Instructions for students

- Write your Name and Roll No. at the top of the first pages of all problems.
- This examination paper consists of **37** pages of problems including answer boxes.
- Total marks for INChO 2014 paper are **98**.
- You have 3 hours to complete all the problems.
- Blank space for rough work has been provided at the end of the paper.
- **Use only a pen to write the answers in the answer boxes. Anything written by a pencil will not be considered for assessment.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- You must show the main steps in the calculations,
- Use only a non-programmable scientific calculator.
- For objective type question, mark **X** in the correct box. Some of the objective questions may have more than one correct answer.
- Values of fundamental constants required for calculations are provided on page 4.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.
- Do not leave the examination room until you are directed to do so.
- The question paper will be uploaded on the HBCSE website by 4th February 2014.

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Fundamental Constants

Avogadro number	$N_A = 6.022 \text{ x } 10^{23}$ mol^{-1}
Electronic charge	$e = 1.602 \text{ x } 10^{-19}$ C
Molar gas constant	$R = 8.314$ J K^{-1}mol^{-1}
	$= 8.314$ K Pa.dm^{3} K^{-1}mol^{-1}
	$= 0.082$ L.atm K^{-1}mol^{-1}
1 atomic mass unit (1u)	$= 931.5$ MeV/C^{2}
1 eV	$= 1.602 \text{ x } 10^{-19}$ J
1 cm^{-1}	$= 11.9 \text{ x } 10^{-3}$ kJ mol^{-1}
Rydberg constant	$R_H = 2.179 \text{ x } 10^{-18}$ J
Mass of electron	$m_e = 9.109 \text{ x } 10^{-31}$ kg
Plancks constant	$h = 6.625 \text{ x } 10^{-34}$ Js
Speed of light	$c = 2.998 \text{ x } 10^{8}$ ms^{-1}
Acceleration due to gravity	$g = 9.8$ ms^{-2}
Density of mercury	$= 13.6 \text{ x } 10^{3}$ kg m^{-3}
Faraday constant	$F = 96485$ C

Name of Student	Roll No

Problem 1 17 marks

Metallurgy

Metallurgy is the technology of obtaining metals from their ores. Depending on the metal and the ore involved, metallurgical operations are divided into three broad divisions as hydrometallurgy, pyrometallurgy and electrometallurgy.

In hydrometallurgy, the metal is extracted into an aqueous solution using oxygen and a complexing agent. Hydrometallurgy is used for noble metals like silver and gold. The process is known as **leaching.** Potassium cyanide is traditionally used for extraction of gold.

In presence of air, native gold dissolves in a solution containing cyanide ions $(CN)^{-1}$ forming $[Au(CN)_2]^{-1}$.

1.1 Write a balanced equation to represent dissolution of gold in KCN solution.

(0.5 mark)

1.2 Calculate the mass of KCN required to extract gold from 100 kg of a rock sample having 2.2% gold on w/w basis.

(1 mark)

Silver and gold both form cyanide complexes $[Ag(CN)_2]^{-1}$, $[Au(CN)_2]^{-1}$ with formation constants as 4.2×10^{20} and 1.0×10^{37} respectively.

1.3 Calculate the equilibrium constant for the reaction.

$$Au^{+1}(aq) + [Ag(CN)_2]^{-1}(aq) \rightleftharpoons Ag^{+1}(aq) + [Au(CN)_2]^{-1}(aq)$$

(0.5 mark)

1.4 Using **1.3** and the information given below, calculate the equilibrium concentrations of $[Au(CN)_2]^{-1}$ and $[Ag(CN)_2]^{-1}$ when solid gold is added in excess to 0.1M $[Ag(CN)_2]^{-1}$ solution. (under standard condition of temperature and pressure)

1) $Ag^{+1}(aq) + e^- \rightleftharpoons Ag(s) \quad E^0 = 0.8V$

2) $Au^{+}(aq) + e^- \rightleftharpoons Au(s) \quad E^0 = 1.83V$

(2 marks)

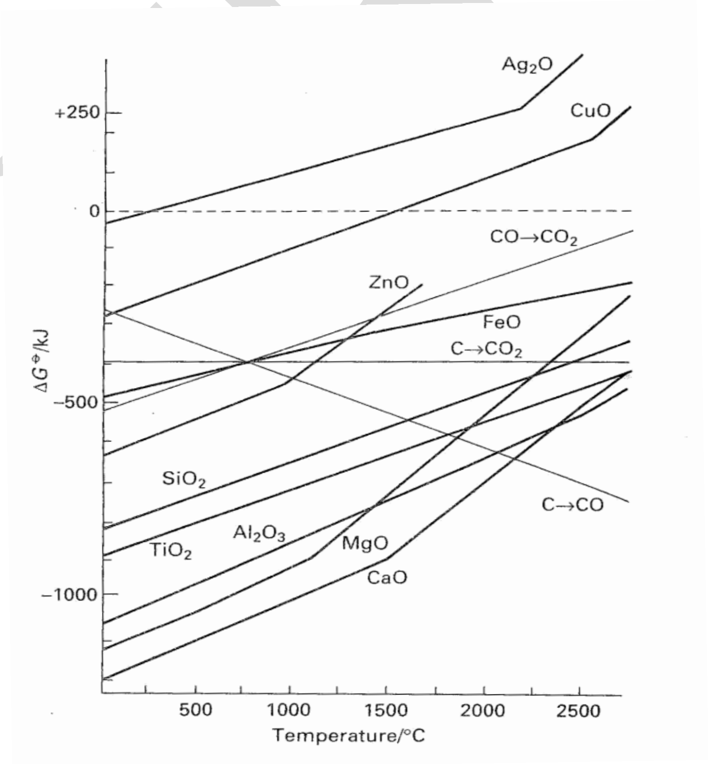
Aqua regia is a mixture of concentrated hydrochloric acid and nitric acid in the ratio of 3:1 on volume basis. It was developed by the alchemists to dissolve gold. In the dissolution process, gold is oxidized and converted to a chloro complex and nitric acid gets reduced to nitrogen dioxide.

1.5 Write a balanced equation for the individual reactions.

(1 mark)

In pyro-metallurgy the metals are extracted from ores and concentrates by heat treatment. This involves conversion to metal oxide. This is followed by the reduction of the oxide to the metal using carbon or carbon monoxide. Metals like iron, copper, zinc and manganese are obtained by this technique.

Ellingham diagram is a graph showing the variation of the standard free energy of formation (ΔG°) of metal oxides with temperature. The diagram also shows lines for formation of CO and CO_2.



Ref: Shriver D.F. and Atkins P.W., *Inorganic Chemistry*, 2nd edition, ELBS, Oxford University Press, (1994), pg no. 278.

1.6 Using the **Ellingham diagram** given above answer the following. Mark **X** in the correct box.

i) The equation of lines in the diagram is given by

a) $\Delta G = \Delta H - T\Delta S$ ☐

b) $\Delta G = \Delta H + T\Delta S$ ☐

c) $\Delta G^0 = \Delta H^0 - T\Delta S^0$ ☐

d) $\Delta G^0 = \Delta H^0 + T\Delta S^0$ ☐

ii) The statement that is true for the line $C \rightarrow CO_2$ is

a) the standard entropy change of the above reaction is positive ☐

b) the standard entropy change of the above reaction is negative ☐

c) the standard entropy change of the above reaction is zero. ☐

iii) The statement that is true for the line $CO \rightarrow CO_2$ is

a) the standard entropy change of the above reaction is positive ☐

b) the standard entropy change of the above reaction is negative ☐

c) the standard entropy change of the above reaction is zero. ☐

iv) The **lowest** temperature below which FeO **cannot** be reduced by coke is

a) 750°C ☐

b) 1300°C ☐

c) 1000°C ☐

v) In a blast furnace at 2000°C the most preferred reaction that will take place for carbon containing species is

a) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$ ☐

b) $\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$ ☐

c) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2$ g) ☐

vi) The preferred temperature for Mg to be used as a reducing agent for SiO_2 is

a) below 2200°C ☐

b) above 2500°C ☐

c) not possible at any temperature ☐

(4.5 marks)

In electrometallurgy, the pure metal is obtained by electrolysis of its appropriate salt.

Aluminum is produced from bauxite by electro-reduction of alumina. The process is known as **Hall- Herault's** process Alumina is dissolved in a conducting medium like cryolite Na_3AlF_6, as it cannot conduct electricity in the molten state. The temperature of melting of cryolite is reduced by adding conducting impurities to it. In the electrolytic bath, aluminum gets deposited at the cathode and oxygen gets liberated at the anode. The liberated oxygen attacks the graphite anode and forms carbon dioxide.

1.7 Write the balanced reactions involved in the electrolysis of alumina.

(1 mark)

The melting point of cryolite (molar mass 210 g) is 1282.7K. However, by adding sodium fluoride cryolite is made to melt at 1233K.

1.8 Calculate the percentage (on w/w basis) of sodium fluoride needed to be added to reduce the melting point to 1233K assuming that it dissociates completely. The heat of fusion of cryolite in this temperature range is 114 kJ mol^{-1}.

(3 marks)

The electrolysis is carried out with a potential difference of 4.5V between the two electrodes and the current passing through the cell is 180kA with the current efficiency of 95%.

1.9 **i)** Calculate the amount of energy required for production of 100kg of aluminum.

(2 marks)

ii) Calculate the rate of production of carbon dioxide per hour.

(1.5 marks)

Name of Student **Roll No**

Problem 2 **15 Marks**

Energy storage devices

A. Hydrogen storage as metal hydrides

Hydrogen is a renewable source of energy and considered as a fuel of the future. One of the problems of its use is storage and transportation. Research has shown that several metal hydrides act as ‘hydrogen tanks’. Large quantities of hydrogen can be absorbed on them and desorbed when needed through absorption/desorption cycles. Lithium nitride, Li_3N is one of the well studied hydrogen storage material. Almost all absorbed hydrogen can be subsequently desorbed if the hydrogenated sample of Li_3N is evacuated to 1 Pa and heated up to 450°C.

The hydrogen uptake of Li_3N is a chemical reaction in two steps. Both steps involve disproportionation of H_2.

2.1 Complete the following equations by identifying **A**, **B** and **C**.

$Li_3N + H_2 \rightarrow$ +

A **B**

(A) + $H_2 \rightarrow$ +

C **B**

(1.5 marks)

2.2 Under standard conditions of temperature and pressure, calculate the maximum volume of hydrogen that can be stored in 1kg of Li_3N.

(1 mark)

When a certain mass of compound **B** was reacted with excess amount of 0.5M HCl, a colourless gas was produced. Passing this gas over CuO(s) resulted in decrease in mass of the solid by 2.096 g.

2.3 (i) Write the balanced equation for the reaction of **B** with HCl

(ii) Calculate the mass of **B** taken in grams.

(1 mark)

Mg and Mg_2Ni also form hydrides which can be desorbed under suitable conditions of temperature and pressure. Mg_2NiH_4 is formed by a technique known as hybriding combustion synthesis. MgH_2 is synthesised by the reaction of H_2 and Mg at high temperatures and pressure in presence of a catalyst.

2.4 In Mg_2NiH_4, Ni(0) atoms form a face centered cubic lattice in which the Mg^{+2} ions occupy interstitial positions. The unit cell length of Mg_2NiH_4 was found to be 6.465×10^{-10} m.

A hydrogen cylinder at 20^0C has number of moles of hydrogen per unit volume which is (1/100) times the number of moles of hydrogen present in unit volume of Mg_2NiH_4. Calculate the pressure (in bar) in this cylinder.

(2 marks)

The desorption equilibrium of Mg_2NiH_4 is as given below

$Mg_2Ni\ H_4\ (s) \rightleftharpoons Mg_2Ni\ (s) + 2H_2\ (g)$

The equilibrium pressure of hydrogen was found to be 7.03 bar and 1.05 bar at 606K and 533K respectively. Assume that the enthalpy values do not change with temperature and $\Delta H_f°\ (Mg_2NiH_4) = -176.0\ kJ\ mol^{-1}$.

2.5 Calculate the standard enthalpy change ($kJmol^{-1}$) for the reaction

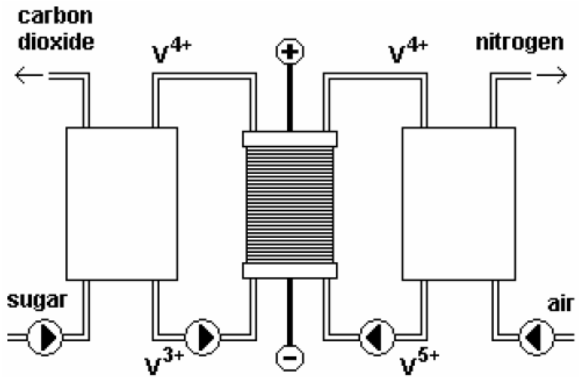
$2Mg(s) + Ni(s) \rightleftharpoons Mg_2Ni(s)$

(1.5 marks)

B. Fuel cells – Green and renewable sources of energy

Fuel cells convert the chemical energy of combustion in a fuel directly into electrical energy without the losses associated with the use of thermodynamic heat engines. A group of researchers have invented a fuel cell using cane sugar ($C_{12}H_{22}O_{11}$). This system consists of two reaction vessels. The reaction vessel on the left hand side contains cane sugar and VO^{2+} ions in a strong acidic solution. Air is pumped in the right hand side vessel which also contains VO^{2+} ions in a strong acidic solution. The assembly contains a battery at the centre that is responsible to generate electricity.

In the left hand side vessel, VO^{2+} is reduced to V^{3+} and cane sugar is oxidised to CO_2. In the right hand side vessel, VO^{2+} is oxidised by oxygen to form VO_2^+. The fuel cell diagram is indicated below.



(Ref: Excell Robert H.B and Spaziante Placido (2004), A fuel power cell powered by sugar, The Joint International Conference on "Sustainable Energy and Environment, Thailand, 1-3 Dec 2004.)

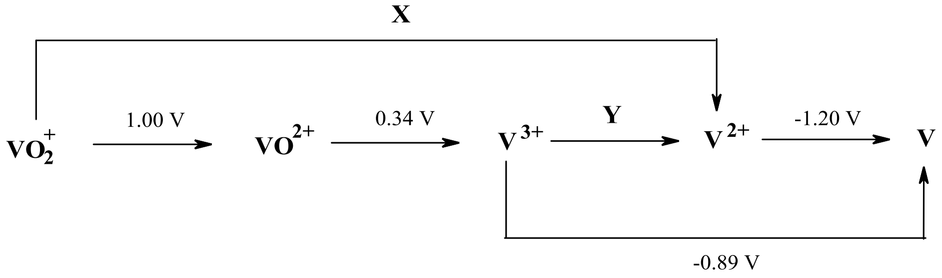
2.6 Write balanced equations for all the reactions in the (a) left side reaction vessel (b) right side reaction vessel.

(2 marks)

2.7 Calculate the volume of air that has to be pumped in at 25°C and 101 kPa into the right side vessel, for the consumption of 10g of cane sugar in the other vessel (air contains 21 % of volume oxygen).

(**1.5 marks)**

2.8 Calculate the values of **X** and **Y** (in volts) from the given information.



(1 mark)

In the battery at the centre between the reaction vessels, the following half cell reactions take place during discharge

V^{3+} (aq)+ $H_2O \rightleftharpoons VO^{2+}$(aq) + $2H^+$(aq) + e^- ....**I**

VO_2^+(aq) + $2H^+$(aq)+ $e^- \rightleftharpoons VO^{2+}$(aq) + H_2O ....**II**

The standard reduction potentials are $E°_{(VO^{2+}/V^{3+})}$ = 0.34 V and $E°_{(VO_2^+/VO^{2+})}$ = 1.00 V respectively. Assume that the concentration of V^{3+}(aq) and VO_2^+(aq) is equal to 2.00 mol L^{-1} (obtained from the reactions taking place in the reaction vessels).

2.9 Determine [V^{3+}], [VO_2^+] and [VO^{+2}] in the battery when the potential of the battery is 0.32V. The temperature of the reaction vessel is 25 °C throughout.

(2.5 marks)

2.10 The standard Gibbs free energy change for the complete combustion of sucrose to carbon dioxide and water is −5684kJ mol^{-1}.

Calculate the theoretical limit on the efficiency of direct conversion of chemical energy in sugar to electricity by this method under standard conditions.

(1 mark)

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Problem 3 25 marks

ALKALOIDS

Alkaloids are naturally occurring nitrogen heterocycles. Although they are poisonous, when used in very small quantities they have medicinal value as well.

Alkaloid **A** (MF $C_{17}H_{23}NO_3$) on hydrolysis with $Ba(OH)_2$ yields two products **B** (MF $C_9H_{10}O_3$) and **C** ($C_8H_{15}NO$).

3.1 Compound **B** does not add bromine and it dissolves in $NaHCO_3$. Heating **B** strongly yields compound **D** (MF $C_9H_8O_2$). Based on these observations which of the following statement/s is/are true for compound **B.**

a) **B** has a hydroxyl group ☐

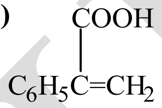
b) **B** is an olefin ☐

c) **B** has a carboxyl group ☐

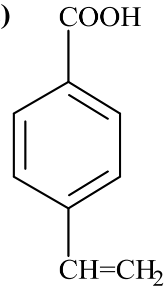
d) **B** is an aromatic compound ☐

(1.5 marks)

3.2 Compound **D** on oxidation gives benzoic acid as one of the products. Based on this observation, the possible structure/s for compound **D** is/ are

a) 
$C_6H_5C(COOH)=CH_2$ ☐

b) $C_6H_5CH=CHCOOH$ ☐

c) 
☐

d) $C_6H_5\ (CH_2)_2\ COOH$ ☐

(2 marks)

3.3 Compound **B** has been synthesized by the following reaction sequence. Draw the structures of the intermediates **E-H** and the structure of **B.**

$$C_6H_5COCH_3 \xrightarrow{HCN} \mathbf{E} \xrightarrow{H_3O^+} \mathbf{F} \xrightarrow[\text{reduced pressure}]{\text{heat}} \mathbf{G} \xrightarrow{HBr} \mathbf{H} \xrightarrow{\text{aq.NaOH}} \mathbf{B}$$

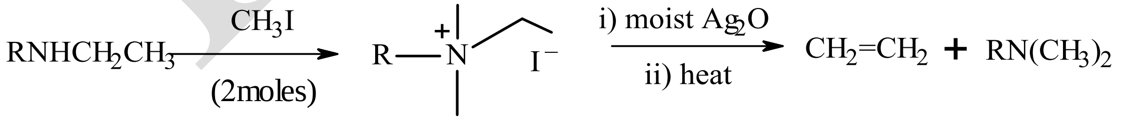
(Note: Product **H** is also obtained on treatment of **G** with HBr in the presence of H_2O_2)

E **F** **G**

H **B**

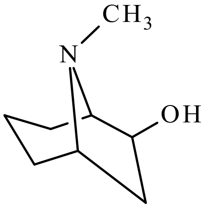
(3 marks)

Structure elucidation of an alkaloid makes use of several chemical and physical methods. One of them is the Hoffman's exhaustive methylation method for determining the nature of the nitrogen heterocylic ring. The heterocyclic ring is opened up with loss of nitrogen as an amine and formation of the less substituted olefin. The reactions involved are shown below.

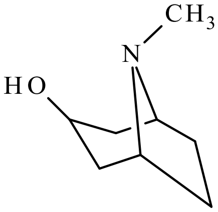


(Note: A cyclic amine undergoes Hoffman's exhaustive methylation twice to give an amine and a diene).

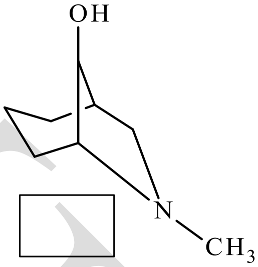
3.4 Compound **C** does not decolorise bromine and dissolves in HCl. **C** on treatment with conc. H_2SO_4 gives **J**. Hoffman's exhaustive methylation of compound **J** gives 1, 3, 5-cycloheptatriene as one of the products. The possible structure /s for compound **C** is /are



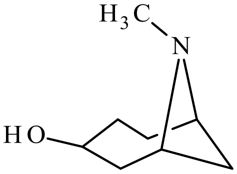
a) ☐



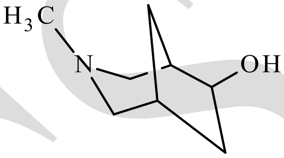
b) ☐



c) ☐



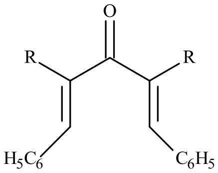
d) ☐



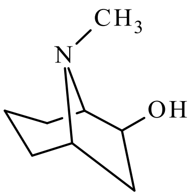
e) ☐

(3 marks)

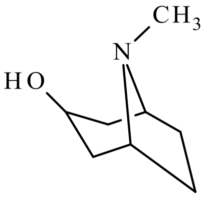
3.5 Compound **C** on controlled oxidation gives a compound **K** which gives a yellow precipitate with 2,4–DNP and also reacts with two equivalents of benzaldehyde in the presence of a base to give a dibenzylidine derivative, the general structure of such derivatives is shown below.



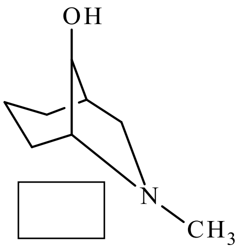
The possible structure /s for compound **C** based on the above observations is /are



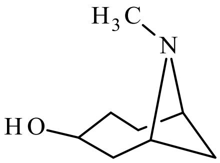
a)



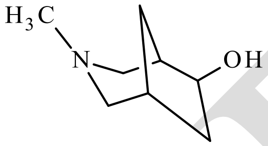
b)



c)



d)



e)

(2 marks)

3.6 **i)** Write the number of chiral atoms in **a** and **b** in **3.5**.

a) **b)**

(1 mark)

ii) For the structures **a-e** in **3.5** the compounds that are optically active are (Mark **X** in the correct box)

a	**b**	**c**	**d**	**e**

(1 mark)

Oxidation of **C** with CrO_3 gives dibasic acid **L. L** on heating with HI at 150-300° C gives one mole of methyl iodide.

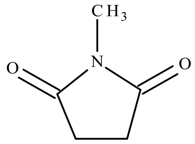
3.7 0.580 g of **L** is dissolved in 100cm^3 of distilled water. 10cm^3 of this diluted solution required 6.2 cm^3 of 0.1 N KOH for neutralisation. Determine the molecular mass of **L.** Show all the steps in the calculation.

(1 mark)

3.8 Write the molecular formula of compound **L.**

(1 mark)

3.9 Oxidation of **L** gives one of the products as **M.** Draw the structure of **L.**



M

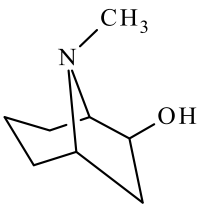
L

(1 mark)

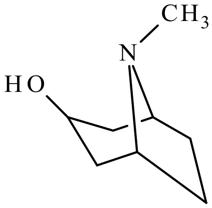
3.10 Draw the possible tautomeric structure/s of **M.**

(1 mark)

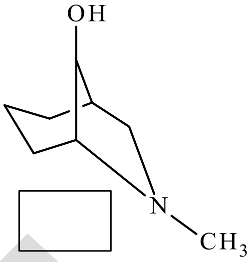
3.11 Based on all the observations from **3.4 -3.9** the structure of **C** is



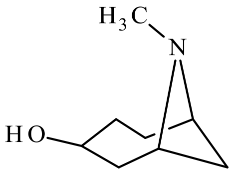
a) ☐



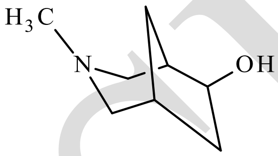
b) ☐



c) ☐



d) ☐



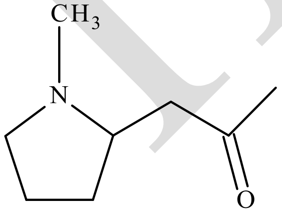
e) ☐

(1 mark)

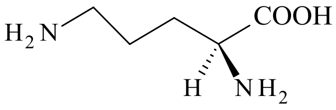
3.12 Draw the possible structure for alkaloid **A**.

(1 mark)

In plant metabolism alkaloids are formed from amino acids. Alkaloid hygrine **(N)** is formed in nature from amino acid Ornithine **(O)**



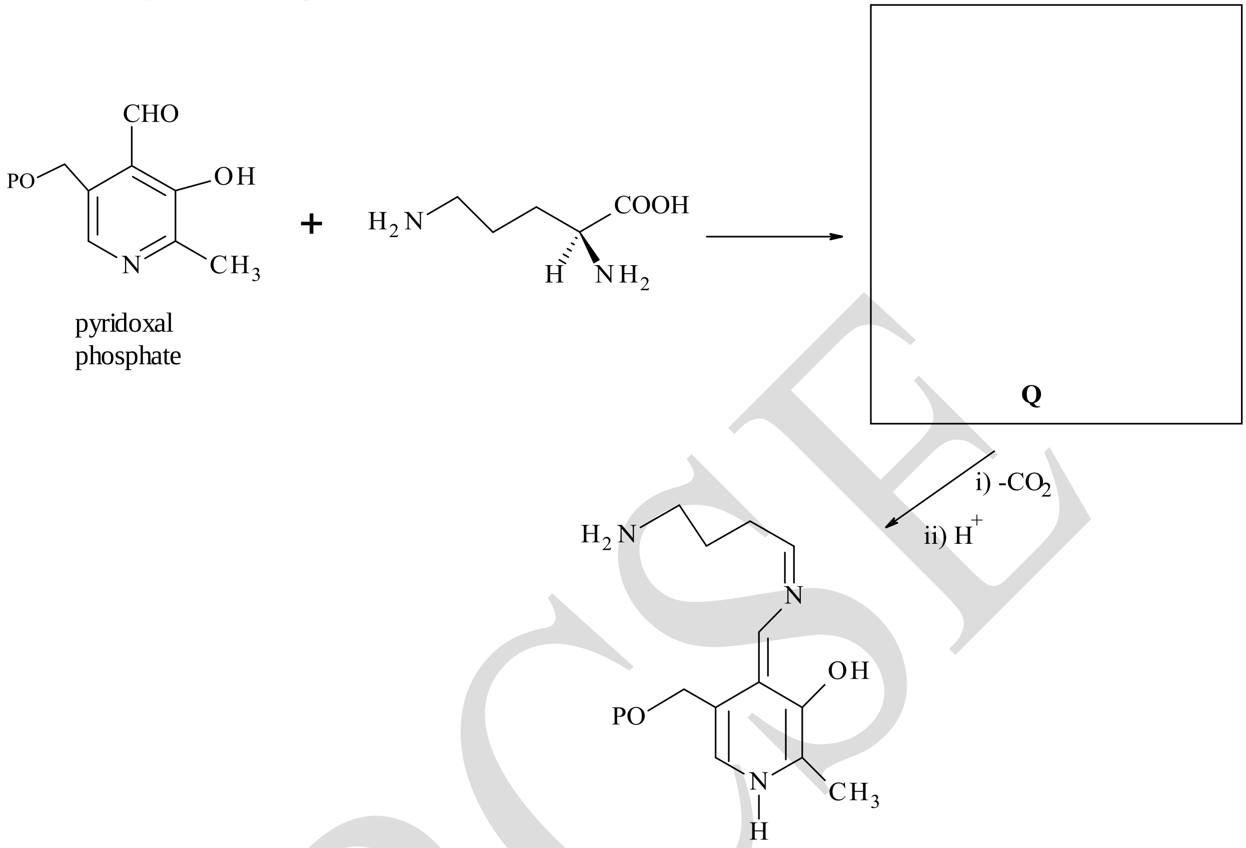
N



O

The first step in the synthesis is the pyridoxal catalysed decarboxylation of Ornithine.

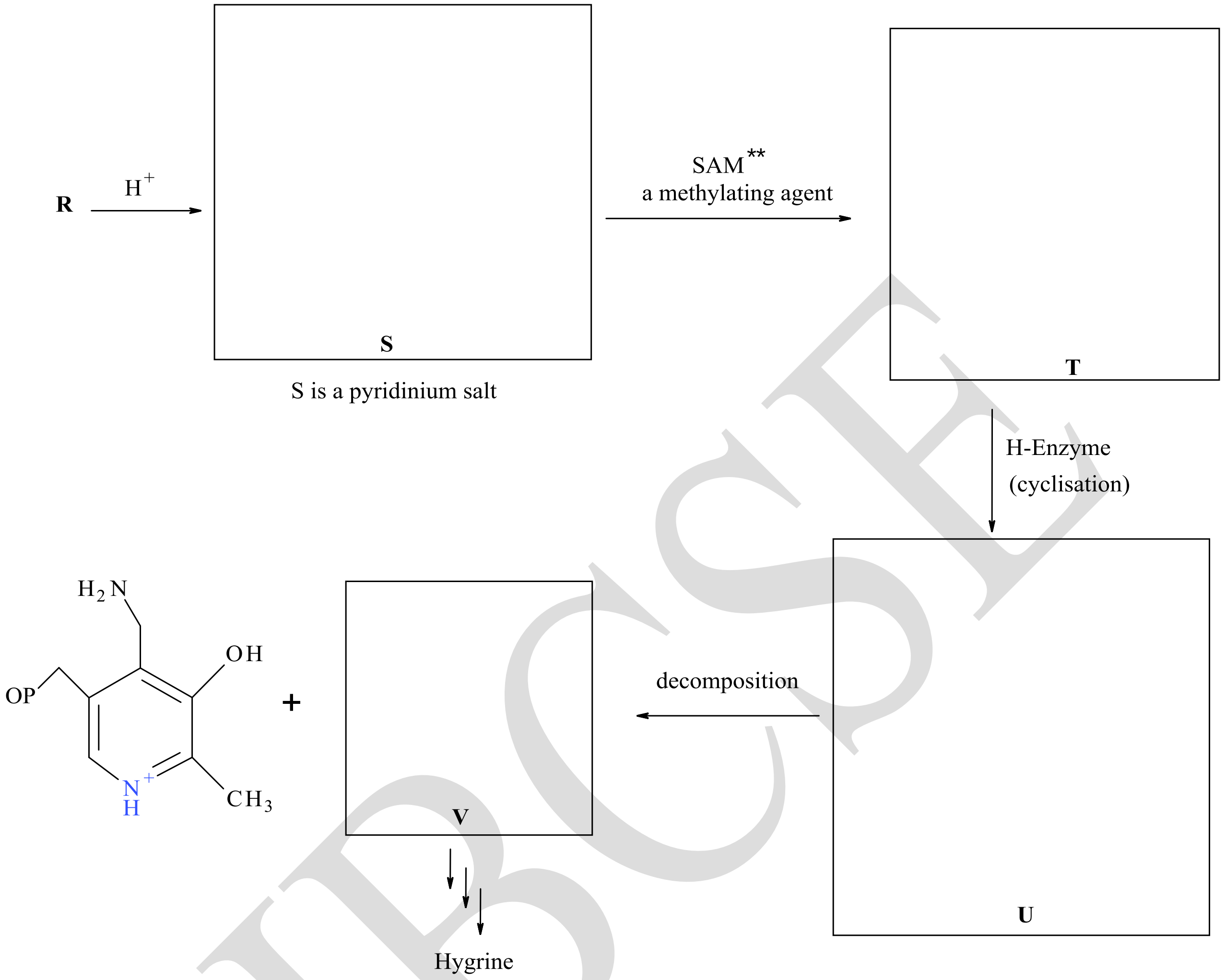
3.13 Identify the missing intermediate **Q.**



R

(1 mark)

3.14 Identify **S**, **T**, **U** and **V** in the following sequence.



****Note: Methylation using SAM takes place at the more nucleophilic nitrogen.**

(3.5 marks)

3.15 Biosynthetic pathways are usually established by isotopic labeling of potential precursors. If ornithine is labeled with ^{14}C at C_2 and ^{15}N at nitrogen on C_2, draw the structure of the hygrine obtained indicating the labeled atoms.

(1 mark)

Name of Student	**Roll No**

Problem 4 **15 marks**

Applications of Transition Metal Complexes

The transition metals are widely distributed in earth's crust. The elements Co, Ir belong to Group IX of the periodic table. These elements as well as their compounds have several applications in chemistry. Cobalt and its compounds are used as catalysts and in making alloys, pigments and glasses.

Silica, on doping with an aqua complex of Co(II) shows light pink colour in wet condition and deep blue colour in dry condition. This colour change is associated with the structural changes in the complex of Co(II) due to partial loss of water.

4.1 Write the formula of the aqua complex of Co(II) that has pink colour.

(0.5 mark)

4.2 With the above formula, write the balanced chemical equation for the reaction responsible for the observed colour change.

(1 mark)

Mercuric tetrathiocyanatocobaltate (II) is another complex of cobalt, used as a standard for calibrating magnetic balances. Its spin only magnetic moment is 3.872 Bohr magnetons.

4.3 Write the formula of the complex.

(0.5 mark)

4.4 Based on the magnetic moment **alone**, can the structure of the complex in **4.3** be predicted correctly to be tetrahedral or square planar?

Yes ☐ No ☐

(1 mark)

B. An oxide of cobalt, Co_3O_4 can exist **either**

(a) as a normal spinel $Co^{II}(Co_2^{III}O_4)$ where 1/8th of the tetrahedral holes are occupied by Co^{II} ions and 1/4th of the octahedral holes are occupied by Co^{III} ions in a cubic lattice, **or**

(b) as an inverted spinel where 1/4th of Co^{II} and Co^{III} exchange their sites.

	Pairing energy P(cm^{-1})	Δ_0(cm^{-1})	Δ_t(cm^{-1})
Co^{3+}	20680	20760	9226
Co^{2+}	20800	9200	4090

(Δ_0 and Δ_t imply the octahedral and tetrahedral splitting parameters respectively for oxygen as the ligand)

4.5 On the basis of the above data, calculate the crystal field stabilization energy (CFSE) in kJ mol^{-1} for

i) a) cobalt (III) in octahedral and b) cobalt (III) in tetrahedral sites.

ii) a) cobalt (II) in octahedral and b) cobalt (II) in tetrahedral sites

(In actual calculations of CFSE values neglect the pairing energies)

(3 marks)

4.6 Calculate the difference of the CFSE values obtained in **4.5 i)** and **4.5 ii)**.

cobalt (III) in octahedral and tetrahedral sites

cobalt (II) in octahedral and tetrahedral sites

(1 mark)

4.7 Based on your above calculations, predict whether Co_3O_4 exists as

a normal spinel ☐ an inverted spinel ☐

(0.5 mark)

4.8 The number of possible isomers for the complex of the type $[Co^{III}AX(en)_2]^{2+}$ (en = ethylene diamine) is

2 ☐ 3 ☐ 4 ☐

(1 mark)

4.9 Draw the possible structure(s) for the *cis* and the *trans* isomers of the above complex. (Represent en by ∩).

(1.5 marks)

Hydrolysis of the above complex (where **X** is the leaving group) proceeds through dissociation mechanism. For the *trans* complex, the reaction proceeds via square pyramidal intermediate but for the *cis* complex it proceeds via trigonal bipyramidal intermediate.

4.10 For the trans form, the hydrolysis will result in

a) Only cis product ☐ b) only trans product ☐

c) Mixture of cis and trans product ☐ **(1 mark)**

4.11 For the cis form, the hydrolysis will result in

a) Only cis product ☐ b) only trans product ☐

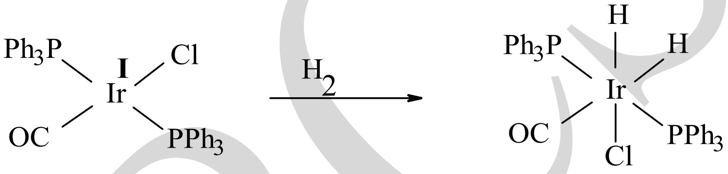
c) Mixture of cis and trans product ☐ **(1 mark)**

C.

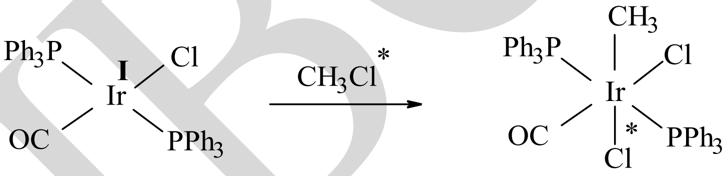
The complex $[Ir^{I}(CO)Cl(PPh_3)_2]$ was first synthesized by Lauri Vaska in 1961 and is known as Vaska's complex. It is a versatile catalyst for several reactions.

The addition of H_2 to $[Ir^{I}(CO)Cl(PPh_3)_2]$ is *cis*, but the addition of CH_3Cl is *trans*. The structures of the complex and the products are given below. These reactions go through intermediate states.

a)



b)



4.12 (i) Draw the structures of the intermediates for the above addition reactions.

Intermediate for a

Intermediate for b

(2 marks)

(ii) State the oxidation number of Ir in the products.

a) ☐ b) ☐

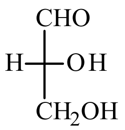
(1 mark)

Problem 5 18 marks

Chemistry of Carbohydrates

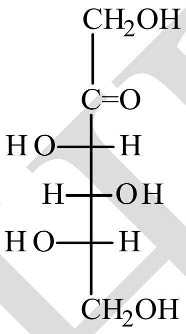
Carbohydrates are biomolecules which perform diverse functions such as being energy sources and constituents of nucleic acids. In solution, monosaccharides, the simplest unit of carbohydrates, exist in cyclic hemiacetal form. The cyclic form is in equilibrium with small quantity of the open chain form.

In a trivial system of naming (D,L-system), the carbohydrates having the configuration at the asymmetric carbon of highest number same as that of R-glyceraldehyde (shown below) are called D forms while those having opposite configuration at the same carbon are called L-forms.

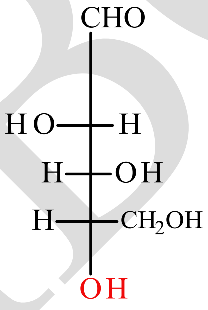


R-glyceraldehyde

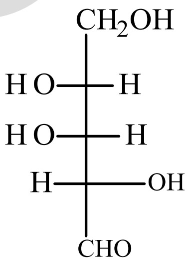
Monosacharides **A**,**B** and **C** have the following structures.



A



B



C

5.1 Classify sugars **A**, **B** and **C** into D or L forms.

A ☐ **B** ☐ **C** ☐

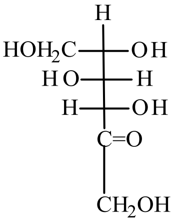
(1.5 marks)

Some terms and their abbreviations are given below.

Term	Identical	Enantiomer	Diastereomer
Abbreviation	I	E	D

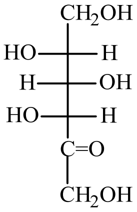
5.2 i) Which is the correct term to describe the relationship of each of the following structure with **A**? (Mark X in the correct box)

a)



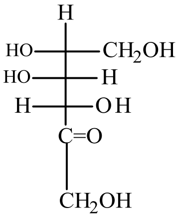
I	E	D

b)



I	E	D

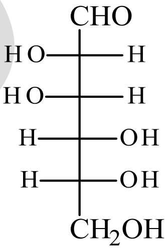
c)



I	E	D

(3 marks)

5.3 **a**) Some reactions of a monosaccharide **U** are given below. Complete them by drawing the structures of the products with correct stereochemistry wherever applicable.



U

i) **U** $\xrightarrow{NH_2OH}$

ii) **U** $\xrightarrow{Br_2/H_2O}$

($C_6H_{12}O_7$)

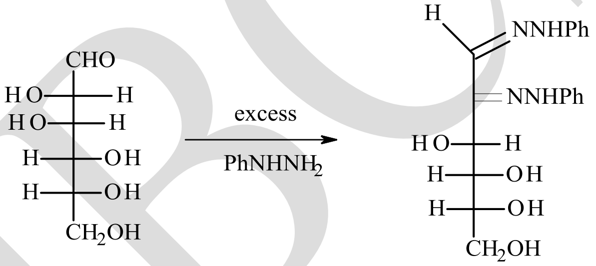
iii) $\mathbf{U} \xrightarrow{\text{Conc. } HNO_3}$ $(C_6H_{10}O_8)$

iv) U $\xrightarrow{\text{excess } (CH_3CO)_2O}$

v) U $\xrightarrow{NaBH_4}$

(2.5 marks)

b) Monosaccharide **U** react with phenylhydrazine in excess to yield a crystalline derivative called osazone.



U

osazone

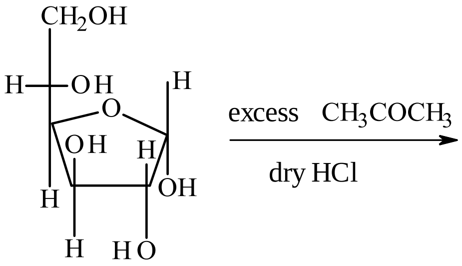
Another aldose **V** and ketose **W** also give the same osazone as **U** on reaction with excess of phenylhydrazine. Draw the structure of **V** and **W** in the Fischer projection formula.

V **W**

(1.5 marks)

1,2 – or 1,3 – diols can be protected by forming cyclic acetals with one equivalent of acetone in acidic conditions. These acetals are hydrolysed back to the original hydroxyl groups in dilute acid solutions.

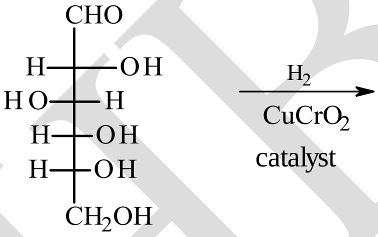
5.4 Draw the structure of the product **G** in the following reaction.



G **(1.5 marks)**

Compound **N** is a vital nutrient essential for the proper growth of the human body. It is commercially synthesized from monosaccharide **H**.

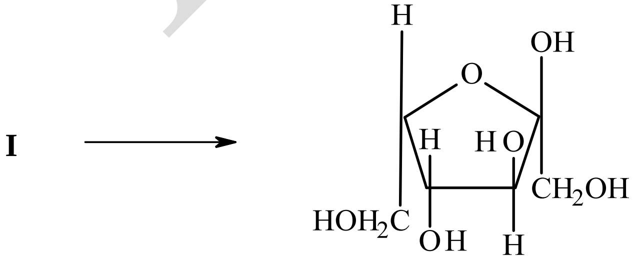
5.5 Draw the structure of the product **I** (with correct stereochemistry) in the first step of the synthesis of **N**.



H

I **(0.5 mark)**

I undergoes microbial oxidation to give **J** whose structure is given as follows



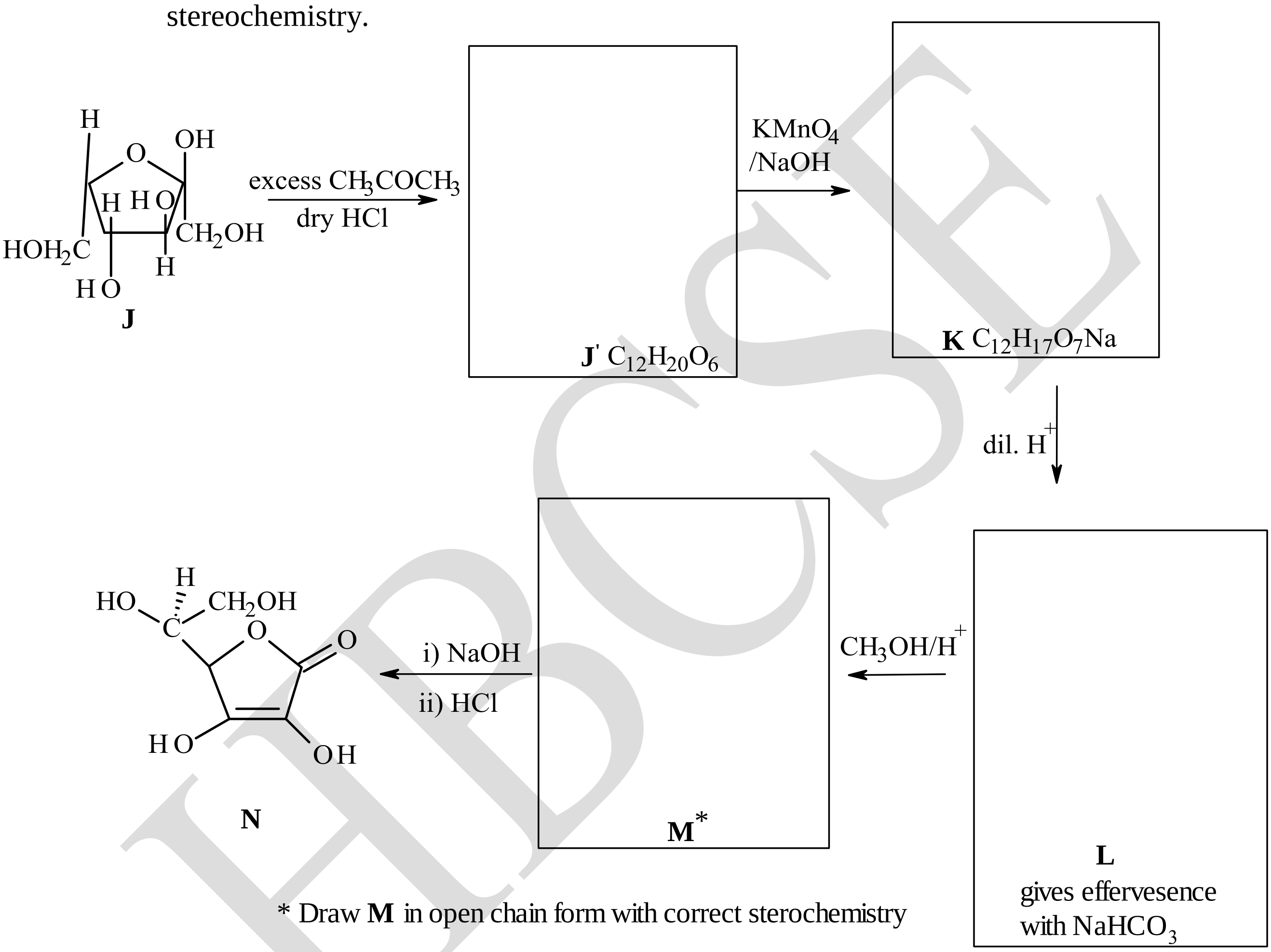
J

5.6 In the conversion of **I** to **J**, which carbon of the original **H** is undergoing this oxidation? (Mark X in the correct box).

C1	C2	C3	C4	C5	C6

(1 mark)

5.7 Complete the synthesis of **N** by drawing structures for **J', K, L** and **M** with correct stereochemistry.

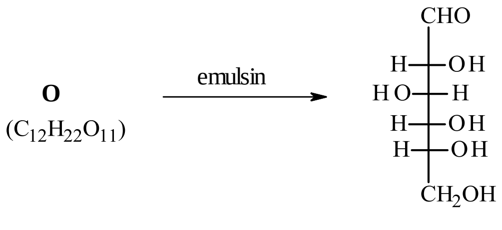


* Draw **M** in open chain form with correct sterochemistry

(3.5 marks)

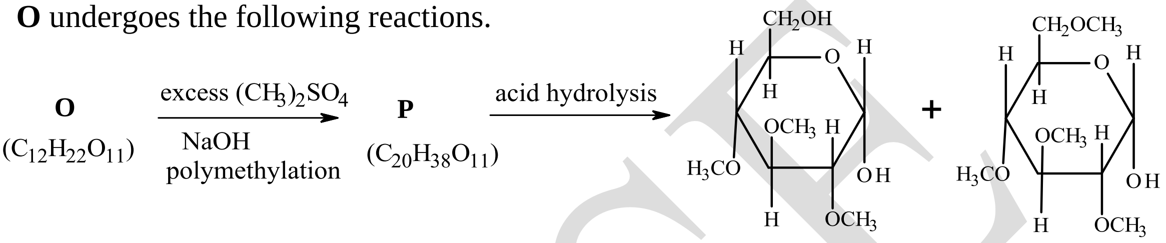
Monsaccharides and oligosaccharides that have a free – OH group on the anomeric carbon give a positive test for Tollen's reagent. Such sugars are called reducing sugars. If this free–OH group at the anomeric carbon is replaced by an ether then the result is a glycoside. The nonsugar part of a glycoside is called an aglycone. Both glycosides and oligosaccharides can be hydrolysed by acids or enzymes into their components.

A disaccharide **O ($C_{12}H_{22}O_{11}$)** is reducing in nature. On hydrolysis by enzyme emulsin (which cleaves only β linkages) **O** gives **H** as the only product.



H

O undergoes the following reactions.



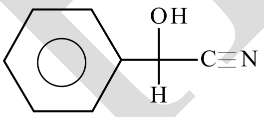
Q **R**

5.8 From the structures of **Q** and **R** draw the structure of **O.**

O

(2 marks)

A glycoside **S** on careful hydrolysis with emulsin gives the disaccharide **O** and the aglycone **T** whose structure is shown below



T

5.9 Draw the structure of the glycoside **S** with the correct stereochemistry.

(1 mark)

Name of student	**Roll No.**

Problem 6 8 marks

Chemical equilibria in quantitative analysis

A. Many metal ions can be precipitated from their aqueous solutions as sulphides using hydrogen sulphide, a weak dibasic acid. The concentration of the sulphide ions in the solution can be controlled by adjusting the pH of the solution and thus the separation of the metal ions from the mixture can be achieved.

Relevant data needed for calculations in different subparts is presented below.

Dissociation constants of H_2S:

$K_1 = 1\times10^{-9}$ and $K_2 = 1.3\times10^{-14}$

Salt	CdS	Tl_2S
Solubility product (K_{sp})	1.0×10^{-27}	6.0×10^{-22}

6.1 Solid NaOH is added to 1L of 0.05M solution of H_2S until the pH reached the value of 12.0. Calculate-

(i) Initial pH of H_2S solution before the addition of solid NaOH.

(ii) Concentration of all the species at pH =12.0 (Use appropriate approximations).

(iii) Total mass of solid NaOH added to the solution.

(3 marks)

A sample solution contains 0.003M each of Cd^{+2} ions and Tl^{+1} ions. The mixture needs to be separated using H_2S at appropriate pH. The separation is assumed to be quantitatively complete when the concentration of Cd^{+2} ions in the sample solution becomes 1×10^{-6} of the initial value.

6.2 Calculate the optimal pH range in which Cd^{+2}(aq) and Tl^{+1}(aq) can be separated quantitatively. (The H_2S concentration in this solution is 0.10 M).

(2 marks)

B. Volhard method is a back titration method and involves excess addition of $AgNO_3$ and its back titration with potassium thiocyanate using ferric alum as the indicator. The end point is the appearance of a reddish brown colour due to the formation of iron thiocyanate complex.

6.3 10g of pesticide sample containing arsenic was treated appropriately to convert its arsenic content to AsO_4^{3-}. Then 25mL of 0.045M $AgNO_3$ was added to precipitate AsO_4^{3-} as Ag_3AsO_4. The precipitate was filtered and the **unreacted** $AgNO_3$ present in the filtrate was then titrated with 0.05M potassium thiocyanate. The observed titre value was 5.0 mL. Calculate the percentage of arsenic as AsO_4^{3-} in the pesticide sample.

(3 marks)

IUPAC Periodic Table of the Elements

Key:

atomic number
Symbol
name
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen [1.007, 1.009]																	2 **He** helium 4.003
3 **Li** lithium [6.938, 6.997]	4 **Be** beryllium 9.012											5 **B** boron [10.80, 10.83]	6 **C** carbon [12.00, 12.02]	7 **N** nitrogen [14.00, 14.01]	8 **O** oxygen [15.99, 16.00]	9 **F** fluorine 19.00	10 **Ne** neon 20.18
11 **Na** sodium 22.99	12 **Mg** magnesium [24.30, 24.31]											13 **Al** aluminium 26.98	14 **Si** silicon [28.08, 28.09]	15 **P** phosphorus 30.97	16 **S** sulfur [32.05, 32.08]	17 **Cl** chlorine [35.44, 35.46]	18 **Ar** argon 39.95
19 **K** potassium 39.10	20 **Ca** calcium 40.08	21 **Sc** scandium 44.96	22 **Ti** titanium 47.87	23 **V** vanadium 50.94	24 **Cr** chromium 52.00	25 **Mn** manganese 54.94	26 **Fe** iron 55.85	27 **Co** cobalt 58.93	28 **Ni** nickel 58.69	29 **Cu** copper 63.55	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.72	32 **Ge** germanium 72.63	33 **As** arsenic 74.92	34 **Se** selenium 78.96(3)	35 **Br** bromine [79.90, 79.91]	36 **Kr** krypton 83.80
37 **Rb** rubidium 85.47	38 **Sr** strontium 87.62	39 **Y** yttrium 88.91	40 **Zr** zirconium 91.22	41 **Nb** niobium 92.91	42 **Mo** molybdenum 95.96(2)	43 **Tc** technetium	44 **Ru** ruthenium 101.1	45 **Rh** rhodium 102.9	46 **Pd** palladium 106.4	47 **Ag** silver 107.9	48 **Cd** cadmium 112.4	49 **In** indium 114.8	50 **Sn** tin 118.7	51 **Sb** antimony 121.8	52 **Te** tellurium 127.6	53 **I** iodine 126.9	54 **Xe** xenon 131.3
55 **Cs** caesium 132.9	56 **Ba** barium 137.3	57-71 lanthanoids	72 **Hf** hafnium 178.5	73 **Ta** tantalum 180.9	74 **W** tungsten 183.8	75 **Re** rhenium 186.2	76 **Os** osmium 190.2	77 **Ir** iridium 192.2	78 **Pt** platinum 195.1	79 **Au** gold 197.0	80 **Hg** mercury 200.6	81 **Tl** thallium [204.3, 204.4]	82 **Pb** lead 207.2	83 **Bi** bismuth 209.0	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium		114 **Fl** flerovium		116 **Lv** livermorium		

57 **La** lanthanum 138.9	58 **Ce** cerium 140.1	59 **Pr** praseodymium 140.9	60 **Nd** neodymium 144.2	61 **Pm** promethium	62 **Sm** samarium 150.4	63 **Eu** europium 152.0	64 **Gd** gadolinium 157.3	65 **Tb** terbium 158.9	66 **Dy** dysprosium 162.5	67 **Ho** holmium 164.9	68 **Er** erbium 167.3	69 **Tm** thulium 168.9	70 **Yb** ytterbium 173.1	71 **Lu** lutetium 175.0
89 **Ac** actinium	90 **Th** thorium 232.0	91 **Pa** protactinium 231.0	92 **U** uranium 238.0	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

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Notes

- IUPAC 2011 Standard atomic weights abridged to four significant digits (Table 4 published in *Pure Appl. Chem.* 85, 1047-1078 (2013); http://dx.doi.org/10.1351/PAC-REP-13-03-02. The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements which lack isotopes with a characteristic isotopic abundance in natural terrestrial samples. See PAC for more details.
- "Aluminum" and "cesium" are commonly used alternative spellings for "aluminium" and "caesium."
- Claims for the discovery of all the remaining elements in the last row of the Table, namely elements with atomic numbers 113, 115, 117 and 118, and for which no assignments have yet been made, are being considered by a IUPAC and IUPAP Joint Working Party.

For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 1 May 2013.