PbXO complex, producing free (yellow) XO. (Charge on XO ignored)
 $H_2Y^{2-} + PbXO^{2+} \rightarrow PbY^{2-} + XO \text{ (yellow)} + 2 H^+$
- 1.9 Below pH 2, F⁻ is protonated and does not compete effectively with Y for Pb²⁺
 $H^+ + F^- \rightarrow HF$.
- 1.10 The percentage by mass of Sn and Pb in the alloy:
 The amount of EDTA in excess from the amount of standard Pb²⁺ titrant:
 $n(\text{EDTA}) = n(\text{Pb}^{2+}) = 0.02405 \text{ dm}^3 \times 0.009970 \text{ mol dm}^{-3} = 2.398 \times 10^{-4} \text{ mol}$.

The original amount of EDTA:

$$n(\text{EDTA})_{\text{init.}} = 0.1 \times 25.00 \text{ dm}^3 \times 0.2000 \text{ mol dm}^{-3} = 5.000 \times 10^{-4} \text{ mol}$$

EDTA consumed by the Pb^{2+} and Sn^{4+} in a 25 cm^3 aliquot:

$$n(\text{EDTA})_{\text{consumed}} = 5.000 \times 10^{-4} - 2.398 \times 10^{-4} \text{ mol} = 2.602 \times 10^{-4} \text{ mol} = n(\text{Pb}^{2+} + \text{Sn}^{4+}) \text{ in a } 25 \text{ cm}^3 \text{ aliquot.}$$

The amount of EDTA released from SnY by reaction with fluoride:

$$n(\text{EDTA})_{\text{released}} = n(\text{Pb}^{2+})_{\text{stand.}} = 15.00 \text{ cm}^3 \times 0.009970 \text{ mol dm}^{-3} = 1.496 \times 10^{-4} \text{ mol} = n(\text{Sn}^{4+}) \text{ in the } 25 \text{ cm}^3 \text{ aliquot}$$

$$\text{in a } 25 \text{ cm}^3 \text{ aliquot } n(\text{Pb}^{2+}) = (2.602 \times 10^{-4} - 1.496 \times 10^{-4}) \text{ mol} = 1.106 \times 10^{-4} \text{ mol}$$

In the original 0.4062 g sample of alloy:

$$m(\text{Sn}) = 10 \times 1.496 \times 10^{-4} \text{ mol} \times 118.69 \text{ g mol}^{-1} = 0.1776 \text{ g}$$

$$m(\text{Pb}) = 10 \times 1.106 \times 10^{-4} \text{ mol} \times 207.19 \text{ g mol}^{-1} = 0.2292 \text{ g}$$

The percentages of tin and lead:

$$\text{Sn: } 100 \times (0.1776 / 0.4062) = 43.7 \%$$

$$\text{Pb: } 100 \times (0.2292 / 0.4062) = 56.4 \%$$

PROBLEM 2

Part A: Dating Historical Events Using Pb-210

Nathan Thompson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of the planting of the seeds is not known. Over the years, pollen produced by the European oak and elm accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive Pb-210 (half-life = 22.0 years) were deposited at the same time. Note that the European oak and elm trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The sediment core was cut into 1 cm slices and examined for pollen and radioactive Pb-210.

The examination of the sediment core found that:

- Pollen of European oak and elm first occur at a depth of 50 cm.
- The activity of Pb-210 at the top of the sediment core is 356 Bq/kg and at 50 cm depth 1.40 Bq/kg.

2.1 In what year did Nathan Thompson plant the seeds?

Radioactive Pb-210 is one of the daughters of U-238. U-238 is present in the earth's crust and for some reason a certain amount of Pb-210 rains out of the atmosphere and attaches itself to sediment particles that accumulate at the bottom of lakes.

- The U-238 decay chain is:
- U-238 – U-234 – Th-230 – Ra-226 – Rn-222 – (Po-218 – Bi-214)* – Pb-210 – Pb-206 (stable)

* Very short half-lives: minutes and days

2.2 Which step in the decay scheme explains how Pb-210 ends up in rainwater while its parent U-238 is only present in the earth's crust?

Part B: Separation of Radionuclides for Nuclear Medicine Applications.

The Ga-67 is used to image lymphoma. It is preferentially produced by bombarding a target enriched in Zn-68 (> 98%) with high energy protons for 11 hrs. Zn-68 has a natural abundance of 18.8%. Due to the target design other radionuclides may be produced (see Table 1). Twelve hours after the end of bombardment, Ga-67 is bound on a cation exchange. Then the other radionuclides and the Zn-68 are eluted in the wash solution leaving Ga-67 bound to the column.

Table 1

Radionuclide	Half-life
Co-55	18.2 hr
Ni-57	36.0 hr
Co-57(daughter of Ni-57)	270 days
Cu-64	12.7 hr
Cu-67	61.7 hr
Zn-65	244 days
Ga-67	78.35 hr
Ga-66	9.4 hr

Cu-64 and Co-55 have ideal half-lives for use in nuclear medicine applications and it would be useful to isolate them from the wash solution.

The distribution coefficient D is a measure of the partition of a metal ion between the ion-exchange resin and the eluant.

For a given ion-exchange resin and eluant, D is given by

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per cm}^3 \text{ of eluant}}$$

For a reasonable separation of two metal ions their D values should differ by at least 10 units.

2.3 The wash solution is evaporated to dryness and the residue resuspended in a small amount of 0.2 M HCl 96 % methanol and loaded onto an anion exchange column. Use the distribution coefficients D given in Figures 1 and 2 and rank the best solvent systems (from given alternatives) for eluting Cu-64 and Co-55.

2.4 Having isolated relevant radionuclides, the presence of some long-lived radionuclides could interfere with medical use of Cu-64 or Co-55 or Ga-67. Indicate which of the following statements is either true or false (one or more may be true).

- a) Ni-57 may be present as a contaminant of Co-55.
- b) Co-57 will interfere with the medical use of Co-55.
- c) Cu-67 will interfere with the medical use of Cu-64.
- d) Ga-66 will interfere with the use of Ga-67.
- e) Ga-67 will interfere with the medical use of Cu-64.

2.5 If radionuclide contamination of Cu-64 or Co-55 or Ga-67 occurred, which method would reduce the amount of radionuclide contaminant/s? Indicate which of the following statements is either true or false. (one or more may be true).

- a) Remove Ni-57 before isolating Co-55.
- b) Separate the Ni-57 from the bombarded target material before isolating the Ga-67.
- c) Separate the radionuclides closer to the end of bombardment.
- d) Allow the Ni-57 to decay before isolation of Co-55.

2.6 If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with high energy protons, indicate which of the following statements is either true or false. (one or more may be true).

- a) Ga-67 would be produced at 5 fold higher yields.
- b) Ga-67 would be produced at 5 fold lower yields.
- c) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would increase.
- d) Ga-67 would be produced at lower yields and contamination of Cu-64, Co-55, Co-57, Ni-57 would remain the same.

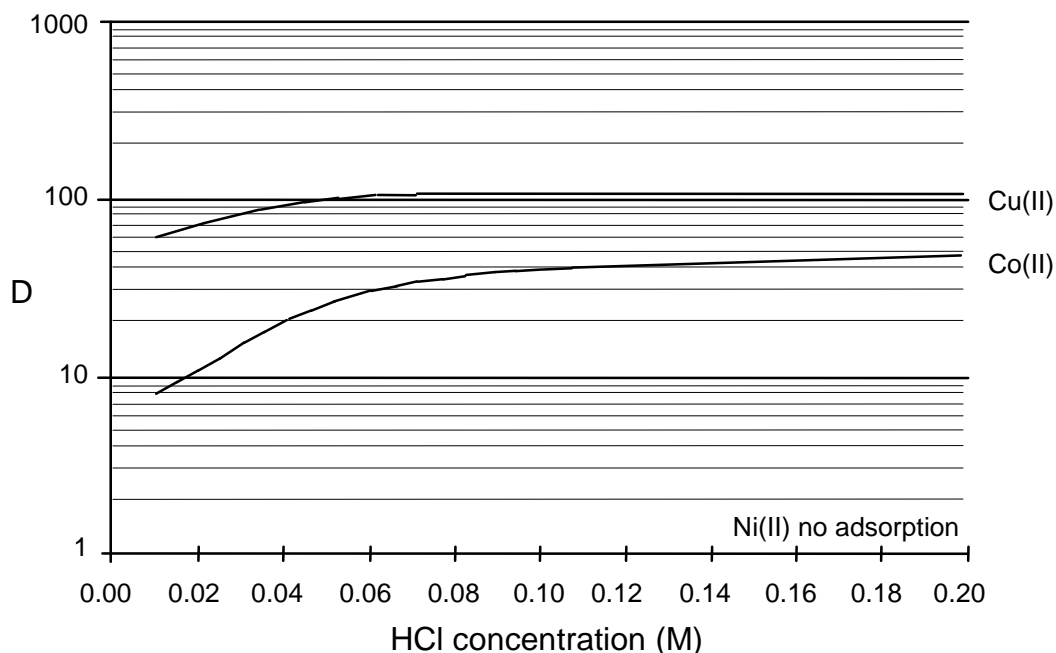


Figure 1. Distribution coefficients, D of metal ions between anion exchange resin and 96 % methanol at varying HCl concentrations. (note D value for Zn > 1000)

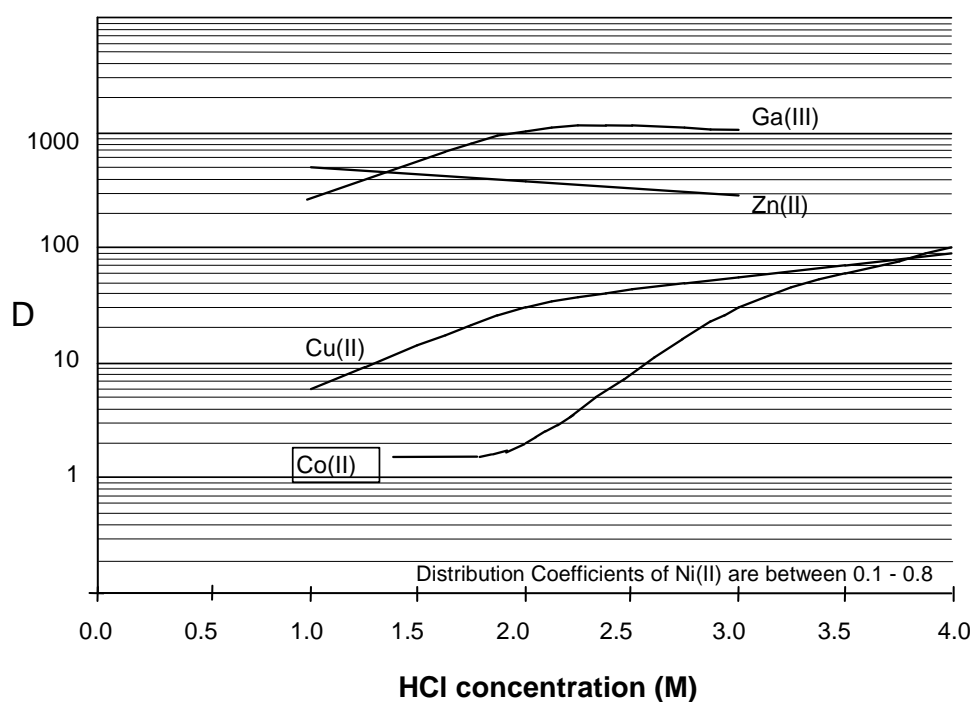


Figure 2. Distribution coefficients, D of metal ions between anion exchange resin and 55 % isopropyl alcohol at varying HCl concentrations.

SOLUTION

2.1 In what year did Nathan Thompson plant the seeds?

Calculations:

Over a depth of 50 cm the apparent decay of Pb-210 was equal to $356 - 178 - 89 - 44.5 - 22.5 - 11.25 - 5.63 - 2.81 - 1.39 = 8$ half-lives = 8×22 years = 176 years

If 1995 was the year of coring then the year of arrival was $1995 - 176 = 1819 (\pm 2)$

2.2 Correct answer: Ra-226 - Rn-222

2.3 Use the distribution coefficients D given in Figures 1 and 2 and rank the following solvent systems for isolating Cu-64 and Co-55 by writing the numbers 1 to 4 in the boxes (1 is best).

- | | | |
|------|---------------------------------|-----------------------------|
| A | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Cu-64 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Co-55 |
|
 | | |
| B | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
|
 | | |
| C | 2.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 1.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |
|
 | | |
| D | 0.2 M HCl 96% methanol | to remove Ni-57 followed by |
| | 3.0 M HCl 55% isopropyl alcohol | to remove Co-55 followed by |
| | 4.0 M HCl 55% isopropyl alcohol | to remove Cu-64 |

The best sequence: B, C, D, A

The other sequences: B, C, A, D or C, B, D, A or C, B, A, D were also accepted but evaluated by less points.

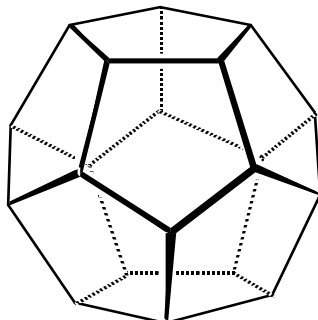
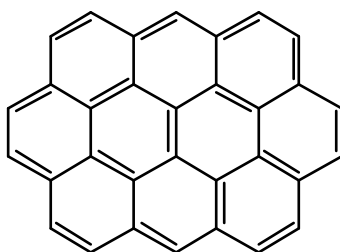
- 2.4** a) False;
 b) True;
 c) True
 d) False
 e) False

- 2.5** a) True
b) True
c) True
d) False

- 2.6** a) False
b) True
c) False
d) True
-
-

PROBLEM 3

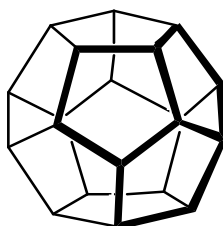
The three-dimensional structures of polycyclic molecules can often be explained in terms of the minimisation of angle strain. Consider the following molecules:

Dodecahedrane, C₂₀H₂₀and Ovalene, C₃₂H₁₄.

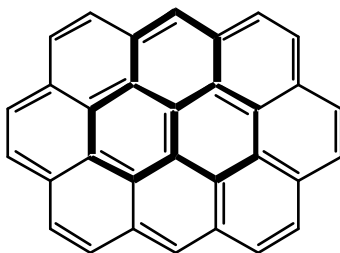
Each C₅ ring of dodecahedrane is a regular pentagon, while each C₆ ring of ovalene can be regarded as a regular hexagon.

- 3.1 What are the $\angle(\text{CCC})$ angles for each of these rings?
- 3.2 Which configuration (trigonal planar, 120°, tetrahedral, 109.5°, or octahedral, 90°) do the above $\angle(\text{CCC})$ angles most closely match?
- 3.3 What is the hybridization (sp , sp^2 , or sp^3) which most closely conforms to the geometric structure of dodecahedrane, and of ovalene?

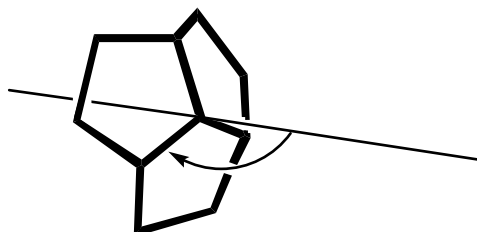
A “junction” is defined here to mean any 3-ring system, sharing a common central carbon atom, within a molecule. Compare the junctions (shown in bold) of three pentagons within dodecahedrane:



and of three hexagons within ovalene:

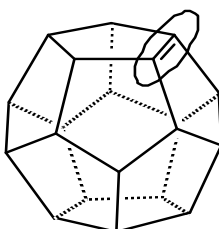


Consider an axis passing through the central carbon atom of each juncture such that the angle the axis forms with all three C-C bonds radiating from this C atom is identical.

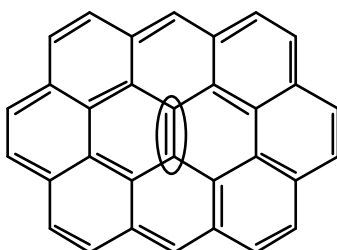


- 3.4** What is the value of this angle for dodecahedrane (make an “educated guess”, to the nearest three degrees), and for ovalene?
- 3.5** Subtracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar ?

Now consider two polycyclic 'alkenes', dodecahedrene ($C_{20}H_{18}$):



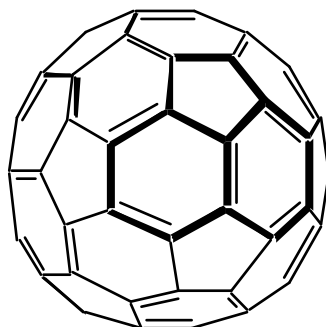
and ovalene:



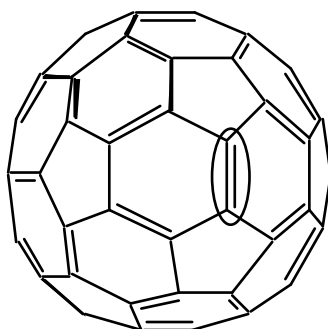
Assume that the molecular framework is rigid and is not significantly distorted by H_2 addition to the (indicated) double bond on each structure. Assume also that all double bonds are localized in assessing these systems.

3.6 Compare the indicated pairs of carbon atoms (encircled above). For which C=C pair is H₂ addition expected to be more exothermic?

And now, on to fullerenes. For all known fullerenes, the deviation from planarity at any juncture is less than is the case for dodecadedrane.



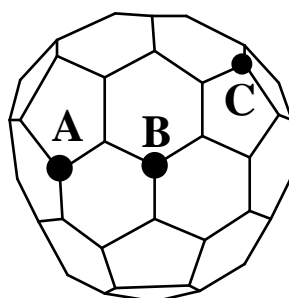
For C₆₀, all junctures are entirely equivalent. Now consider H₂ addition at a C=C bond of C₆₀:



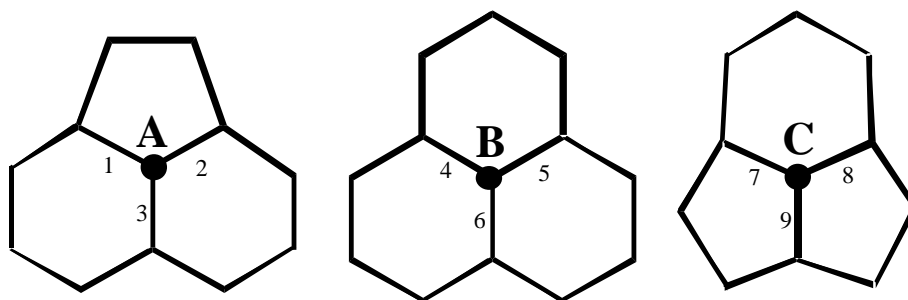
3.7 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition most exothermic? (Again, assume localization of double bonds.)

3.8 For which of C₆₀, dodecahedrene, or ovalene is H₂ addition least exothermic?

There is evidence for fullerenes smaller than C₆₀, such as C₅₈. The C₅₈ structure (ignoring any distinction between 'double' and 'single' bonds) is shown below:

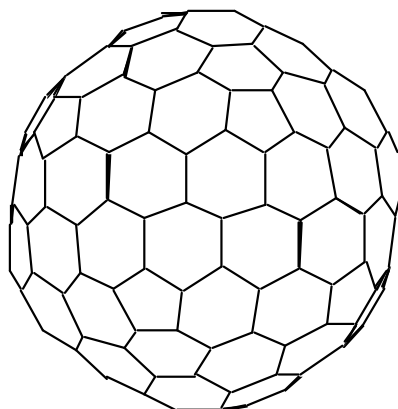


The junctures centred on atoms **A**, **B** and **C** on the above structure can be redrawn for greater clarity:



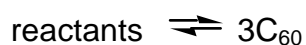
- 3.9 Which juncture has the least deviation from planarity ?
- 3.10 Which juncture has the greatest deviation from planarity ?
- 3.11 Of the above carbon-carbon bonds, numbered from 1 to 9, which represents the most favourable site for H₂ addition?

Finally, consider a larger fullerene, C₁₈₀:

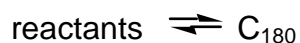


To a first approximation, both C₆₀ and C₁₈₀ are "perfect" spheres.

- 3.12 Which has the larger average deviation from planarity at each juncture? C₆₀ or C₁₈₀?
- 3.13 Compare the geometries of C₆₀ and C₁₈₀, and graphite. Which of the statements shown on the answer sheet (concerning enthalpies of formation, in kJ g⁻¹ units) is correct?
- Fullerenes are generated on a very rapid timescale, typically milliseconds. In all techniques, C₆₀ is produced in much greater quantities than C₁₈₀.
- 3.14 Which of the graphs shown on the answer template best represents the dependence of potential energy upon reaction progress for the two processes:



and



SOLUTION

- 3.1 Dodecahedrane: 108°
 Ovalene 120°

- 3.2 Dodecahedrane: tetrahedral
 Ovalene: trigonal planar

The $\angle(\text{CCC})$ angle for dodecahedrane is only slightly lower than the tetrahedral angle, but is much higher than the 90° required for octahedral coordination and is obviously too low for a trigonal planar arrangement. The corresponding angle for ovalene is identical to that for trigonal planar.

- 3.3 Dodecahedrane: sp^3
 Ovalene: sp^2

Reasoning: As above, dodecahedrane conforms quite closely to a tetrahedral arrangement at each C atom, thus sp^3 . Ovalene corresponds exactly to a trigonal planar arrangement, so sp^2 .

- 3.4 Dodecahedrane, $\text{C}_{20}\text{H}_{20}$ 109 -115 degrees
 ovalene, $\text{C}_{32}\text{H}_{14}$ 90 degrees

Reasoning: For dodecahedrane, the three rings are not coplanar. Determination of the exact axis angle is complicated; but note that the $\angle(\text{CCC})$ angle for a C_5 ring is very close to the tetrahedral angle. Therefore distortion from a tetrahedral configuration at each carbon in dodecahedrane is slight: therefore the axis angle is about 109.5° (more probably $\sim 112^\circ$). For ovalene, all rings are coplanar. The axis angle is clearly 90° .

- 3.5 Correct: Ovalene, $\text{C}_{32}\text{H}_{14}$

- 3.6 H_2 addition is more exothermic dodecahedrene.

Reasoning: The C=C pair within the dodecahedrene skeleton is more suited to sp^3 -hybridization than sp^2 -hybridization: this favours dihydrogenation to yield dodecahedrane. For ovalene, sp^3 -hybridization is disfavoured relative to sp^2 -

hybridization, so dihydrogenation at the indicated site is disfavoured on the grounds of angle strain.

(This is quite apart from any reduction in ovalene's aromaticity, which is also likely to disfavour hydrogenation!)

3.7 H₂ addition from among C₆₀, dodecahedrene, ovalene is most exothermic for dodecahedrene.

Reasoning: The deviation from planarity, in a C₆₀ juncture, is less than in dodecahedrene (which has very close to tetrahedral, i.e. sp³, coordination at each carbon) but is clearly more than in ovalene (which is flat, i.e. ideal for sp² hybridization). Thus C₆₀ is intermediate between dodecahedrene and ovalene in its preference for hydrogenated versus dehydrogenated structures. The junctures in dodecahedrene are all pentagons [C₅,C₅,C₅]. The junctures in ovalene are all [C₆,C₆,C₆]. Those in C₆₀ are [C₅,C₆,C₆]. The implication is that, the more pentagons are found in a juncture, the greater the deviation from planarity and hence the greater the relative stability of sp³ hybridization, rather than sp², at the central carbon atom.

3.8 H₂ addition from among C₆₀, dodecahedrene and ovalene is the least exothermic for ovalene.

3.9 The least deviation from planarity is in **B**.

3.10 The greatest deviation from planarity is in **C**.

Reasoning: The juncture centred on atom 'A' features two hexagons and a pentagon: this is the same pattern as that seen in the Ceo junctures. For 'B', the three surrounding rings are all hexagons, while for 'C', the juncture contains two pentagons and a hexagon. The trend for increasing deviation from planarity with increasing number of pentagons in the juncture indicates that the deviation from planarity will be most severe at 'C', and least severe at 'B'.

3.11 The most favourable site for H₂ addition is at bond number 9.

Reasoning: Bonds 1,2,7, and 8 are each flanked by a pentagon and a hexagon. Bonds 3-6 are each 'sandwiched' between two hexagons. Bond 9 is between two adjacent pentagons. Of these configurations, bond 9 represents the geometry which is most distorted from planarity (preferred by sp^2 hybridization) and is closest to the dodecahedrane skeleton (for which the bond angles are almost ideal for sp^3 hybridization). Thus, bond 9 is the most favourable site for dihydrogenation.

3.12 The larger average deviation from planarity at each juncture is in C₆₀.

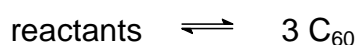
Reasoning: C₁₈₀ obviously has a larger diameter than C₆₀, so its average deviation from planarity at a given juncture is less than that found for C₆₀. [To visualize this, it may help to note that the 'equator' of C₁₈₀ will be defined by more atoms than are found along C₆₀'s 'equator'.]

3.13 The correct statement:

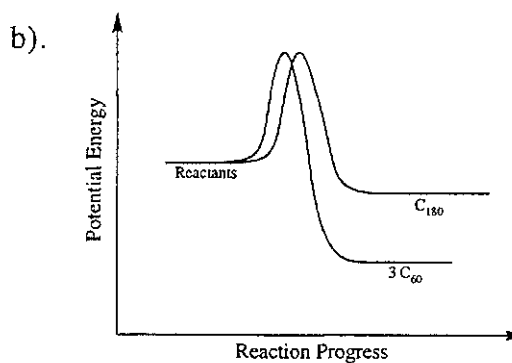
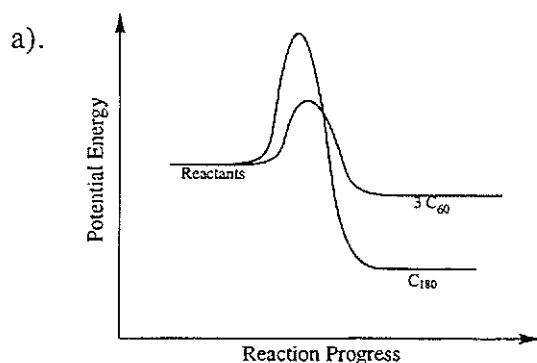
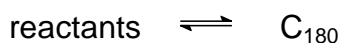
$$\Delta_f H^\circ (\text{C}_{60}) > \Delta_f H^\circ (\text{C}_{180}) > \Delta_f H^\circ (\text{graphite})$$

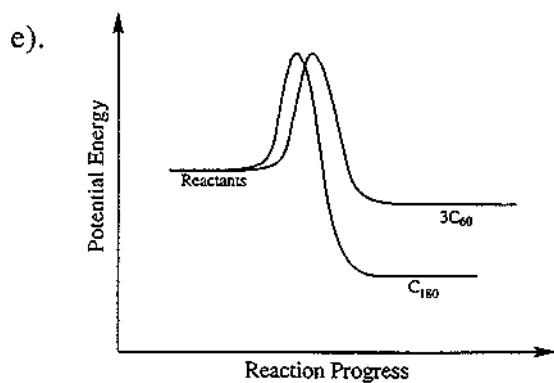
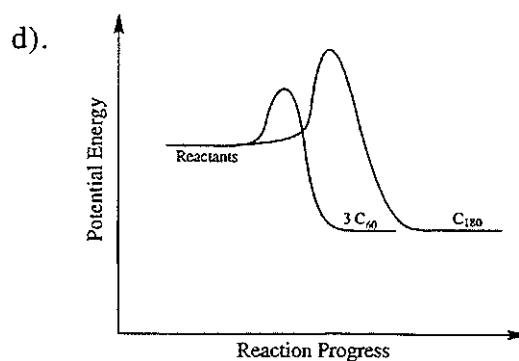
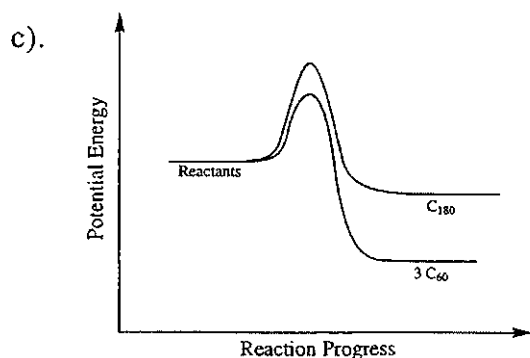
Reasoning: C₆₀ has a larger average deviation from planarity than C₁₈₀, so sp^2 hybridization is less favourable for the smaller fullerene. However, both fullerenes are non-planar and therefore less amenable to sp^2 hybridization than graphite (which additionally gets stabilization from inter-layer electronic effects, although this last point does not have to be considered to attain the correct answer).

3.14 Which of graphs best represents the dependence of potential energy upon reaction progress for the two processes:



and





The best graph is: a)

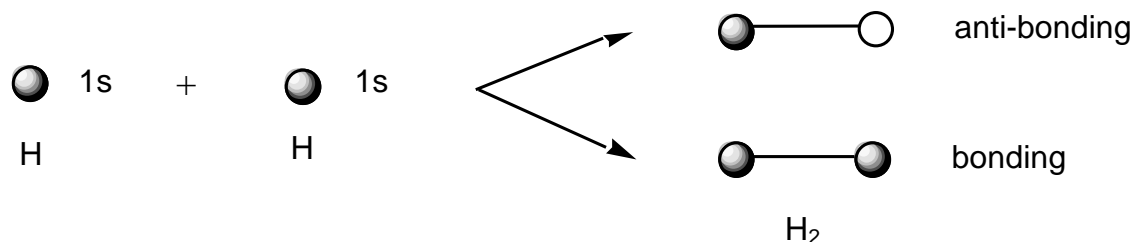
Reasoning: The equilibrium reaction



is characterized by a large positive energy change in going from left to middle, and a negative energy change of smaller magnitude in going from middle to right. Formation of C_{180} is thermodynamically favoured over three C_{60} molecules. However, C_{60} is found to predominate, implying that the reaction is under kinetic control and does not have sufficient time to reach equilibrium.

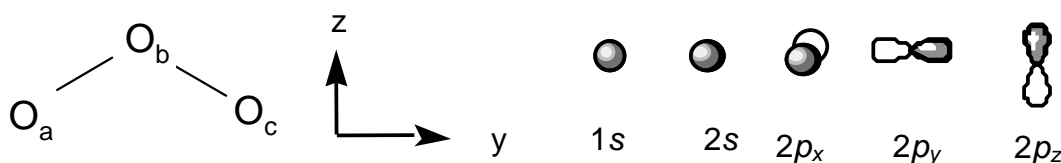
PROBLEM 4

When two hydrogen atoms come together, the 1s atomic orbitals combine to form bonding and anti-bonding molecular orbitals:



In a similar way, we may combine the atomic orbitals of more complicated atoms to form molecular orbitals, taking into account the symmetry of the molecule.

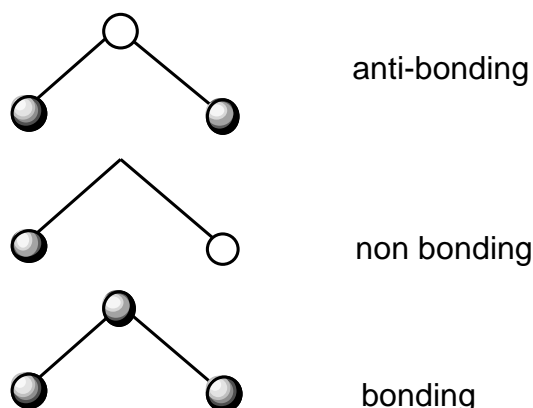
Consider the ozone molecule, O_3 , which is shaped like an Australian boomerang. We can arrange the oxygens as follows (in the yz plane) and assume that there are 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on each atom.



The atoms O_a and O_c are "related by symmetry" and the 1s orbitals on these atoms form symmetric and anti-symmetric combinations:



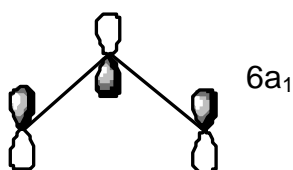
In this molecule the 1s atomic orbital on O_b is classified as symmetric. It can combine with the symmetric combination of O_a and O_c given above (but not with the anti-symmetric combination) to form bonding and anti-bonding molecular orbitals. The anti-symmetric combination is non-bonding. The final three molecular orbitals are:



- 4.1** On the answer sheet, use a similar approach to construct the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. (Remember to form the symmetric and anti-symmetric combinations of O_a and O_c first.)

We may now rearrange these molecular orbitals in order of increasing energy. This can be generalised to other triatomic molecules. The energy of these orbitals is different in a bent triatomic molecule (like ozone) compared to a linear molecule (like carbon dioxide). The variation in orbital energy may be represented in a "Walsh diagram" for XY_2 molecules as shown on the answer sheet. It shows a plot of the energy of each orbital versus the $Y-X-Y$ bond angle. The orbitals have been given labels which we call "symmetry labels".

The $6a_1$ orbital referred to in the Walsh diagram is shown below.



- 4.2** Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ?

Only occupied molecular orbitals affect the geometry, and a doubly occupied orbital has more influence than a singly occupied orbital. For example, O_3 has 24 electrons and so at a bond angle of 135° the orbitals are doubly occupied up to $6a_1$. Thus, the lowest-energy geometry of ozone (taking into account steric repulsion and the contrasting energy

behaviour of the $4b_2$, $1a_2$ and $6a_1$ orbitals) is probably towards the left of the Walsh diagram, which is consistent with the observed bond angle of 116° .

4.3 At a bond angle of 135° , what are the highest occupied orbitals for the molecules BO_2 , CO_2 , NO_2 and FO_2 ?

4.4 The bond angles of BO_2 , CO_2 and O_3 are known experimentally to be 180° , 180° and 116° , respectively. Use the Walsh diagram on the answer sheet to predict whether NO_2 and FO_2 are more or less bent than O_3 .

SOLUTION

4.1 Construction of the molecular orbitals arising from the separate interaction of the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals is shown on the next page.

4.2 Why does the energy of the $6a_1$ orbital increase so rapidly as the bond angle changes from 90° to 180° ? (Choose one)

- Because the bonding character decreases.
- Because the anti-bonding character increases.
- Both (a) and (b).
- Because the overlap decreases.

The correct answer is c).

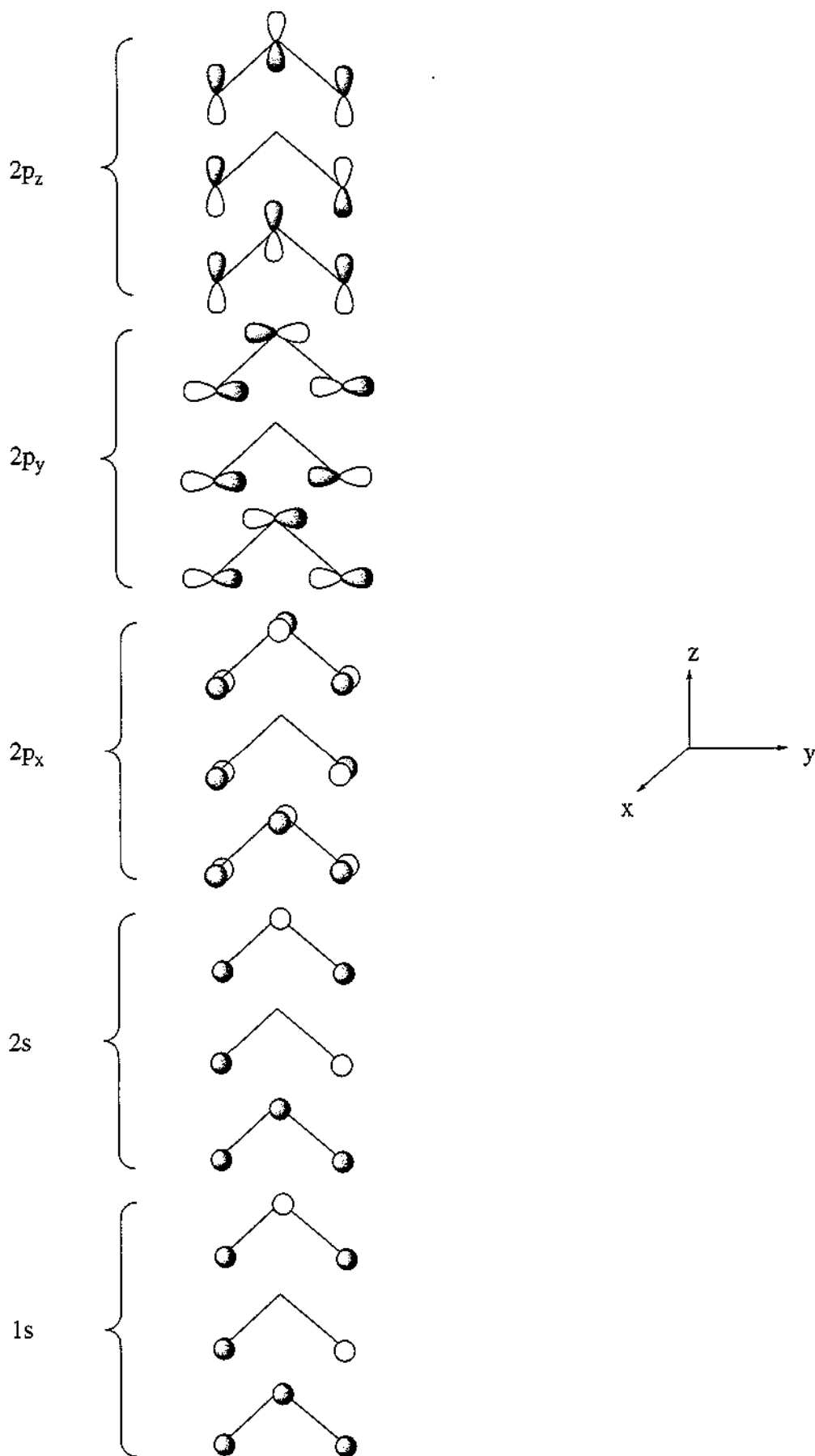
Reasoning: The energy changes so rapidly because the overlap is bonding between all three atoms in the bent molecule, but becomes more and more anti-bonding as the molecule approaches linearity:

4.3

O_3	BO_2	CO_2	NO_2	FO_2
$6a_x$ (24e ⁻)	$4b_2$ (21e ⁻)	$4b_2$ (22e ⁻)	$6a_1$ (23e ⁻)	$2b_x$ (25e ⁻)

4.4 The correct answer is (d): NO_2 is less bent than O_3 , and FO_2 is more bent than O_3 .

Atomic orbitals Molecular orbitals



PROBLEM 5

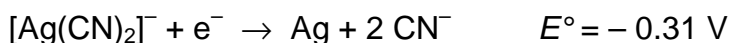
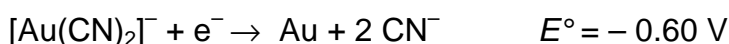
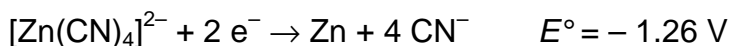
Metallic gold frequently is found in aluminosilicate rocks and it is finely dispersed among other minerals. It may be extracted by treating the crushed rock with aerated sodium cyanide solution. During this process metallic gold is slowly converted to $[\text{Au}(\text{CN})_2]^-$, which is soluble in water (reaction 1).

After equilibrium has been reached, the aqueous phase is pumped off and the metallic gold is recovered from it by reacting the gold complex with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$ (reaction 2).

5.1 Write balanced ionic equations for reactions (1) and (2).

Gold in nature is frequently alloyed with silver which is also oxidized by aerated sodium cyanide solution.

5.2 Five hundred litres (500 L) of a solution 0.0100 M in $[\text{Au}(\text{CN})_2]^-$ and 0.0030 M in $[\text{Ag}(\text{CN})_2]^-$ was evaporated to one third of the original volume and was treated with zinc (40 g). Assuming that deviation from standard conditions is unimportant and that all these redox reactions go essentially to completion, calculate the concentrations of $[\text{Au}(\text{CN})_2]^-$ and of $[\text{Ag}(\text{CN})_2]^-$ after reaction has ceased.

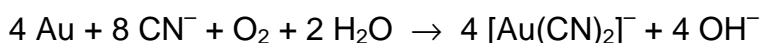


5.3 $[\text{Au}(\text{CN})_2]^-$ is a very stable complex under certain conditions. What concentration of sodium cyanide is required to keep 99 mol% of the gold in solution in the form of the cyanide complex? $\{[\text{Au}(\text{CN})_2]^- : K_f = 4 \times 10^{28}\}$

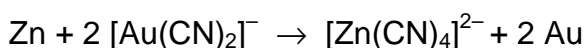
5.4 There have been several efforts to develop alternative gold extraction processes which could replace this one. Why? Choose one of the options on the answer sheet.

SOLUTION

5.1 Reaction 1:



reaction 2:



$$5.2 \quad E^{\circ}(\text{Ag}/\text{Zn}) = -0.31 - (-1.26) = 0.95 \text{ V}$$

$$E^{\circ}(\text{Au}/\text{Zn}) = -0.60 - (-1.26) = 0.66 \text{ V}$$

$$E^{\circ}(\text{Ag}/\text{Zn}) > E^{\circ}(\text{Au}/\text{Zn})$$

Therefore the Ag(I) complex will be reduced first.

$$(i) \quad \text{mol Ag(I) in } 500 \text{ dm}^3 = 500 \times 0.0030 = 1.5 \text{ mol}$$

$$(ii) \quad \text{mol Au(I) in } 500 \text{ dm}^3 = 500 \times 0.010 = 5.0 \text{ mol}$$

$$(iii) \quad \text{mol Zn in } 40 \text{ g} = 40 / 65.38 = 0.61 \text{ mol}$$

1 mol zinc reacts with 2 mol of Ag(I) or Au(I)

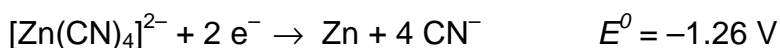
Therefore 0.61 mol Zn will consume 1.2 mol $[\text{Ag}(\text{CN})_2]^-$

$$[\text{Ag}(\text{CN})_2]^- \text{ remaining} = 1.5 - 1.2 = 0.3 \text{ mol}$$

$[\text{Au}(\text{CN})_2]^-$ will not be reduced.

$$\text{Concentration of } [\text{Au}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.010 \times 3 = 0.030 \text{ M}$$

$$\text{Concentration of } [\text{Ag}(\text{CN})_2]^- \text{ when reaction has ceased} = 0.3 \times (3 / 500) = 0.002 \text{ M}$$



$$5.3 \quad \text{Au}^+ + 2 \text{CN}^- \rightarrow [\text{Au}(\text{CN})_2]^- \quad K_f = 4 \times 10^{28}$$

99 mol % $[\text{Au}(\text{CN})_2]^-$

$$K_f = \frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+][\text{CN}^-]^2}$$

$$\frac{[\text{Au}(\text{CN})_2]^-}{[\text{Au}^+] + [\text{Au}(\text{CN})_2]^-} = 99 / 100$$

$$\text{Thus: } 100 \times [\text{Au}(\text{CN})_2]^- = 99 \times [\text{Au}^+] + 99 \times [\text{Au}(\text{CN})_2]^-$$

$$\text{Therefore } [\text{Au}^+] = [\text{Au}(\text{CN})_2]^- / 99$$

Substituting into K_f :

$$4 \times 10^{-28} = 99 / [\text{CN}^-]^2$$

$$[\text{CN}^-] = 5 \times 10^{-14}$$

- 5.4** Sodium cyanide escapes into ground water and produces hydrogen cyanide which is toxic to many animals.
-
-

PROBLEM 6

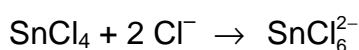
Unlike carbon, tin can increase its coordination number beyond four. Like carbon, tin forms a chloride, SnCl_4 .

6.1 Draw two alternative geometries for SnCl_4 .

Lewis acids such as SnCl_4 react with Lewis bases such as chloride ion or amines. In the case of chloride the following two reactions are observed.



and



6.2 Draw three alternative geometries for SnCl_5^- .

6.3 Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for SnCl_5^- .

6.4 Draw three alternative geometries for SnCl_6^{2-} .

6.5 Use VSEPR theory to predict which of these geometries is likely to be preferred for SnCl_6^{2-} .

A solution containing SnCl_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z = 295$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{35}Cl .

6.6 Write the empirical formula for the tin-containing species detected by this technique.

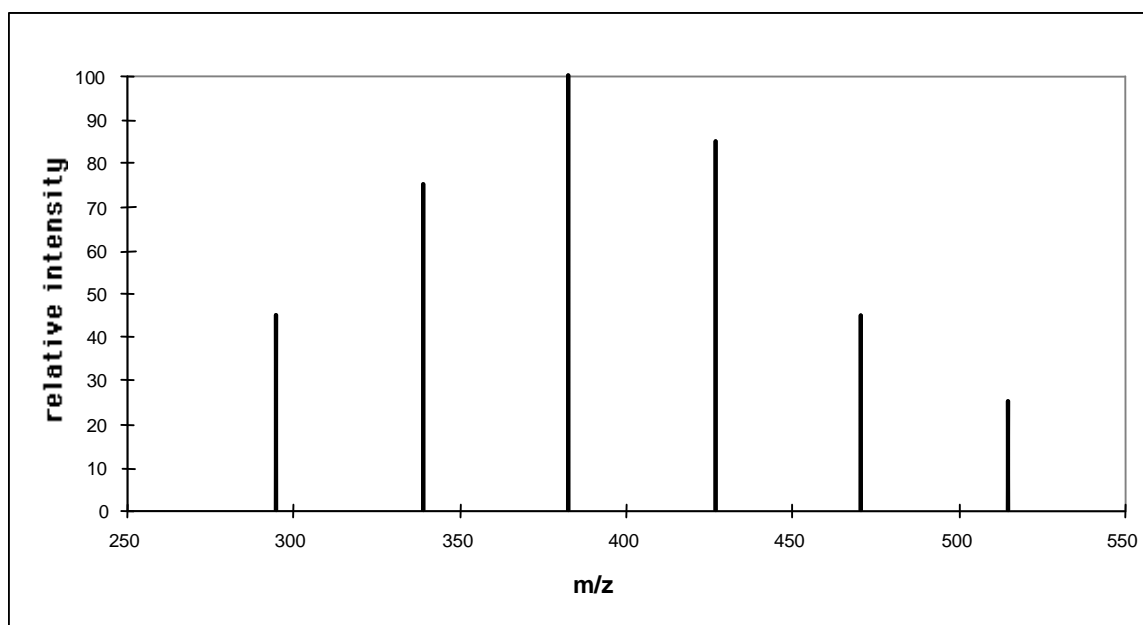
A solution containing SnBr_6^{2-} (as the tetrabutylammonium salt) was examined by negative ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z=515$.

You may assume that the only isotopes observed in this species are ^{120}Sn and ^{79}Br .

6.7 Write the formula for the tin-containing species detected by this technique.

The ESMS spectrum of a solution made by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} (as tetrabutylammonium salts) shows six major species (Fig. 1).

Fig. 1



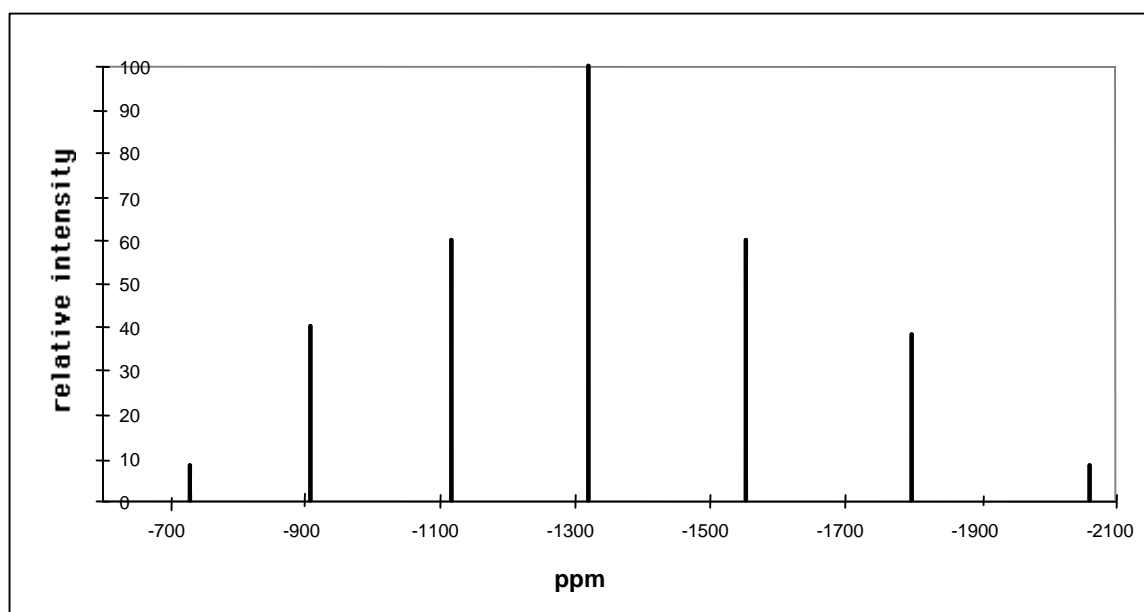
6.8 Write the empirical formula for each of the four new species.

^1H and ^{13}C NMR spectroscopy of molecules enable detection of a separate signal for each proton and ^{13}C nucleus which is in a different environment. These signals are recorded on dimensionless parts per million (ppm) scale relative to some agreed standard reference compound. Similarly, ^{119}Sn NMR gives a signal for each tin atom which is in a different environment.

The ^{119}Sn NMR spectrum of a solution of SnCl_6^{2-} (as the tetrabutylammonium salt) contains only one signal which occurs at -732 ppm (relative to tetramethyltin, Me_4Sn). The ^{119}Sn NMR spectrum of a solution of SnBr_6^{2-} (as the tetrabutylammonium salt) occurs at 2064 ppm. The ^{119}Sn NMR spectrum at 60°C of a solution formed by mixing equimolar amounts of SnCl_6^{2-} and SnBr_6^{2-} contains seven peaks (Fig. 2).

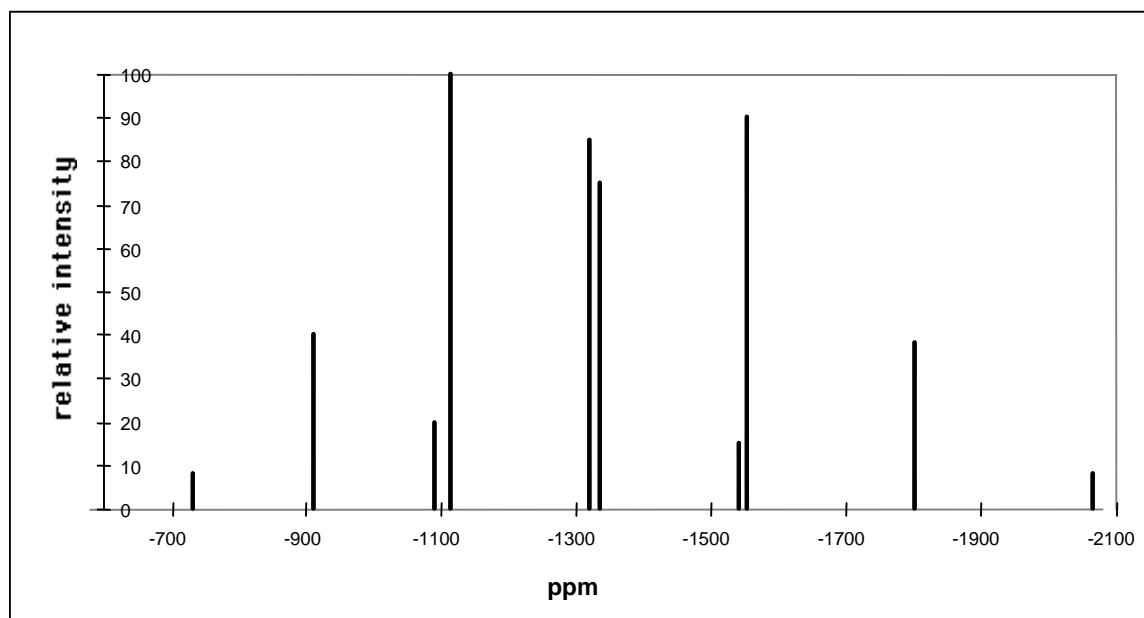
6.9 Write the empirical formula for the tin-containing species in this mixture that give rise to the peaks listed on the answer template.

Fig. 2



Cooling the solution causes a change to this ^{119}Sn NMR spectrum and at $-30\text{ }^\circ\text{C}$ ten peaks are observed (Fig. 3).

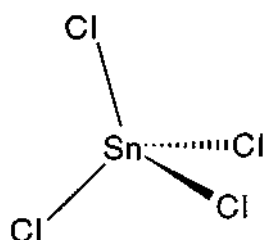
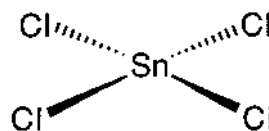
Fig. 3



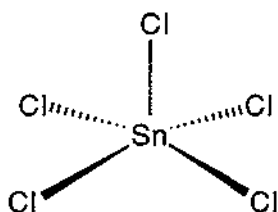
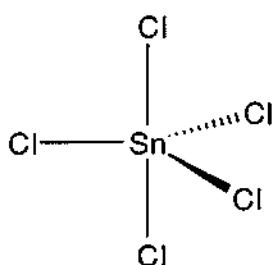
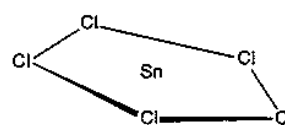
6.10 Draw the geometry for the four tin-containing species present in this solution at $-30\text{ }^\circ\text{C}$ that give rise to the peaks at -1092 and -1115 , -1322 and -1336 ppm.

SOLUTION

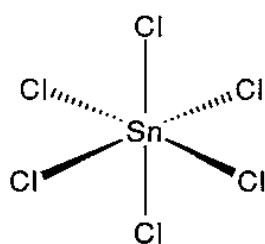
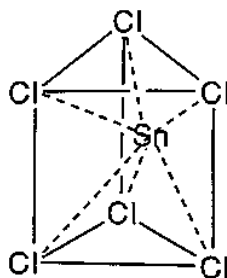
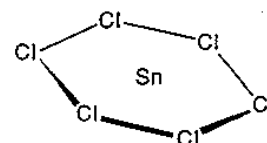
6.1

A

B


6.2

C

D

E

 6.3 In accordance with VSEPR theory geometry D is likely to be preferred for SnCl_5^- .

6.4

F

G

H

 6.5 In accordance with VSEPR theory geometry of F is likely to be preferred for SnCl_5^-

 6.6 SnCl_5^-

 6.7 SnBr_5^-

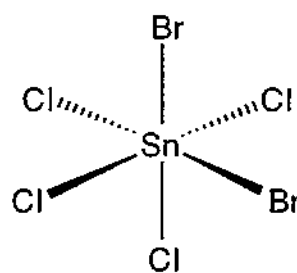
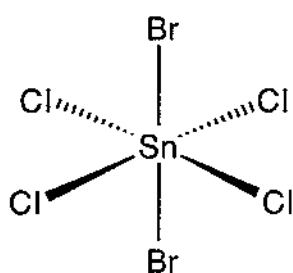
 6.8 $m/z = 339$: SnCl_4Br^- $m/z = 427$: $\text{SnCl}_2\text{Br}_3^-$
 $m/z = 383$: $\text{SnCl}_3\text{Br}_2^-$ $m/z = 471$: SnClBr_4^-

6.9

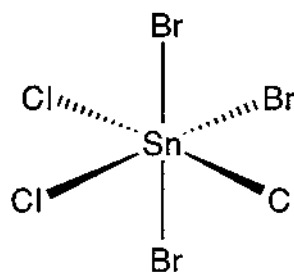
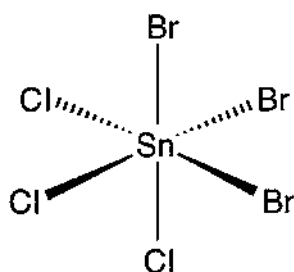
- 912 ppm:	$\text{SnCl}_5\text{Br}^{2-}$
-1117 ppm:	$\text{SnCl}_4\text{Br}_2^{2-}$
-1322 ppm:	$\text{SnCl}_3\text{Br}_3^{2-}$
-1554 ppm:	$\text{SnCl}_2\text{Br}_4^{2-}$
-1800 ppm:	SnClBr_5^{2-}

6.10

-1092 ppm and -1115 ppm (2 compounds)



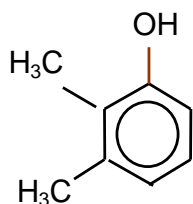
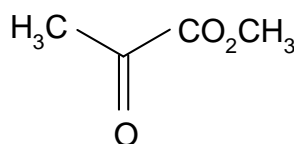
-1322 ppm and -1336 ppm (2 compounds)



PROBLEM 7

The structures needed to read this question are shown in the answer template.

The fungus *Aspergillus nidulans* produces two isomeric aromatic lactones (cyclic esters) **A** and **B** ($C_{10}H_{10}O_4$) each of which dissolved in cold aqueous NaOH but not in aqueous NaHCO₃. Both **A** and **B** gave a violet colour with aqueous FeCl₃. Reaction of **A** with CH₃I in the presence of K₂CO₃ gave **C** ($C_{11}H_{12}O_4$) which was shown by ¹H NMR spectroscopy to contain three non-identical methyl groups one of which was bonded directly to an aromatic ring. Selective demethylation of **C** with BCl₃ followed by aqueous work up gave **D** a new isomer of **A**. The ¹H NMR spectrum of compound **D** clearly showed the presence of an intramolecularly hydrogen bonded hydroxyl group at δ 11.8 ppm.

**E****I**

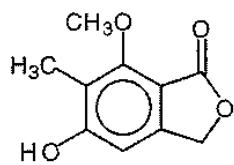
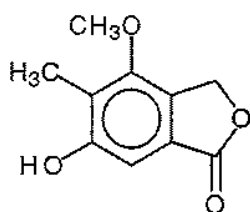
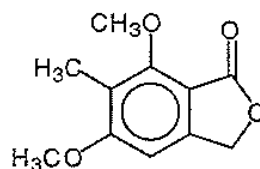
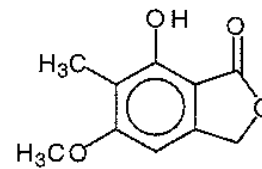
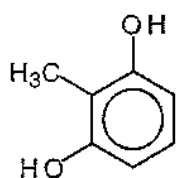
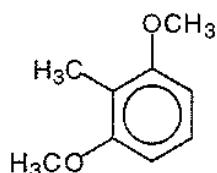
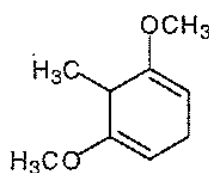
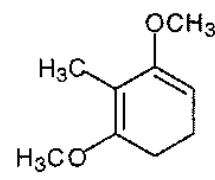
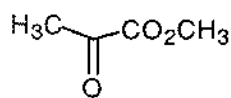
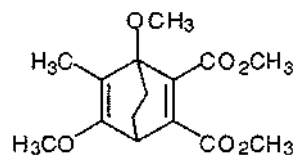
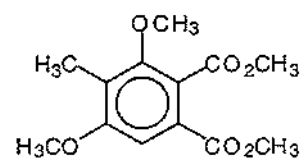
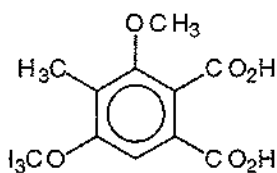
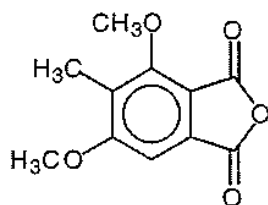
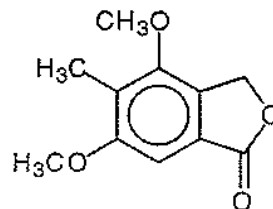
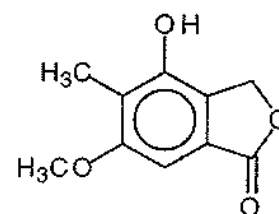
Compound **D** was synthesised as follows: The phenol **E** was methylated (MeI/K₂CO₃) to afford **F** ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methyl-propan-2-ol to give the symmetrical unconjugated diene **G**. Conjugation of this diene was achieved by reaction with KNH₂ in liquid ammonia followed by aqueous work up, a process which afforded only one product **H**. Ozonolysis of **H** followed by non reductive work up afforded amongst other products the ketoester **I**. Compound **H** underwent a Diels-Alder reaction with dimethyl but-2-ynedioate **J** to give the adduct **K** ($C_{15}H_{20}O_6$) which upon heating expelled ethene to afford an aromatic ester **L**. Basic hydrolysis of **L** followed by acidification of the solution gave **M** ($C_{11}H_{12}O_6$) which when heated under vacuum yielded **N** ($C_{11}H_{10}O_5$). Reduction of **N** with NaBH₄ in dimethylformamide gave **C** and an isomeric lactone **O** which could also be obtained by the methylation of **B**.

7.1 Using the answer template provided fill in the structures **A** to **O**.

7.2 Using the last space on the answer template provide a second structure for **B**.

SOLUTION

7.1 and 7.2

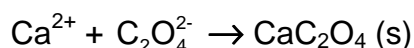
**A****B****C****D****E****F****G****H****I****J****K****L****M****N****O**Other structure for **B**

PRACTICAL PROBLEMS

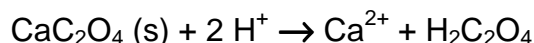
PROBLEM 1 (Practical)

Determination of Calcium by Precipitation with Oxalate Followed by Titration with Permanganate.

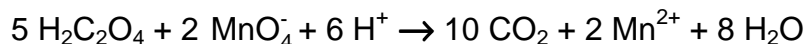
In this exercise, you must determine the amount of calcium ion in a solution that contains both calcium and magnesium, by selectively precipitating only the calcium as calcium oxalate, then quantitatively removing the precipitate from the solution by filtration.



The precipitate must then be re-dissolved in acid:



The liberated oxalic acid is titrated with standard permanganate solution:



Formation of the calcium oxalate precipitate

- Use a 25.00 cm³ pipette and 250.0 cm³ volumetric flask to accurately dilute (by a factor of 10), the calcium/magnesium solution that has been provided for you.

Analyse two samples of the dilute calcium/magnesium solution. You have sufficient reagents for three analyses, but you must plan your time and use of equipment carefully. Take each of your samples through the following procedure:

- Transfer a 25.00 cm³ aliquot of the dilute calcium/magnesium solution into a 250 cm³ beaker, add approximately 10 cm³ of 3 M H₂SO₄ and about 50 cm³ of water.

CARE! 3 M H₂SO₄ is very corrosive! The following steps involve hot (nearly boiling) solutions. Be careful and beware of steam!

- Cover the beaker with a watch glass and gently heat on a hotplate until the solution is very hot, but not boiling.
- Remove the beaker from the heat, then carefully add solid ammonium oxalate (1.5 g) and swirl the beaker until most of the ammonium oxalate dissolves.

CARE! Oxalate solutions are toxic. Do not wash solutions that contain oxalate down the sink. Place them in the "Permanganate/Oxalate residues" bottle at the end of your bench.

5. Add 5 –10 drops of methyl red indicator to the beaker, then while the solution is hot, increase the *pH* of the solution by slowly adding 1 : 1 ammonia solution with constant stirring, until the colour just changes from pink to orange. If you add too much ammonia, the solution will turn yellow. To correct this problem, add 1 drop of 3 M H₂SO₄ to lower the *pH* again, then repeat the *pH* adjustment with ammonia solution.

CARE! 1 : 1 ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.

6. Allow the solution to stand for at least 60 minutes to quantitatively precipitate the calcium oxalate. Do not stir the solution during this time.

You should complete Laboratory Task 2 during this waiting period.

Do not proceed to the next step until you are confident that precipitation is complete.

Filtration of the calcium oxalate precipitate

7. Prepare a filter paper in a filter funnel supported in the neck of a 250 cm³ conical flask. Rinse the paper with a few cm³ of water then decant most of the supernatant solution from step 6. into the filter funnel. Collect the filtrate in the conical flask. Use a wash bottle to rinse the watch glass into the filter funnel.
8. Test the filtrate for the presence of calcium ion by adding a drop of ammonium oxalate test solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, the calcium oxalate precipitation in step 6 was unfortunately not complete. Perhaps the *pH* was not adjusted correctly or insufficient time was allowed for precipitation. Depending on the time you have left, you may start the analysis again or you may continue with the present experiment.
9. If there is no detectable calcium ion in the filtrate, use a wash bottle to carefully wash the calcium oxalate precipitate into the filter. Use the rubber “policeman” on the end of a glass rod to remove the last traces of precipitate from the beaker, and rinse these into the filter.
10. Wash the precipitate 4 times with approximately 10 cm³ portions of water, collecting the washings in the conical flask.

11. Discard the combined filtrates from the previous steps into the residue bottle labeled "Permanganate/Oxalate residues" then carefully rinse the conical flask with water into the residue bottle.
12. Wash the precipitate one more time with 10 cm³ of water. Collect this filtrate in the conical flask and test it for the presence of oxalate by adding a drop of saturated calcium nitrate solution to a drop of the filtrate on a black plastic sheet. If a white precipitate (or cloudiness) is formed, continue washing and testing until the washings are free from oxalate.
13. When the precipitate is free of oxalate, discard the washings and rinse and drain the conical flask.

NOTE! Show your demonstrator your precipitates. You must ask your demonstrator to sign your results sheet before proceeding to the next step.

14. Use a glass rod to break a small hole in the bottom of the filter paper and wash the precipitate through the hole into the conical flask with approximately 20 cm³ water. Take care to rinse the rod and the creases of the filter paper.
15. Use a Pasteur pipette to dissolve any traces of calcium oxalate that remain in the paper with 25 cm³ 3 M sulphuric acid, collecting the acid in the conical flask. Finally, rinse the paper with ~ 20 cm³ water.

Titration with permanganate

16. Make the volume up to about 100 cm³ with water, heat the solution to about 60 °C, then when all the calcium oxalate precipitate is dissolved, carefully titrate the hot solution with standard potassium permanganate solution.

CARE! It is not necessary to measure the temperature of the solution with a thermometer. 60 °C is uncomfortably hot to touch.

17. Discard the titrated solution into the residue bottle labelled "**Permanganate/Oxalate residues**".

Calculate the average concentration of calcium ion in the original calcium/magnesium solution that was provided.

Molar masses in g mol⁻¹: Ca 40.08, Mg 24.31, Mn 54.94, C 12.01, O 16.00.

SOLUTION

Model solution

Analysis of calcium/magnesium solution

Permanganate titration

Concentration of standard KMnO₄ solution: 0.02039 mol dm⁻³

Titration number	1	2	3
initial burette reading (cm ³)	0.90	0.80	3.00
final burette reading (cm ³)	28.55	28.45	30.80
volume of standard KMnO ₄ (cm ³)	27.65	27.65	27.80
Average titre (cm ³)	27.70		

In a 25 cm³ aliquot of dilute Ca/Mg solution:

$n(\text{KMnO}_4)$ required to titrate oxalate from dissolved calcium oxalate precipitate

$$n(\text{KMnO}_4) = 0.0198 \text{ mol dm}^{-3} \times 0.0277 \text{ dm}^3 = 5.485 \times 10^{-4} \text{ mol}$$

$n(\text{oxalate})$ from dissolved calcium oxalate precipitate:

$$n(\text{oxalate}) = 5/2 \times 5.485 \times 10^{-4} \text{ mol} = 1.371 \times 10^{-3} \text{ mol}$$

$$n(\text{Ca}^{2+}) \text{ from dissolved calcium oxalate precipitate} = n(\text{oxalate}) = 1.371 \times 10^{-3} \text{ mol}$$

$$c(\text{Ca}) = 1.371 \times 10^{-3} \text{ mol} / 0.02500 \text{ dm}^3 = 0.0548 \text{ mol dm}^{-3}$$

In original Ca/Mg solution:

$$c(\text{Ca}) = 0.0548 \text{ mol dm}^{-3}$$

PROBLEM 2 (Practical)**Analysis of a Mixture of Cobalt(III) Complexes**

When the complex $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is prepared in the laboratory, it often contains a considerable amount of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ by-product.

In this exercise, you must determine the amount of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ in a sample that also contains only $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as a by-product, using a cation-exchange procedure. The cation exchange resin used in this exercise is a cross-linked polystyrene resin of the strong acid type. It contains $-\text{SO}_3\text{H}$ groups from which the H^+ can be exchanged. When a solution containing 1 mol of M^{n+} is allowed to react with the resin this liberates n mol of H^+ . In this exercise, the solution resulting from ion exchange of the mixture of the two different complex cations is used to titrate a standardised NaOH solution.

Preparation of the cation exchange resin

You are provided with about 10 g of wet resin in the H^+ form. Wash the resin using the following procedure to remove all traces of free acid:

1. Transfer your resin to a 250 cm³ beaker, washing it from the container with about 50 cm³ of water, then let the resin settle. This will take a few minutes.
2. Carefully pour off (decant) as much of the acidic solution as possible into a 'waste' beaker. Try to minimise loss of any of the resin in this process. Wash the resin with ~20 cm³ portions of distilled water and test a drop of washing solution using a glass rod and pH paper until the excess acid is completely removed ($\text{pH} \sim 5$). You should not need to use more than 200 cm³ of water to do this.
3. Drain off all but enough water to leave the resin just covered with water.

Be sure to put all your acidic wash solutions into a waste bottle labelled "acid waste" - not down the sink! Do not allow the resin to dry out.

Preparation and standardisation of approximately 0.0125 M NaOH

4. Prepare 250.0 cm³ of approximately 0.0125 M NaOH by accurately diluting your ~0.125 M NaOH with distilled water in a volumetric flask.
5. With the standard 0.01253 M HCl that is provided, titrate 25.00 cm³ aliquots of the diluted NaOH solution, using phenolphthalein indicator.

Analysis Procedure

You are provided with approximately 40 cm³ of a 0.00500 M solution of HCl that contains 0.2000 g of a mixture of the cobalt(III) complexes [Co(NH₃)₅NO₂]Cl₂ and [Co(NH₃)₆]Cl₃ in 40.00 cm³.

- Use a pipette to transfer a 25.00 cm³ aliquot of the cobalt complex solution into a 250 cm³ beaker (beaker No 1) and add ~25 cm³ water.
 - Use a plastic spoon to add about half (~5 g) of your wet resin to the cobalt(III) solution and allow to stand for at least 5 minutes for ion-exchange to take place, liberating H⁺. You should occasionally gently swirl the mixture to hasten the ion-exchange process.
 - Carefully wash the acidic solution into a second 250 cm³ beaker (beaker No 2) with about 20 cm³ of distilled water. Try to leave as much as possible of the resin behind. Notice that the solution is now much lighter in colour, indicating that most, but not all of the cobalt complex mixture is stuck to the resin. You must now remove the last traces of cobalt(III) from solution (liberating more acid in the process), with a second batch of resin.
 - Add most of the remainder of your resin (~4 g) to the solution in beaker No 2 and again allow to stand for at least 5 minutes to allow the cation exchange to take place, liberating more H⁺.
- At the end of this process, the solution should be colourless - if not, (perhaps you did not wait long enough for ion-exchange to take place) repeat the ion-exchange and washing steps with the last portion (~1 g) of your ion-exchange resin.
- Filter the two resin samples through a carefully washed filter paper, and collect the acidic filtrate in a 100 cm³ volumetric flask. Carefully wash the resin with small portions of water into the volumetric flask and make up to the mark with water.
 - With this acid solution titrate 25.00 cm³ aliquots of your standardized NaOH solution.

Calculate the number of moles of H⁺ liberated by the 25 cm³ aliquot of your mixture of cobalt(III) complexes and report the percentage of [Co(NH₃)₅NO₂]Cl₂ that is present in your sample.

Molar masses in g mol⁻¹: Co 58.93; N 14.01; H 1.01; Cl 35.45; O 16.00.

SOLUTION**Model solution**Standardization of 0.0125 M NaOHConcentration of standard HCl in bottle: 0.01253... mol dm⁻³

Titration number	1	2	3
aliquot of NaOH	25.00	25.00	25.00
initial burette reading (cm ³)	13.60	17.40	10.35
final burette reading (cm ³)	37.75	41.50	34.45
volume of standard KMnO ₄ (cm ³)	24.15	24.10	24.10
Average titre (cm ³)	24.12		

$$c(\text{NaOH}) = 0.01250 \text{ mol dm}^{-3} \times 0.02412 \text{ dm}^3 = 0.01206 \text{ mol dm}^{-3}$$

Aliquot of cobalt complex solution used for ion-exchange: 25 cm³

Titration number	1	2	3
initial burette reading (cm ³)	26.25	16.10	3.80
final burette reading (cm ³)	48.50	38.40	26.20
volume of standard KMnO ₄ (cm ³)	22.25	22.30	22.40
Average titre (cm ³)	22.32		

Calculations $c(\text{H}^+)$ collected in 100 cm³ flask:

$$c(\text{H}^+) = 0.01206 \text{ mol dm}^{-3} \times (25.00 \text{ cm}^3) / (22.32 \text{ cm}^3) = 0.01351 \text{ mol dm}^{-3}$$

total $n(\text{H}^+)$ collected from column:

$$n(\text{H}^+) = 0.01351 \text{ mol dm}^{-3} \times 0.100 \text{ dm}^3 = 1.351 \times 10^{-3} \text{ mol}$$

 $n(\text{H}^+)$ from aliquot put onto column:

$$n(\text{H}^+) = 0.00500 \text{ mol dm}^{-3} \times 0.02500 \text{ dm}^3 = 1.250 \times 10^{-4} \text{ mol}$$

 $n(\text{H}^+)$ ion-exchanged from complexes in aliquot put onto column:

$$n(\text{H}^+) = 1.351 \times 10^{-3} \text{ mol} - 1.250 \times 10^{-4} \text{ mol} = 1.226 \times 10^{-3} \text{ mol}$$

let y = mass [Co(NH₃)₅NO₂]Cl₂ in 25.00 cm³ aliquot of mixture added to column mass of

$$\text{mixture added to column} = (25.00 \text{ cm}^3 / 40 \text{ cm}^3) \times 0.2000 \text{ g} = 0.1250 \text{ g}$$

then mass $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in aliquot = $(0.1250 - y)$ g

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$:

$$n(\text{H}^+) = 2 y / 261.00 \text{ g mol}^{-1} = 0.007663x \text{ mol}$$

$n(\text{H}^+)$ ion-exchanged from $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$:

$$n(\text{H}^+) = 3 (0.1250 - y) \text{ g} / 267.50 \text{ g mol}^{-1} = (0.001402 - 0.011214 y) \text{ mol}$$

Thus, $0.007663 y + (0.001402 - 0.011214 y) = 0.001226$ or $y = 0.04956$ g

$$\% [\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2 = 100 (0.04956 \text{ g} / 0.1250 \text{ g}) = 39.6 \%$$
