Indian National Chemistry Olympiad 2019
Theory (3 hours)

Roll No. ☐☐☐☐–☐☐☐☐–☐☐☐☐

Exam Centre: ________________________ **Date:** February 2, 2019

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Question No	1	2	3	4	5	Total
Marks	**23**	**17**	**19**	**20**	**24**	**103**
Marks Obtained						
Signature of Examiner						

Instructions for students

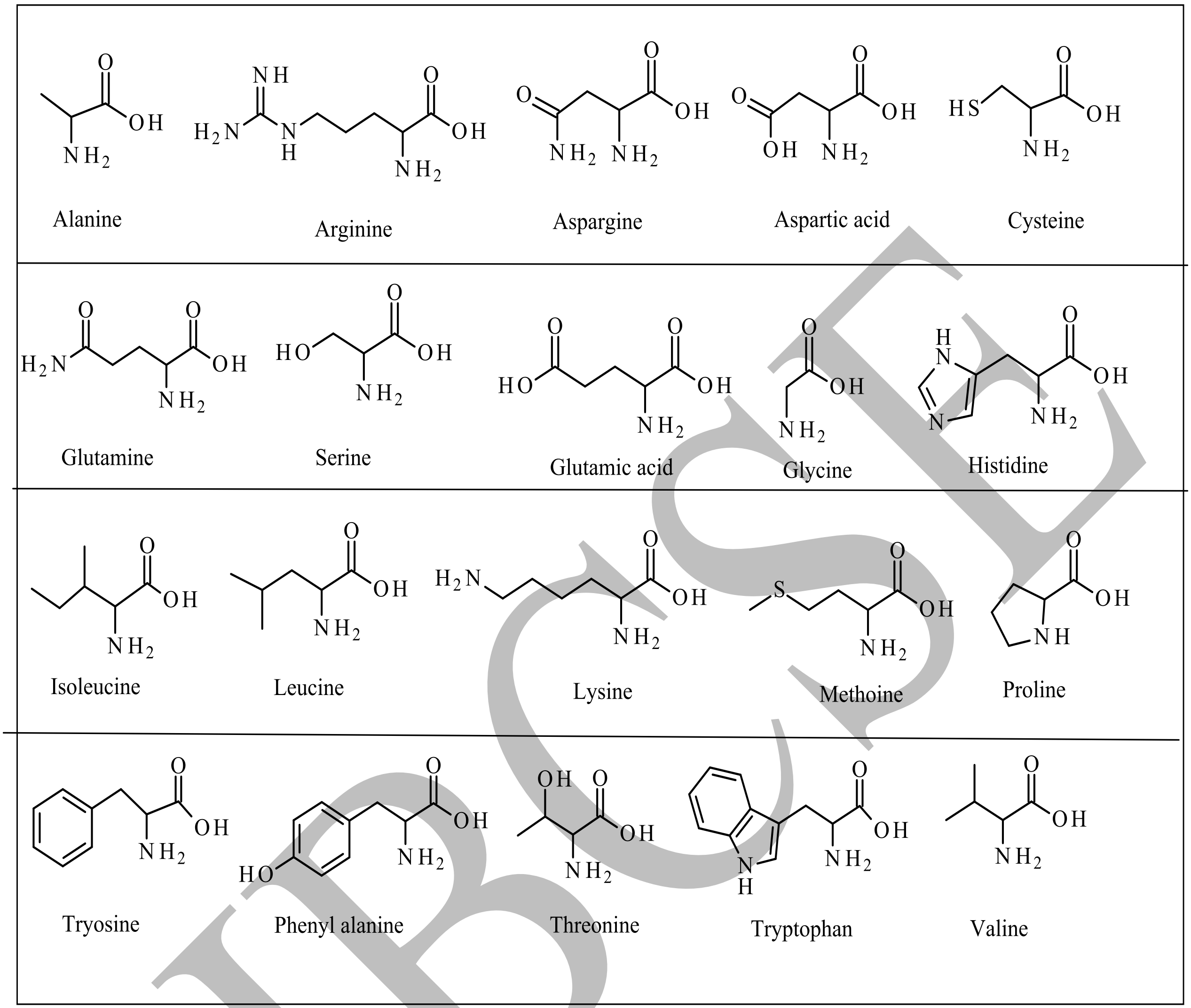
- Write last four digits of your Roll No. at the top of all pages.
- This examination booklet consists of **27** pages of problems including answer boxes.
- **Kindly check that the booklet has all the pages. If not, report to the invigilator immediately**.
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- Adequate space has been provided in the answersheet for you to write/calculate your answers. In case you need extra space to write, you may request for additional blank sheets from the invigilator (**Please draw a box and write the Q.no in the box on this sheet for evaluation**). Remember to write your roll number on the extra sheets and get them attached to your answersheet.
- **Use only a pen to write the answers in the answer boxes. Answers written in pencil (except for graph) will be penalized.**
- You **must** show the main steps in the calculations.
- For objective type question, mark **X** in the correct box. Some of the objective questions may have more than one correct answer.
- Structure of common α-amino acids is provided at the back of this page.
- A copy of the Periodic Table of the Elements is provided at the end.
- Do not leave the examination room until you are directed to do so.

Fundamental Constants

Avogadro number	$N_A = 6.022 \times 10^{23}$ mol^{-1}	Mass of electron	$m_e = 9.109 \times 10^{-31}$ kg
Electronic charge	$e = 1.602 \times 10^{-19}$ C	Speed of light	$c = 2.998 \times 10^{8}$ m s^{-1}
Molar gas constant	$R = 8.314$ J K^{-1} mol^{-1} 0.08205 L atm K^{-1} mol^{-1}	1 atomic mass unit Density of mercury	(1 amu) = 1.660×10^{-27} kg $= 13.6 \times 10^{3}$ kg m^{-3}
Faraday constant	F = 96485 C mol^{-1}		

$pH = -\log [H^+]$ $pK_a = -\log K_a$ $pK_{sp} = -\log K_{sp}$

Structures of common α-amino acids



Problem 1 **23 marks**

Common and Uncommon Amino Acids

Proteins are the most diverse class of biologically important compounds, derived from structurally varied α-amino acids. However, α-amino acids are not just found as the building blocks of proteins, but serve a variety of other functions too. This capacity of amino acids is derived due to their unique structure. Here, we will first look at the common properties of amino acids and then two special amino acids.

Part I

α-Amino acids have at least two pK_a values, one of the –COOH group and the other of the conjugate acid of the amino group. The two pK_a values of the amino acid proline are $pK_{a1} = 1.95$ and $pK_{a2} = 10.64$.

1.1 Write the predominant equilibria in aqueous solutions of proline at pH = 1.95 and 10.64.

α-Amino acids are usually characterized by their isoelectric pH (written as pI), which is the pH at which the degree of protonation at one functional group in the amino acid equals the degree of deprotonation at another functional group in the amino acid. At this pH, the amino acid shows minimum/zero electrical conductivity in aqueous solution and predominantly exists in electrically-neutral zwitter ionic form.

1.2 Based on the above definition of pI, derive a relation between pI, pK_{a1}, pK_{a2} for proline.

1.3. Consider the following statements for the amino acid and mark **X** in the correct box/es.

a. The pK_a of –COOH group in an α-amino acid is lower than the pK_a of acetic acid.

True ☐ **False** ☐

b. The pK_a of $–NH_3^+$ group in an α-amino acid is lower than the pK_a of $–NH_3^+$ group derived from a primary amine.

True ☐ **False** ☐

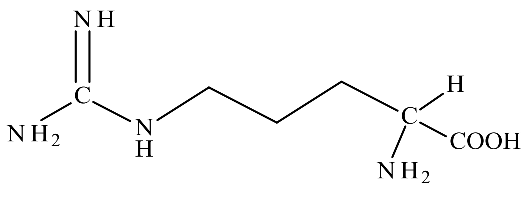
1.4. When the side chain of the α-amino acid bears an additional acidic or basic functional group, they are classified as acidic or basic amino acids, respectively. The amino acid arginine has three pK_a's in the pH range 0 – 14.

a. For arginine, the most likely pK_a values are (Mark **X** in the correct box)

i. 1.2, 2.0, 9.0 ☐ ii. 3.1, 5.0, 12.3 ☐

iii. 3.0, 6.7,12.1 ☐ iv. 2.2, 9.0, 12.5 ☐

b. In the following structure of arginine, circle the groups involved in proton exchange and assign appropriate pK_a values based on your answer in **1.4a**.



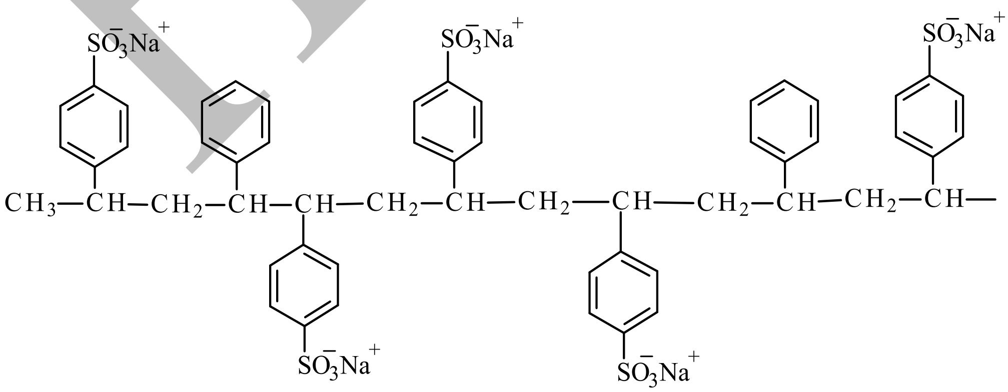
c. Write the structure for the zwitter ionic form of **arginine** amino acid and also for the species that is formed by the addition of one H^+ to this zwitter ion.

Zwitter Ion	**Zwitter ion + H$^+$**

d. Calculate the pI value of arginine. Show the steps involved in calculations.

Chromatography is a technique used to separate species in a mobile phase (liquid or gaseous) on the basis of their distribution between stationery and mobile phases. The ion exchange chromatographic technique exploits the interaction between charged entities in the mobile phase and the charged groups present in the solid stationary phase—usually an ion exchange resin.

The following figure indicates one type of ion exchange resin (**X**) that contains SO_3^- Na^+ groups as shown. The counter ion Na^+ can be exchanged with the positive ions present in the mobile phase and hence, the resin is called cation-exchange resin.



1.5. An equimolar mixture of tryptophan (**A**, pI = 5.88), histidine (**B**, pI = 7.6) and aspartic acid (**C**, pI = 2.98) was made in a buffer solution of **pH = 6.0**. This mixture was poured into column of **X.** The order in which these amino acids will come out of the column is (Mark **X** in the correct box)

i) **A, B, C** ☐ ii) **C**, **A**, **B** ☐ iii) **B, C, A** ☐

iv) **A, C, B** ☐ v) **C, B, A** ☐ vi) **B, A, C** ☐

Part II

Keratin (hair protein) contains unusually large number of cysteine units. These units from different part of the protein chains on mild oxidation form disulphide linkages which are responsible for the 3-D structure of hair.

$$2\text{R-SH} \xrightarrow{(\text{O})} \text{R-S-S-R} + 2\text{H}^+ + 2e^-$$

Curling or straightening of hair involves rearranging these –S-S- linkages of keratin.

Thus, the amino acids with mercapto (thiol) groups can act as reducing agents.

1.6. a. The simplest β-mercapto-α-amino acid reduces Cu(II) ions to Cu(I). Write a balanced chemical equation for this reaction.

Compound **P,** a β-mercapto α-amino acid with one chiral centre, is a biochemical breakdown product of the antibiotic penicillin. Excess of **P** when reacted with copper(II) chloride at its **pI (6.2)** gives a yellow precipitate of compound **Q**. Elemental analysis showed that **Q** contains 26.14% C, 5.26% H and 27.66% Cu. The compound **Q** (molar mass = 229.5 g mol^{-1}) also has one water molecule of hydration.

b. Deduce the molecular formula of **Q** showing the appropriate steps.

c. Draw the structure of **P**.

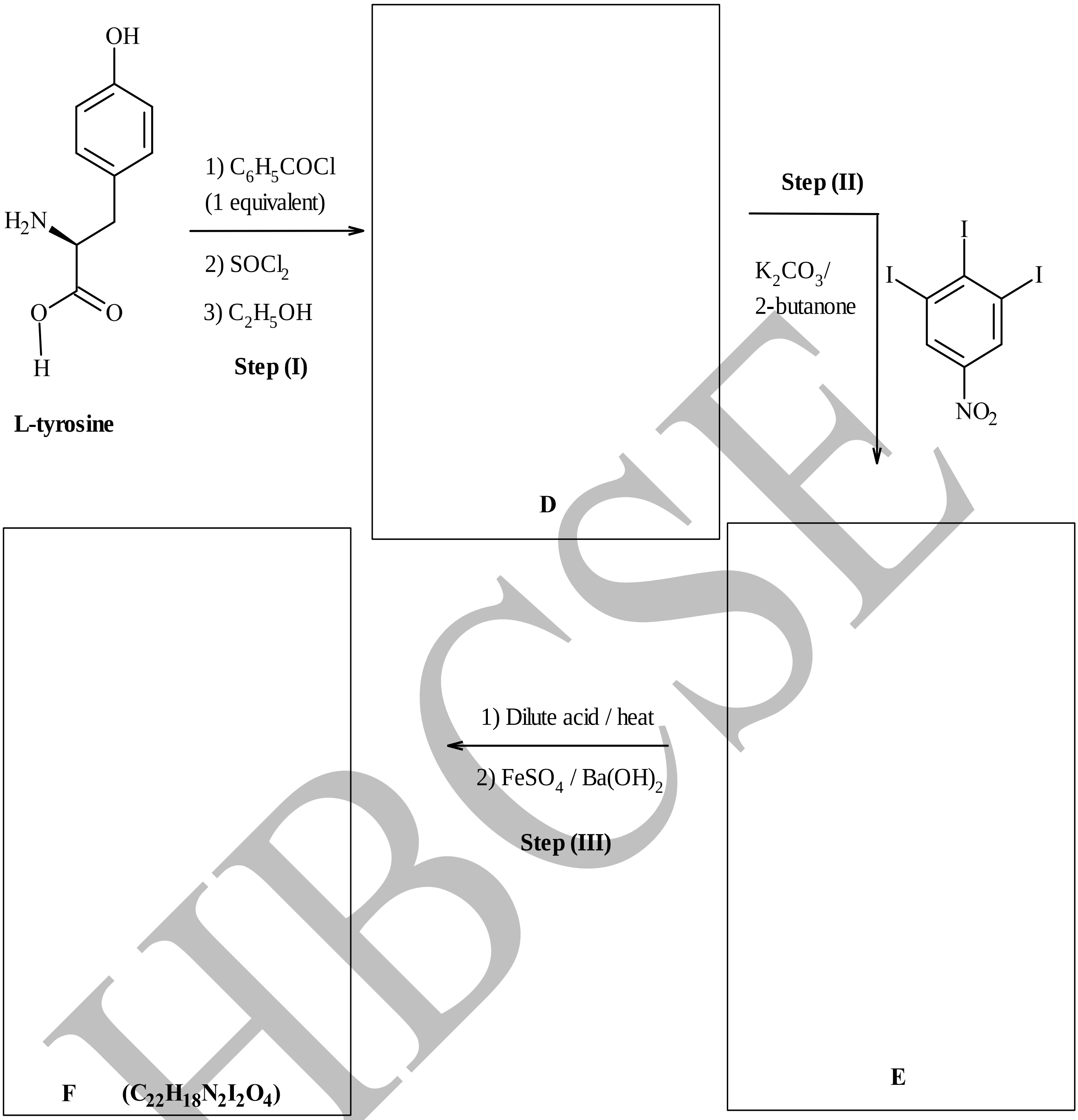
Wilson's disease is a genetic disease of copper assimilation in humans. This condition is effectively treated using agents such as **P** that can chelate copper. Lewis bases like thioethers and thioelates make stable complexes with Cu(I) with 2 to 4 coordination at the metal center, in preference to Cu(II) ions. However, Cu(II) ions gives 4 to 6 co-ordinations with Lewis bases like amino, amido and carbonyl oxygen.

d. Write the balanced chemical equation(s) for the reaction of **P** (excess) with copper(II) chloride at its pI **= 6.2** leading to the formation of **Q.**

Part III: Thyroxine

Thyroid hormones are derivatives of the amino acid **tyrosine** having iodine bound covalently to aromatic carbon atoms. There are two thyroid hormones: the principal one is **thyroxine**. Thyroxine's chemical structure was deciphered in 1927 and was found to be optically active, but its stereochemical configuration was difficult to decipher. In 1934, researchers of Pathological Chemistry in a medical college in London were able to get the configuration of Thyroxine by the following method based on **L-tyrosine**.

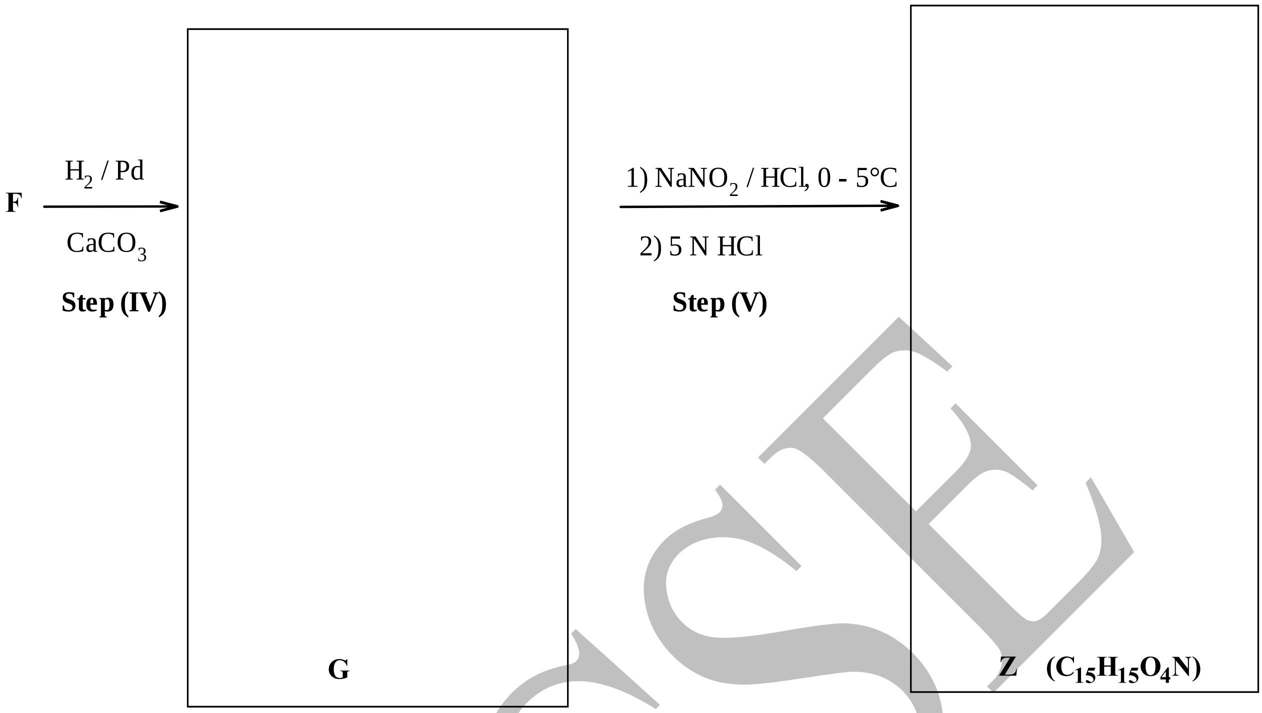
1.7.i) The researchers used **L-tyrosine** to prepare **Z** via the following route. Complete the following sequence of reactions by drawing structures **D – F** with correct stereochemistry.



ii) The reagent mixture $FeSO_4$/ $Ba(OH)_2$ in **Step III** is acting as

a) Reducing agent ☐ b) Precipitating agent ☐ c) Complexing agent ☐

iii) The Compound **F** was further treated as follows.



An aqueous solution of **thyroxine ($C_{15}H_{11}O_4NI_4$)** on treatment with Pd/$CaCO_3$ in an atmosphere of H_2 also gave the same compound **Z** on workup (the reaction mixture on acidification and evaporation)**.** This **Z** had the same specific rotation as when obtained from L-tyrosine.

iv) Draw any one possible structure of **thyroxine** consistent with the above information, with correct stereochemistry.

****During the exam, the following additional was communicated to the students.**

Q 1.7(iii) Draw the structures of compounds **G** and **Z** with stereochemistry.

Problem 2 **17 marks**

Boron Compounds through the Ages

Boron has been widely found in nature in form of Borax, known as "*Buraq*" in Arabic, *suhaga* in Hindi, and *tankan* in Sanskrit. In 1807, Sir Davy isolated the element boron from boric acid. However for another century, synthetic chemists found no interest in boron. Around 1910 in Germany, Alfred Stock prepared a series of compounds called boranes, which had high reactivities with many substances.

Around World War II, chemists found boranes could be used for chemical storage of hydrogen for weather balloons and military needs. A popular compound for this purpose was $NaBH_4$ which reacted with water to give hydrogen.

2.1 The gas obtained by reacting 100 g of $NaBH_4$ with water at 25°C was used to fill a balloon. Write the balanced equation for the reaction of $NaBH_4$ with water. Assuming the pressure inside the balloon to be approximately equal to outside pressure, estimate the volume of the balloon after the reaction is over. Show the main steps in calculations used to arrive at the answer.

Synthesis method for $NaBH_4$ was developed by H. C. Brown in USA not to make boranes but to refine uranium. His Ph.D. supervisor Schlesinger had found that uranium forms a volatile complex $[U(BH_4)_4]$ which could be used to separate isotopes of uranium.

2.2 Borohydride anion acts as a ligand in complexes where the metal ion coordinates to the B-H bond and not to any atomic center. Neutron diffraction studies of $[U(BH_4)_4]$ in gas phase show the coordination number of U(IV) to be greater than 8, whereas in solid phase, it exists as a polymeric structure with U(IV) center having coordination number 14. Draw the most stable structures of $[U(BH_4)_4]$ in gaseous and solid phase. You may use dot-wedge notations to represent bonds wherever needed. (Note: steric effects may play a major role here in determining the structures)

Gas phase **Solid phase**

Due to developments of other better methods, $[U(BH_4)_4]$ method was eventually not used for uranium refining, but it led to method developments for large scale synthesis of $NaBH_4$, which became an important reagent in organic synthesis. In 1979, H. C. Brown received the Nobel prize in chemistry for the same.

Another property of boron attracted the attention of nuclear scientists. One of its isotopes, ^{10}B has a very high affinity to absorb neutrons. Therefore, boron rods could be used as moderators in nuclear reactors to control the fission reaction.

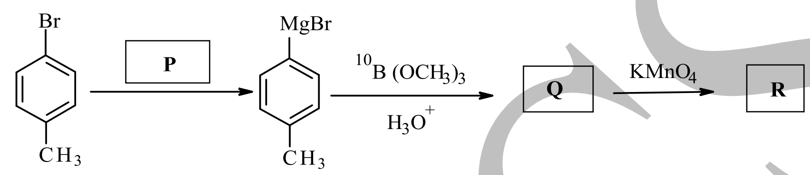
$$^{10}B + {}^{1}n \longrightarrow [^{11}B] \longrightarrow {}^{4}He + {}^{7}Li + 2.79\ \text{MeV}$$

2.3 The average atomic weight of boron is 10.81 amu and consists of only two isotopes: ^{10}B and ^{11}B. The masses of these isotopes are 10.0129 amu and 11.0093 amu, respectively. What is the percentage of ^{10}B atoms in natural Boron samples? Show the steps involved in calculations.

Solutions of boron compounds can also be used to control the number of neutrons (referred as Chemical shims) in nuclear reactors or in case of a nuclear accident.

2.4 Among saturated aqueous solutions of boric acid (H_3BO_3) and of borax ($Na_2B_4O_7.10H_2O$), which will be more effective as chemical shims? Show the calculations needed to arrive at the answer. The solubilities of Boric acid and Borax in water are 52 g L^{-1} and 58 g L^{-1}, respectively.

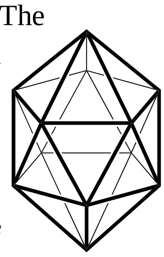
The neutron absorption property of ^{10}B is also being used for cancer treatment (in Boron Neutron Capture Therapy, BNCT). If one can place a boron-containing molecule inside a cancer cell, then a neutron irradiation will react with boron and the emitted alpha particle can kill selectively the cancer cell, while sparing the normal cells lacking boron. One way of preparing ^{10}B enriched molecules for BNCT applications is given below:



2.4 Identify **P**, **Q** & **R**.

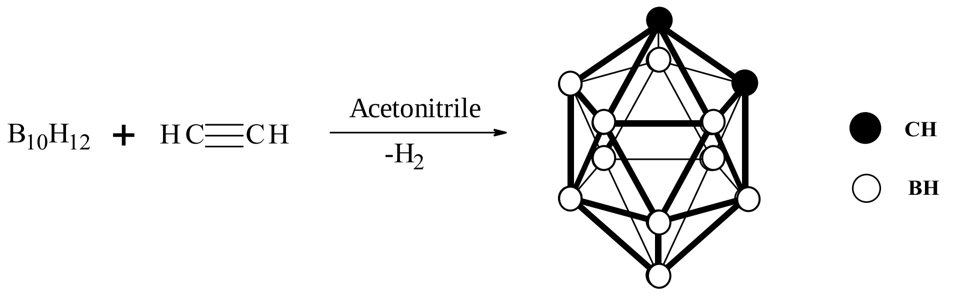
P **Q** **R**

Theoretical explainations of bonding in boranes had always been a challenge. The crystalline form of elemental boron consists of B_{12} icosahedra units, each of which in turn is bonded to neighboring icosahedra via boron-boron bonds. A typical structure of icosahedron is given here:



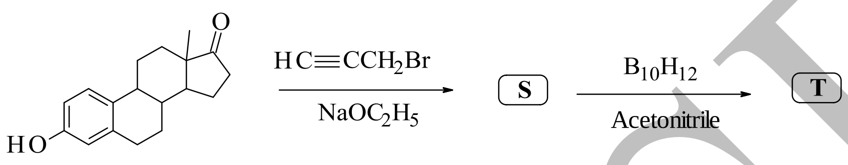
2.5 The maximum number of bonds for a boron atom in this crystalline form of boron is

More surprise came when scientists succeeded in preparing similar cage compounds with some of the B atoms replaced with C atoms having the same number of bonds. One such compound is C_2-carborane, whose method of synthesis is indicated below.



C_2-carborane

For BNCT, the tumour cells can be preferentially targeted by attaching a boron-containing molecule to the hormones, as some tumours depend strongly on hormones for growth. In one of the first studies, estrone was used for the purpose, as shown below.

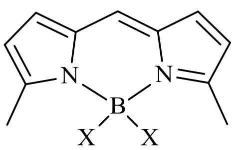


2.6 Draw the structures of **S** and **T**.

S **T**

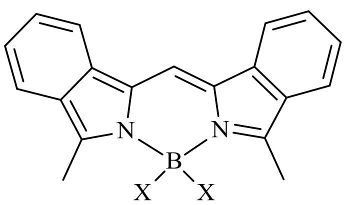
2.7 Boron compounds are not only used for therapeutic but also for diagnostic applications. A class of pyrrole-containing boron compounds are used as dyes to stain and image various (transparent) organelles inside the living cells, which are ordinarily difficult to see. The B–N bonds in these compounds are very stable even under biochemical condition, and hence the compounds do not interfere with cellular processes. Two representative examples of such dyes are given below:

a)



X = F/Cl/Br

b)



i. What is the oxidation state of boron in **a**?

ii. What is the geometry around boron in **a**?

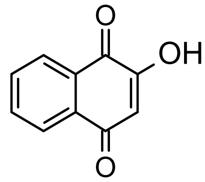
iii. Out of all three halides (X = F/Cl/Br) in the class of compounds **a**, which is the most stable species in aqueous conditions?

iv. For a given X (among the stable compounds in aqueous solutions), which dye among **a** and **b** will preferentially stain fat tissues?

Problem 3 — 19 Marks

Chemistry behind Henna – Lawsone

Mehendi or *henna* is known to us as colourant for hands, hair, and fabrics. The orange colour observed from henna is due to a compound called lawsone.



Lawsone

Part I: Properties of Lawsone

Henna leaves, however, do not contain lawsone, but have a class of compounds called hennosides. When the plant cells are ruptured by crushing the leaves, hennosides undergo enzymatic cleavage to generate one equivalent of glucose ($C_6H_{12}O_6$) and a triol **A** which on air oxidation produces lawsone. Compound **A** also gives a positive test with 2, 4-Dinitrophenylhydrazine.

3.1 Draw structures for the possible hennosides and of the triol **A**.

Hennosides	**A**

3.2 Which of the following common substances can promote the hydrolysis of hennoside? (Mark **X** in the correct box)

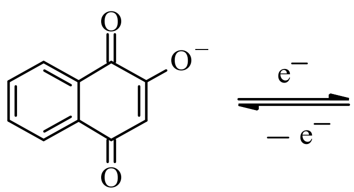
a) Lemon juice ☐ b**)** Glucose syrup ☐ c) $NaHCO_3$ ☐

3.3 Lawsone undergoes tautomerisation in water. Draw the structure of its tautomer **B**.

B

Lawsone is yellow in colour at pH below 3.6, above which it undergoes de-protonation in solutions and becomes orange in colour. In strong solutions of alkalies, lawsone undergoes reduction forming a species that is highly stable due to resonance.

3.4 Draw the species obtained by 1 e^- reduction of deprotonated lawsone. Also draw most stable resonance structures of this reduced species.



Reduced Species **Resonance Structures**

Juglone (5-hydroxy derivative of 1,4-naphthalene dione) is a compound structurally similar to lawsone, and occurs in root, leaves, and bark of walnut. Juglone and lawsone, both have intramolecular hydrogen bonding.

3.5 Draw the structures of lawsone and juglone with intramolecular hydrogen bonding.

3.6 Planar molecules would be present in (Mark **X** in the correct box/es)

Lawsone ☐ Juglone ☐

3.7 Out of lawsone and juglone, the compound that is more acidic is (Mark **X** in the correct box/es)

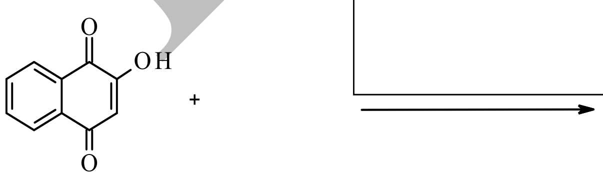
Lawsone ☐ Juglone ☐

Part II: Lawsone in Polymers

Lawsone-based polymers can be used for dyeing of wool and other textiles. A monomer (**C**) for these polymers was prepared by the following method:

Lawsone (0.4 g) was dissolved in 10 mL water-free tetrahydrofuran (THF) under argon gas at room temperature. After 10 min, 0.12 mL (density = 1.12 g cm^{-3}) 2-propenoyl chloride was added to this solution, followed by the addition of 0.254 g triethylamine (Mol. Mass = 101.2 g mol^{-1}). A deep red color appeared immediately. The reaction was allowed to undergo completion for 4 h. The solvent was then removed by evaporation. Next, 30 mL of toluene was added to the mixture, and this solution was shaken with dilute sulfuric acid, and then the aqueous layer was removed. After removing toluene by evaporation, a dark red product (**C**) was obtained with a yield of 95%.

3.8 Based on the above procedure, give the balanced chemical equation for the reaction leading to formation of **C.** Also write the reaction conditions (in box above the arrow) necessary for the **formation** of **C**.



3.9 In the above synthesis procedure, triethyl amine acts as a (Mark **X** in the correct box)

a) Base ☐ b) Catalyst ☐ c) Nucleophile ☐ d) Acid ☐

3.10 In the above synthesis procedure, which of the reagents is the limiting reagent? Show all the steps in the calculations that help in indicating the limiting reagent.

3.11 Give the reaction involving dilute H_2SO_4 taking place when it is shaken with the reaction mixture. Specify the phase in which this reaction occurs.

One student tried this synthesis on a rainy day, and coincidently forgot to attach the Ar gas supply and left the reaction flask open. She could not observe the red product **C** in the flask.

3.12 Write the balanced equation for the side reaction due to which the product **C** was not formed.

The monomer **C** obtained can undergo polymerization in presence of radical initiators.

3.13 Give the structure of the product of the following polymerization reaction of **C**.

$$\mathbf{C} \xrightarrow[\text{Ar, 80}^{o}\text{C, 72 h}]{\text{Toluene, AIBN (radical initiator)}}$$

3.14 For each of the given statements below, mark **X** in the appropriate box.

	True	**False**
(i) Lawsone and Juglone will have the same physical properties.		
(ii) Lawsone can act as an acid-base indicator.		
(iii) Lawsone-metal ion system can be used as an oxidizing agent.		

Problem 4 **20 Marks**

Gold Refining

Even though gold is found in elemental form in nature, separating the element from other minerals found in its ores is a difficult process. Earlier, this separation was achieved by using liquid mercury or chlorine gas. Around 1887, leaching metallic gold in cyanide solution in air was found to be the most effective method which is still used in many parts of the world, including in India.

Part I: Cyanidation Method

This dissolution of gold in NaCN solution is an oxidation-reduction process resulting in a strong complex of cyanide ion with Au^+ ion. This reaction is considered to proceed via two chemical pathways, wherein H_2O_2 is formed in one pathway and consumed in the second.

4.1 Write balanced chemical reactions for the two leaching pathways of Au in aqueous CN^- solution in presence of air leading to the formation of the gold complex.

Solubility of O_2 in water at room temperature and 1 atm pressure is very low (8.2 mg L^{-1}). Interestingly, this process is economical even with this concentration of oxygen. Therefore, cyanide concentrations used for effective leaching are also not very high.

4.2 Assuming that the leaching reactions proceed to completion faster than the diffusion of atmospheric O_2 in water, what minimum concentration of NaCN (in g L^{-1}) is desirable for maximum gold leaching at room temperature and 1 atm?

4.3 Write the most preferable geometry and spin magnetic moment ($\mu_{spin\ only}$) value of the gold cyanide complex formed.

The reduction potential for Au^+(aq) ion ($E°_{Au^+/Au}$= +1.69 V) is much higher than that of O_2, indicating that gold is stable with respect to oxidation by oxygen at all pH values. Presence of strong complexing agents such as CN^-, which can stabilize gold in either +1 or +3 oxidation states, significantly shifts the reduction potential of gold. Cyanide ions affect the equilibria of the reaction $Au^+(aq) + e^- \rightleftharpoons Au(s)$ due to the following additional equilibrium:

$$[Au(CN)_2]^-(aq) \rightleftharpoons Au^+(aq) + 2CN^-(aq) \qquad pK = 38.3 \text{ (at 25°C)}$$

4.4 Find the E° value for the following half-cell reaction and write its Nernst equation.

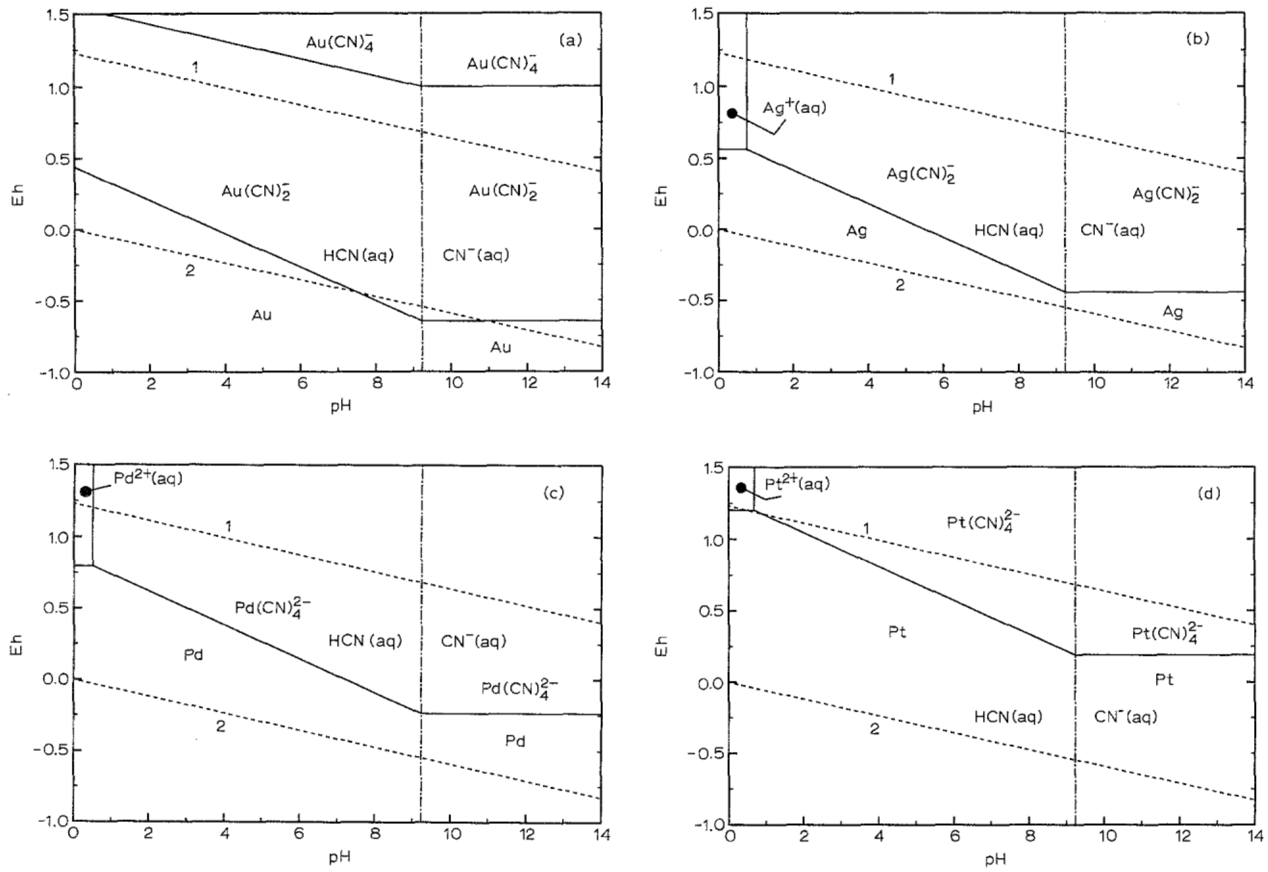
$$[Au(CN)_2]^-(aq) + e- \rightleftharpoons Au\,(s) + 2CN^-(aq)$$

Electrochemical potentials of several redox systems change with pH. This dependence is graphically represented in form of the E_H (potential) vs pH diagrams. The reduction potential E_H of a half-cell reaction relative to Standard Hydrogen Electrode is plotted on the y-axis with pH on the x-axis. Regions on different sides of plotted lines indicate domains of E and pH values at which specific species will be predominant (due to thermodynamic stability) under equilibrium conditions. These diagrams are based on the Nernst equation (based only on thermodynamics), but give no information about the reaction kinetics.

The E_H vs pH diagrams of (a) Au, (b) Ag, (c) Pd and (d) Pt in 0.02 M NaCN solution at 25°C are shown below. The H_2O stability limits are represented by the two dotted lines which correspond to the equilibria:

$$O_2\,(g) + 4H^+\,(aq) + 4e^- \rightleftharpoons 2H_2O\,(aq)$$
$$2H^+(aq) + 2e^- \rightleftharpoons H_2\,(g)$$

Regions **1** and **2** represent stability domains for O_2 and H_2 (both at unit activity), respectively.



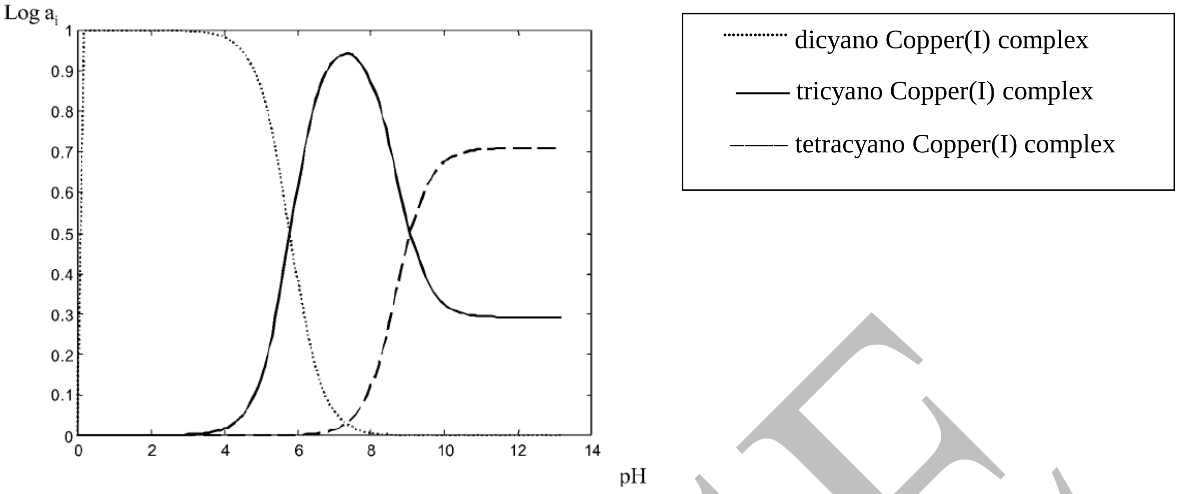
4.5 Based on the information given in above diagrams for Au, Ag, Pd, and Pt at pH = 7,
(i) identify the metals which can be leached out using NaCN solution in presence of O_2.

(ii) arrange the leachable metals identified in (**i**) in descending order of ease of leaching using the above cyanidation process at the given pH.

4.6 The most suitable pH for Au extraction using NaCN solution in presence of O_2 is

Many gold ores also contain copper minerals. Thus, during cyanidation, some copper minerals readily dissolve forming several copper(I)-cyanide complexes. These can reduce the process efficiency (and economics) due to high cyanide consumption, leading to reduced gold leach rates and poor gold recovery.

The pH dependency of the speciation of copper (I) cyanide complexes is shown in the following plot, where a_i is the ratio between concentrations of a cyanide complex and of total dissolved copper.



4.7 Write the formulae of copper(I) cyano complexes most likely to be extracted along with Au during the cyanidation process at the most suitable pH condition (identified in **4.6** above).

To separate the dissolved gold complexes from dissolved copper complexes, activated carbon is added to the leached solution. The Au(I) cyanide complex ions preferentially move into the pores of activated carbon compared to the Cu(I) cyanide complex.

4.8 Mark the correct reason/s for the above observation from the following options (Mark **X** in the correct box/es)

(a) Lower hydration of Au(I) cyanide complex anion.

(b) Lower hydration of Cu(I) cyanide complex anion.

(c) Higher charge density of Au(I) cyanide complex anion.

(d) Higher charge density of Cu(I) cyanide complex anion.

The gold complexes are then removed from activated carbon by elution with a NaOH/NaCN solution, from which gold is recovered by electrowinning.

Part II: Thiourea Method

The use of thiourea, NH_2CSNH_2, as an extracting agent for precious metals like gold has shown promise as it is less toxic compared to the reagents used in the cyanidation process.

4.9 Write the balanced chemical equation for reaction of Au with thiourea in presence of ferric ion (which is used as an oxidant) leading to the formation of the gold complex.

One of the factors that prevents the economic viability of thiourea use in gold leaching is the irreversible loss of thiourea by oxidation.

4.10 Write the structure of the product formed by oxidation of thiourea in presence of ferric ions in the following (balanced) reaction.

$$2CS(NH_2)_2 + 2Fe^{3+} \longrightarrow \boxed{} + 2H^+ + 2Fe^{2+}$$

When thiourea is separately mixed with Fe^{3+} solution, the oxidation reaction was found to be second-order reaction with a rate constant of $1.55 \times 10^{-6}\ m^3mol^{-1}s^{-1}$ at 303 K. The activation energy for the process was found to be 79 kJ mol^{-1}.

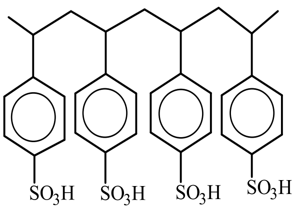
For the leaching reaction of Au by thiourea and Fe^{3+}, activation energy is 8.5 kJ mol^{-1}.

4.11 Determine the ratios of the rate constants at temperature 303 K to 295 K for the leaching and the thiourea oxidation reactions. Based on the ratios, deduce whether Au recovery per kg of thiourea will be more at 295 K or at 303 K under identical conditions? Show steps to arrive at the answers.

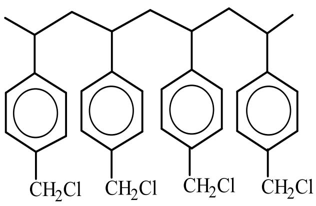
The Au-thiourea complex is separated from the leaching solution using ion-exchange resins. Ion exchange resins are polymeric compounds having side groups, with which some of the ions in the solution can bind or can exchange for an ion associated with the resin.

4.12 Of the following, the ion-exchange resin(s) that will lead to adsorption of Au-thiourea complex are (Mark **X** in the correct box/es)

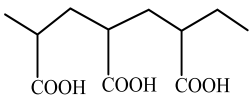
(A)



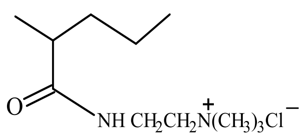
(B)



(C)



(D)



The Au-thiourea complex is extracted from the ion exchange resin into a solution and then pure gold is obtained by electrowinning of this solution. In this process, current is passed through an inert anode, the metal is deposited onto the cathode and thiourea remains in the electrolyte. The amount of thiourea is determined by titrating with KIO_3 solution in the presence of starch indicator.

4.13 Thiourea is oxidized by potassium iodate in acid solution and forms $[CS(NH_2)_2]_2^{2+}$. Write down the balanced equation for the associated reaction.

4.14 Standard KIO_3 solution was prepared by dissolving 5.35 g of KIO_3 in 1 litre of distilled water. 50.0 mL of thiourea sample (after electrowinning) was taken in a beaker. Few mL of H_3PO_4 solution and 4-5 drops of starch indicator was added to it and the mixture was titrated using KIO_3 solution. The equivalence point was observed after addition of 20.0 mL of KIO_3 solution. Calculate the amount of gold (in g) recovered from 1 L of the Au-thiourea complex solution that was used for electrowinning.

Problem 5 **24 marks**

Phosphate and Struvite

Part I: Struvite from Phosphate

Phosphorus is an essential element in living organisms, critical for bones and biomolecules like glyophosphates, DNA, RNA, ATP, etc. For plants also, phosphorus fertilizers are considered important (among NPK fertilizers) – the most common being the orthophosphate salts.

On the other hand, high concentrations of phosphates in rivers and lakes is a serious environmental concern as these cause toxic algal blooms, 'dead zones' and health hazards. Important sources of phosphorus in water bodies include sewage discharges and run-offs from agricultural fields. Since phosphorus is mostly present in wastewaters as phosphates, one of the parameters defining the performance of a sewage treatment plant is the phosphate reduction in the wastewater during the treatment.

Concentration of phosphorus (as phosphates) in a solution can be estimated by adding $MgSO_4$ and NH_3. Mass of the resulting precipitate $MgNH_4PO_4.6H_2O$ i.e. magnesium ammonium phosphate hexahydrate (MAP, also known as struvite) indicates the concentration of phosphorus in the sample.

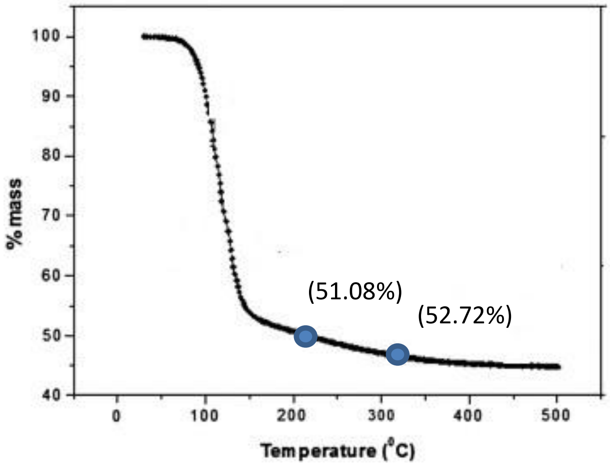
5.1 If 100 mL of a standard phosphate salt solution yields 10.496 mg of MAP precipitate after addition of excess of $MgSO_4$ and NH_3, calculate the phosphorus content (in mg L^{-1}) of the sample.

5.2 Phosphorus content in a wastewater sample was determined by the MAP method as well as a standard spectroscopic method. The estimated phosphorus content by the MAP method had an error of 2%. The error in a measurement is defined as

Error = |Measured value – Actual Value| / Actual Value

Chemical analysis of the precipitate showed that the molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} deviated from 1:1:1. Further the precipitate also had some $MgKPO_4.6H_2O$ (MKP), due to high K^+ concentration in the wastewater which could explain the 2% error. What is the molar ratio of MAP:MKP in the precipitate?

5.3 On heating, a pure sample of MAP undergoes change in mass due to gradual loss of volatile components. The mass percentage of solid remaining at each temperature is given as follows:



The figures in the brackets indicate the approximate % **mass loss** at 205 K and 315 K, respectively. The solid at 205 K is a single compound **A**, whereas at 315 K is a mixture of **A** and another compound **B** in approximately equal mass ratio. Identify **A** and **B**, and **their molar masses**. Show steps needed to arrive at answer.

Part II: Precipitation Conditions for Struvite

Sewage often contains NH_4^+ and Mg^{2+} ions along with phosphates in appreciable concentrations. Thus, struvite precipitation is common in sewage, causing blockage in pipes. Precipitation of struvite from a solution, however, highly depends on the pH, as several ionic equilibria affect its dissolution equilibrium. To understand the precipitation conditions for struvite, we shall first try to understand some of the equilibria involved. Consider an element that can exist in form of multiple species $X_1,\ldots,X_n$ in a system. The relative percentage of the specie X_n is given as

$$\%X_n = \frac{[X_n]}{\sum_n [X_n]} \times 100$$

For example, phosphate can exist as PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4 in solutions depending on the pH.

5.4 Given that H_3PO_4 has $pK_{a1} = 2.30$, $pK_{a2} = 7.20$, and $pK_{a3} = 12.32$, estimate the relative ratios $[PO_4^{3-}] : [H_2PO_4^{-}]$ at pH = 7, and $[PO_4^{3-}] : [HPO_4^{2-}]$ at pH = 11.

Another relevant pH-dependent process is the equilibrium between ammonium ions and ammonia

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad pK_a = 9.24$$

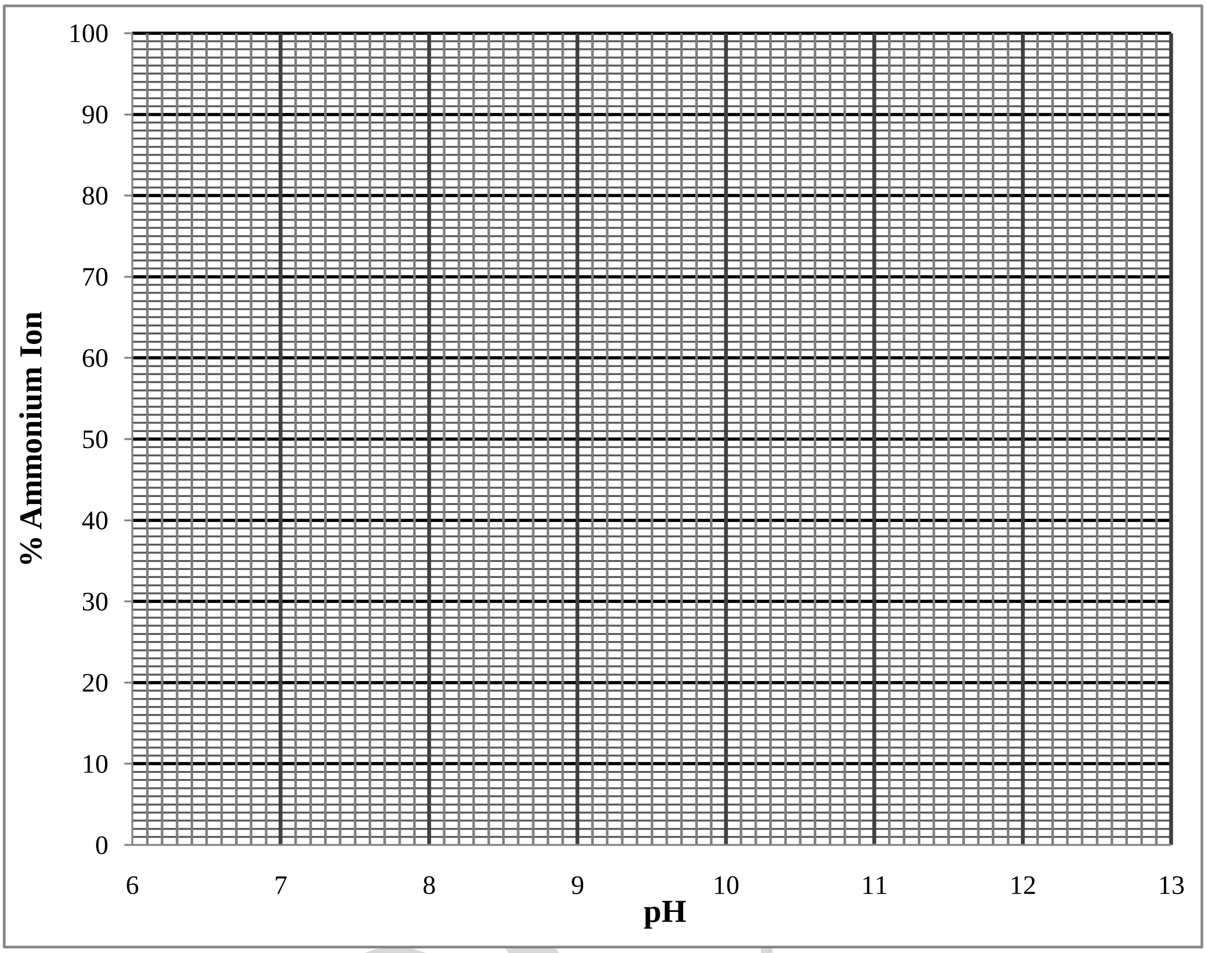
5 .5 Assuming no ammonia escapes from the solution at any time, plot a graph of % NH_4^+ as a function of pH, by determining the required coordinates corresponding to the following three points

a) pH = pKa (point $\mathbf{Z_1}$)

b) pH = 11.0 (point $\mathbf{Z_2}$)

c) pH where %NH_4^+ ~ 99% (point $\mathbf{Z_3}$)

Show calculations for the coordinates of the three points. Also, label the three points on the curve.



5.6 Depending on the pH of the solution, Mg^{2+} ions may hydrolyze to water soluble $MgOH^+$ species or precipitate as $Mg(OH)_2$.

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \qquad K_{sp} = 5.61 \times 10^{-12}$$

$$Mg^{2+}(aq) + OH^-(aq) \rightleftharpoons MgOH^+(aq) \qquad K_1 = 3.98 \times 10^2$$

Consider a solution of 0.002 M $MgCl_2$ prepared in a buffer of pH = 11. Determine $\%Mg^{2+}$ (relative to all soluble Mg species) in this solution. Show the steps involved.

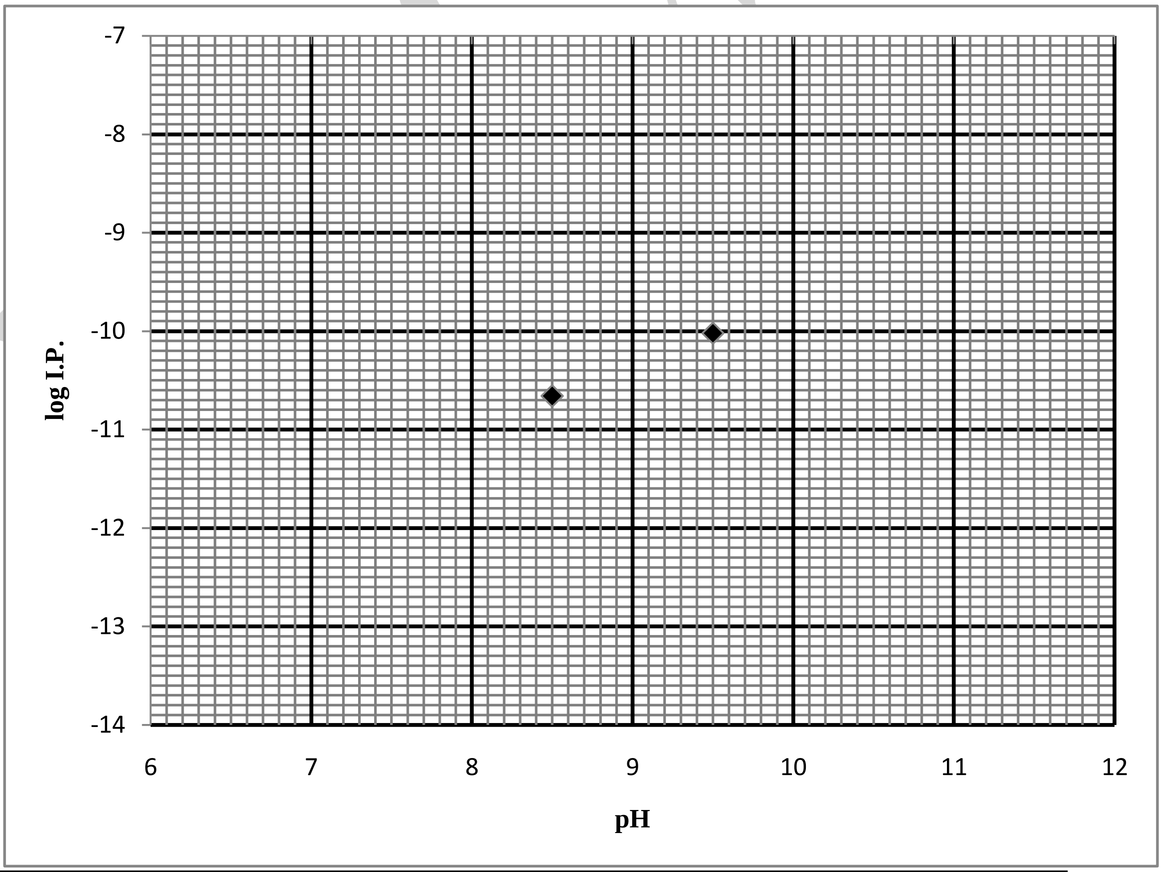
Precipitation of struvite at any given pH will take place only if the ionic product (I.P., product of concentrations of the three ions) exceeds its solubility product (K_{sp} of struvite = 5.0×10^{-12}).

$$I.\,P. = [Mg^{2+}][NH_4^+][PO_4^{3-}]$$

5.7 Suppose a sewage water sample contains 2 mM total dissolved Mg^{2+}, 30 mM total dissolved NH_3 and 3 mM total soluble phosphate at pH = 7.

(**i**) Determine the I. P. values at pH = 7 and pH = 11. Assume no other ionic equibria exists involving the three ions, other than those mentioned in this problem. Assume the temperature to be same for all calculations.

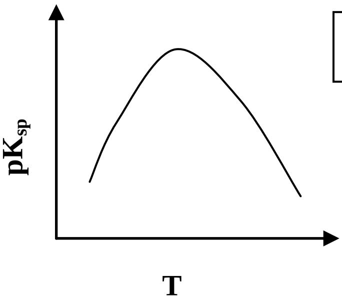
(ii) In the graph below, plot log (I.P.) values for pH = 7 and pH = 11 based on your calculations in **5.7 (i)**. Two points corresponding to pH = 8.5 and 9.5 are given here. Plot the dependence of log (I.P.) vs pH based on the four points and thus, deduce the pH range in which struvite will precipitate under equilibrium conditions. Assume the temperature to be same for all calculations.



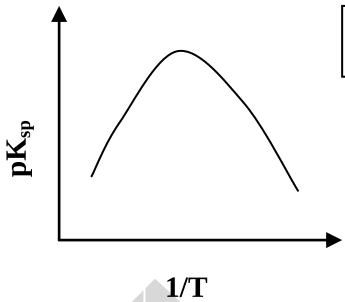
pH Range:

5.8 The dissolution of struvite has a peculiarity that it is endothermic at lower temperature and exothermic above a certain temperature. Which of the following graph/s qualitatively indicates this property of struvite (mark **X** in the correct box/es)

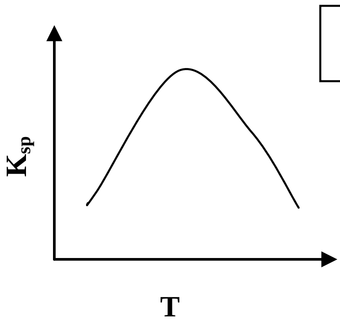
a)



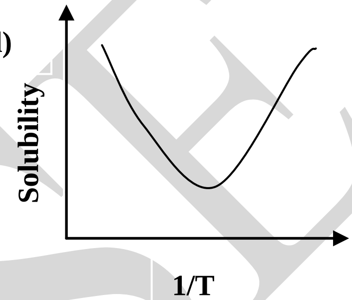
b)



c)



d)



Controlled precipitation of struvite in sewage treatment plants is being used in some countries to recover valuable phosphorus for use as a slow-release fertilizer. In this approach, the sewage water (usually at pH ~ 7.0) is retained in a reactor and subject to conditions which promote struvite precipitation. The struvite precipitation in reaction reduces the phosphorus content in the effluent as well as the precipitation and clogging in pipes.

5.9 Given below are four interventions possible in the sewage tank. State the effect of each of these on the struvite precipitation (**Write the statement number i-iv, as applicable for each option**)

(i) no effect (ii) increase in precipitation

(iii) decrease in precipitation (iv) need more information.

Condition	**Effect**
a) Addition of mineral acid	
b) Addition of water	
c) Passing carbon dioxide	
d) Partial Removal of struvite precipitate	

IUPAC Periodic Table of the Elements

Key:

atomic number **Symbol** **name** conventional atomic weight standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.95 [39.792, 39.963]
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	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	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	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

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 1 December 2018.

United Nations
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Cultural Organization

2019 IYPT
International Year
of the Periodic Table
of Chemical Elements

IUPAC

Rough Page

Rough Page

"Any alternative method of solution to any question that is scientifically and mathematically correct, and leads to the same answer will be accepted with full credit. Partially correct answers will gain partial credit."

For questions requiring calculations, full credit is given only if necessary steps of the calculations are written.

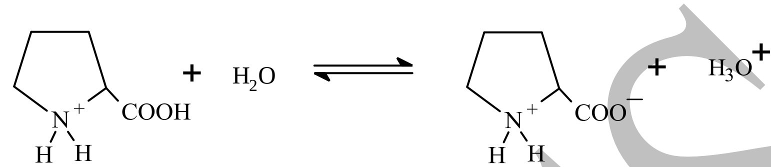
Frozen Solutions

Problem 1 **23 marks**

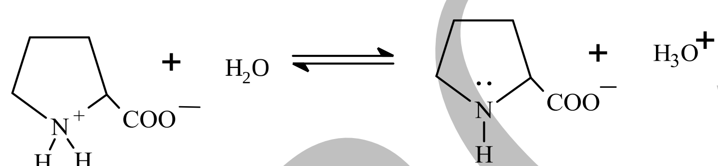
Common and Uncommon Amino Acids

1.1

Equilibrium at pH = pK_{a1}



Equilibrium at pH = pK_{a2}



(1 mark)

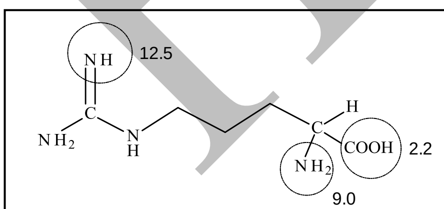
1.2 $pI = \frac{pK_{a1}+pK_{a2}}{2}$ **(2.5 marks)**

1.3. **a.** **True** X

b. **True** X **(1 mark)**

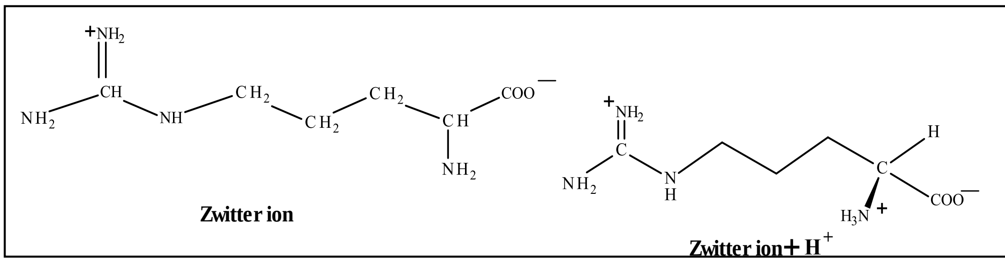
1.4. **a.** iv. 2.2, 9.0, 12.5 X **(1 mark)**

b.



(1 mark)

c.

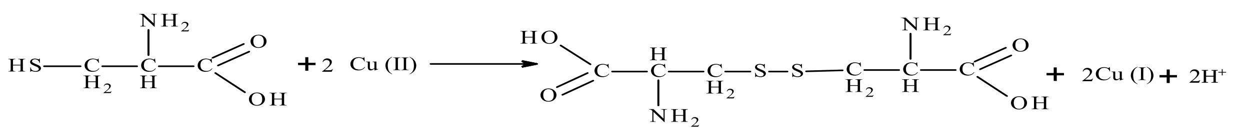


(1.5 marks)

d. pI = 10.75 **(1 mark)**

1.5. ii) **C**, **A**, **B** X **(1.5 marks)**

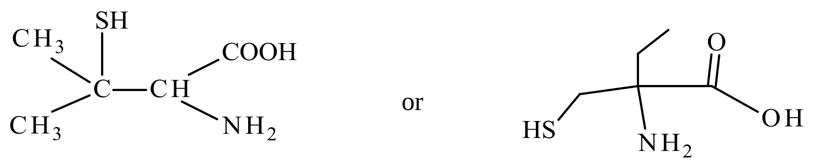
1.6. a.



(0.5 mark)

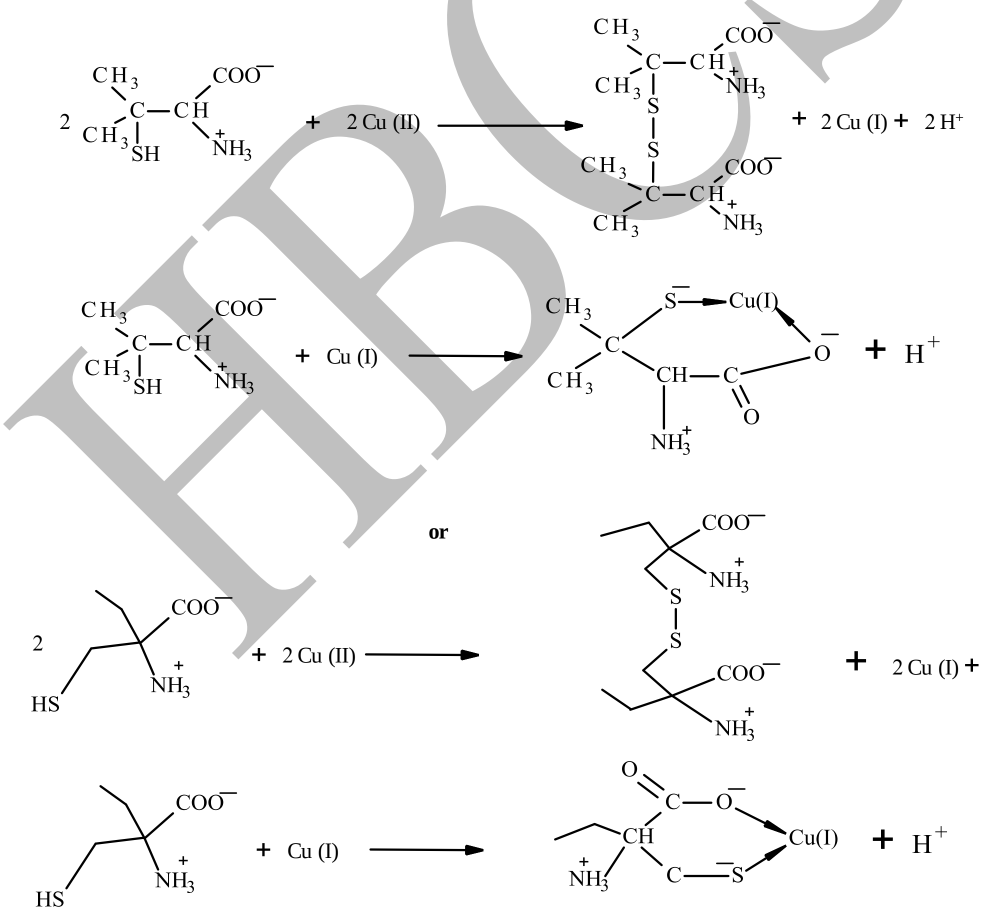
b. **Q** = $CuC_5H_{10}NO_2S.H_2O$ **(3 marks)**

c.



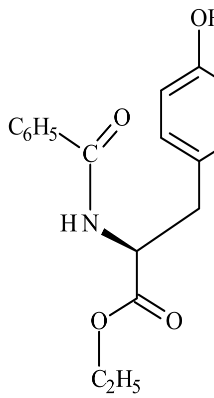
(1 mark)

d.

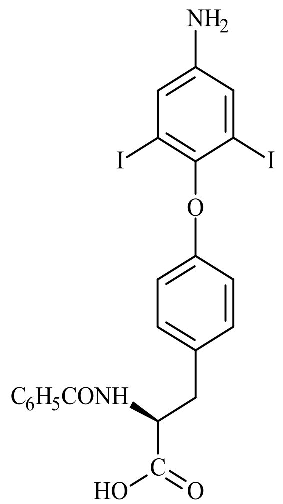


(2 marks)

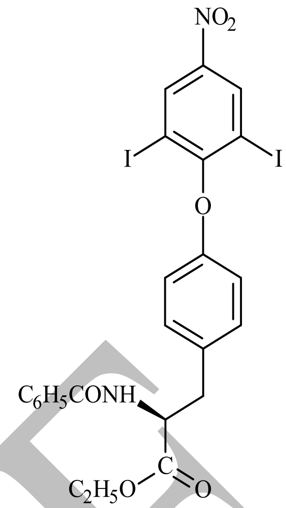
1.7.i)



D



F **($C_{22}H_{18}N_2I_2O_4$)**

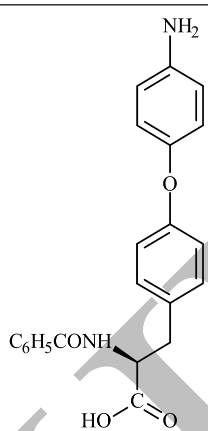


E

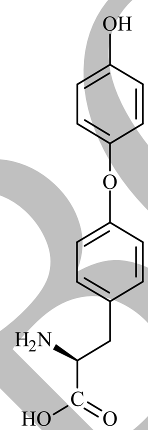
(3 marks)

ii) a) Reducing agent X **(0.5 mark)**

iii) **



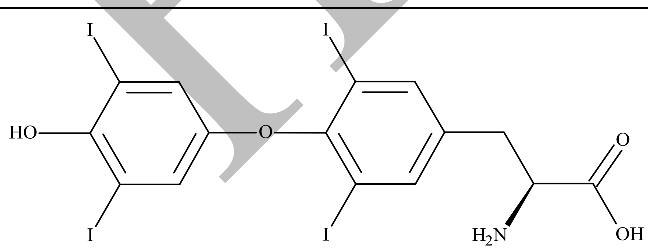
G



Z **($C_{15}H_{15}O_4N$)**

(1.5 marks)

iv)



(I atoms attached to any other aromatic C atom will also be accepted)

(1 mark)

****During the exam, the following additional instruction was communicated to the students.**

Q. 1.7(iii) Draw the structures of compounds **G** and **Z** with stereochemistry.

Problem 2 **17 marks**

Boron Compounds through the Ages

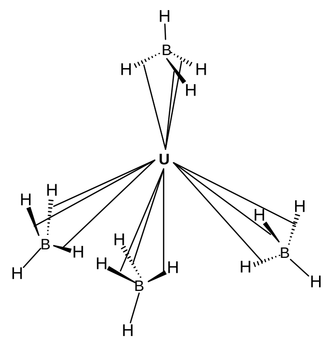
2.1

$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaB(OH)_4$

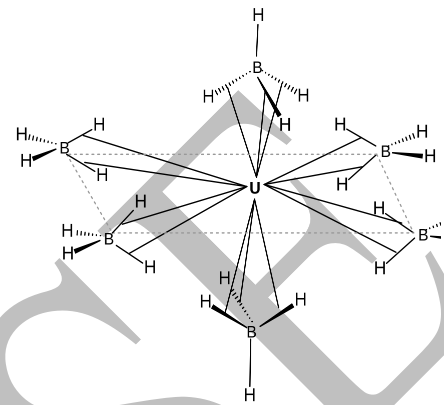
Volume V= 257.6 L

(2.5 marks)

2.2



Gas phase



Solid phase

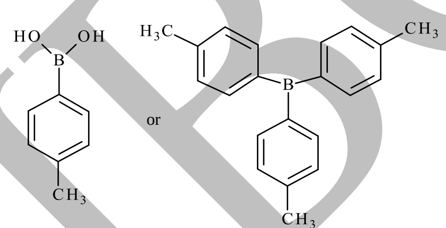
(3.5 marks)

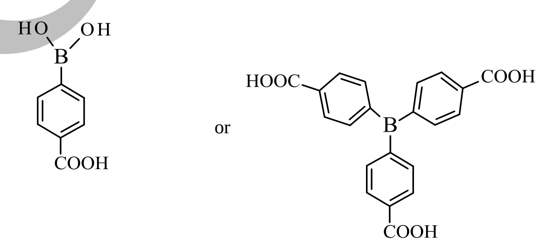
2.3 ^{10}B = 20% **(1.5 marks)**

2.4 Saturated solution of H_3BO_3 **(2.5 marks)**

2.5

Mg/Dry ether



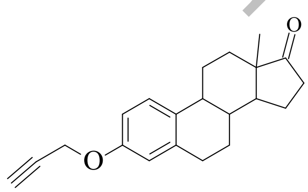


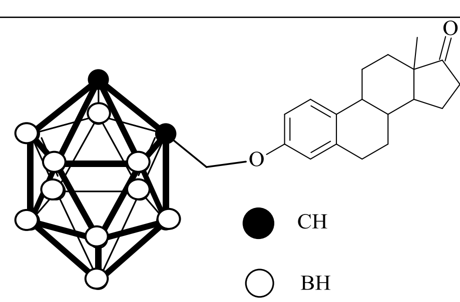
P **Q** **R**

(2 marks)

2.6 6 **(1 mark)**

2.7





(2 marks)

2.8 i. +3 ii. Tetrahedral

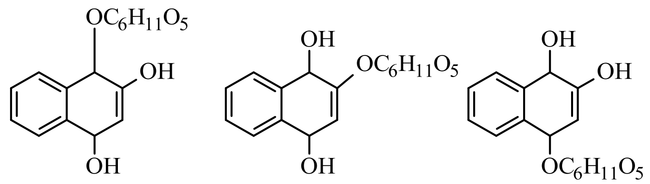
iii. X= F iv. **b** **(2 marks)**

Problem 3 **19 Marks**

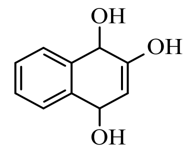
Chemistry behind Henna – Lawsone

Part I: Properties of Lawsone

3.1



Hennosides

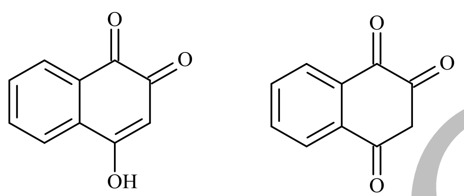


A

(2.5 marks)

3.2 a) Lemon juice [X] **(1 mark)**

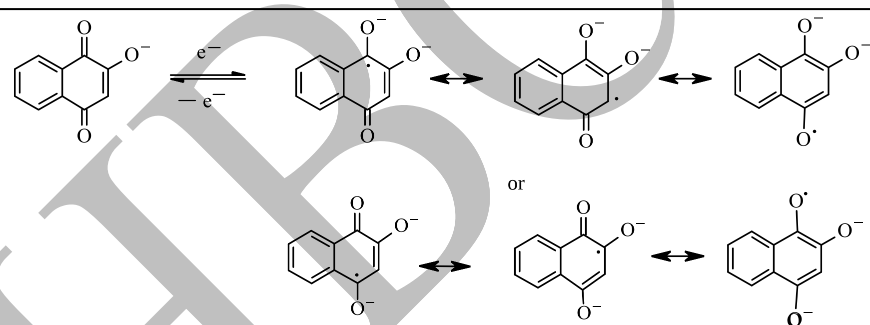
3.3



B

(0.5 mark)

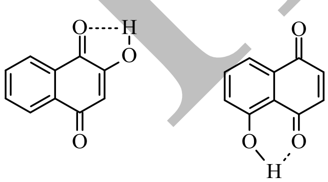
3.4



Reduced Species **Resonance Structures**

(2 marks)

3.5



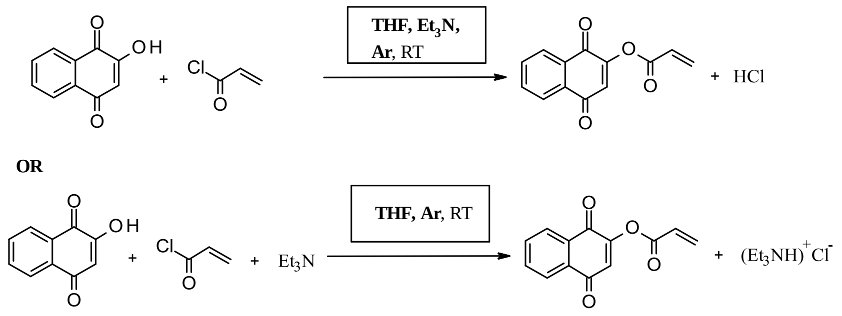
Lawsone Juglone

(1 mark)

3.6 Lawsone [X] Juglone [X] **(1 mark)**

3.7 Lawsone [X] **(1 mark)**

3.8

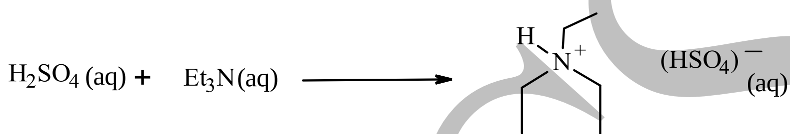


(2.5 marks)

3.9 a) Base [X] **(0.5 mark)**

3.10 2-propenoyl chloride **(2 marks)**

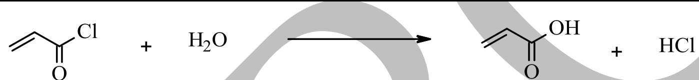
3.11



Aqueous phase (organic/aqueous interface also accepted)

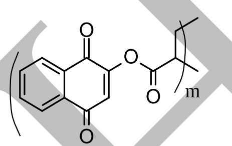
(1.5 marks)

3.12



(1 mark)

3.13



(1 mark)

3.14

	True	**False**
(i)		X
(ii)	X	
(iii)	X	

(1.5 marks)

Problem 4 **23.5 Marks**

Gold Refining

Part I: Cyanidation Method

4.1

$2Au(s) + 4NaCN(aq) + O_2(aq) + 2H_2O \rightarrow 2Na[Au(CN)_2](aq) + 2NaOH(aq) + H_2O_2(aq)$

$2Au(s) + 4NaCN(aq) + H_2O_2(aq) \rightarrow 2Na[Au(CN)_2](aq) + 2NaOH(aq)$

Or [ionic equation]

$2Au(s) + 4CN^-(aq) + O_2(aq) + 2H_2O \rightarrow 2[Au(CN)_2]^-(aq) + 2OH^-(aq) + H_2O_2(aq)$

$2Au(s) + 4CN^-(aq) + H_2O_2(aq) \rightarrow 2[Au(CN)_2]^-(aq) + 2OH^-(aq)$

Or

$2Au(s) + 4CN^-(aq) + O_2(aq) + 2H^+ \rightarrow 2[Au(CN)_2]^-(aq) + H_2O_2(aq)$

$2Au(s) + 4CN^-(aq) + H_2O_2(aq) + 2H^+ \rightarrow 2[Au(CN)_2]^-(aq) + 2H_2O(aq)$

(1.5 marks)

4.2 Net reaction: $4Au(s) + 8CN^-(aq) + O_2(aq) + 2H_2O \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$

NaCN concentration = 0.105 g L^{-1}.

(2 marks)

4.3 Linear, $\mu_{spin} = 0$ **(1mark)**

4.4 **(2.5 marks)**

$$E_{(Au(CN)_2)^-/Au} = -0.57 - 0.059 \log \frac{[CN^-]^2}{[Au(CN)_2]^-}$$

4.5 **(i)** Au, Ag, Pd, Pt

(ii) Au > Ag > Pd > Pt **(3 marks)**

4.6 pH ≈ 9.1 **(1 mark)**

4.7 $[Cu(CN)_4]^{3-}$, $[Cu(CN)_3]^{2-}$ **(1 mark)**

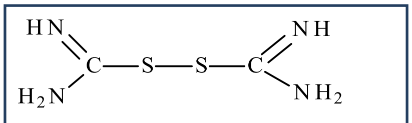
4.8 a) X d) X **(2 marks)**

Part II: Thiourea Method

4.9 $Au + 2CS(NH_2)_2 + Fe^{3+} \longrightarrow [Au(CS(NH_2)_2)_2]^{+} + Fe^{2+}$

(1 mark)

4.10



(1 mark)

4.11 295 K **(2.5 marks)**

4.12 (A) X (C) X **(1 mark)**

4.13 $6CS(NH_2)_2 + KIO_3 + 6H^{+} \rightleftharpoons 3[CS(NH_2)_2]_2^{2+} + 3H_2O + KI$

(1 mark)

4.14 Mass of gold recovered = 5.91 g L^{-1} **(3 marks)**

Problem 5 **24 marks**

Phosphate and Struvite

Part I: Struvite from Phosphate

5.1 13.26 mg L^{-1} **(1.5 marks)**

5.2 Molar ratio MAP: MKP = 3.3: 1 **(2 marks)**

5.3
A = $MgHPO_4$, Molar mass = 120.4 g mol^{-1}
B = $Mg_2P_2O_7$, Molar mass = 222.6 g mol^{-1}
(3 marks)

Part II: Precipitation Conditions for Struvite

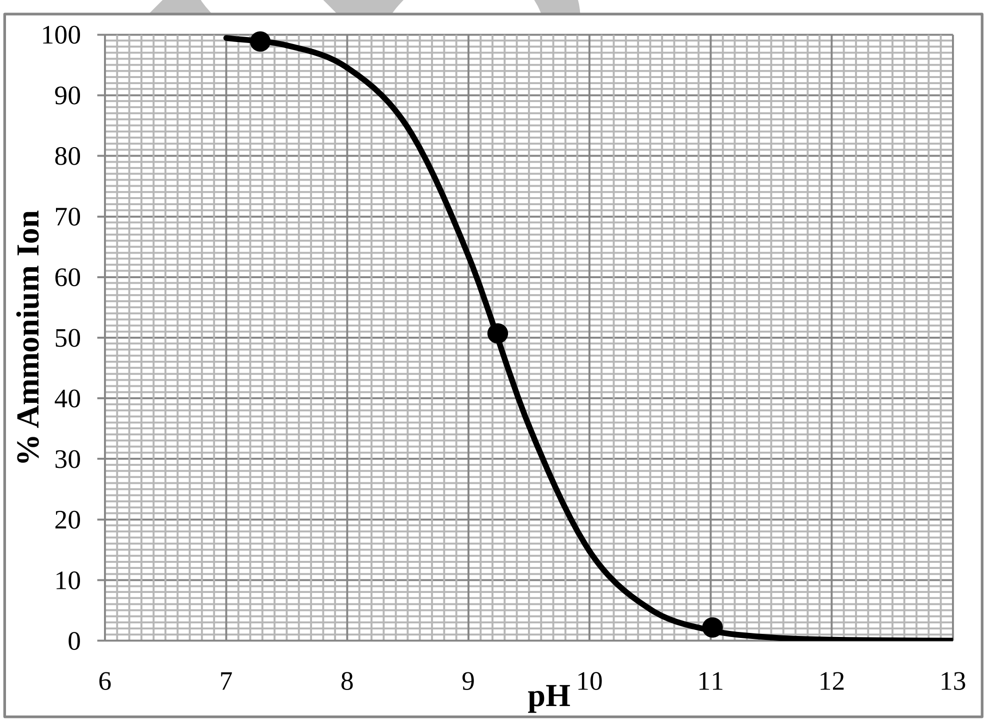
5.4
At pH 7,
$([PO_4^{3-}]/[H_2PO_4^-])$ = 3.02×10^{-6}:1
At pH 11,
$[PO_4^{3-}]/[HPO_4^{2-}]$ = 0.048:1
(2 marks)

5 .5
a) % NH_4^+ = 50%

b) % NH_4^+ = 1.67%

c) pH ≈ 7.24

(2.5 marks)



(1.5 marks)

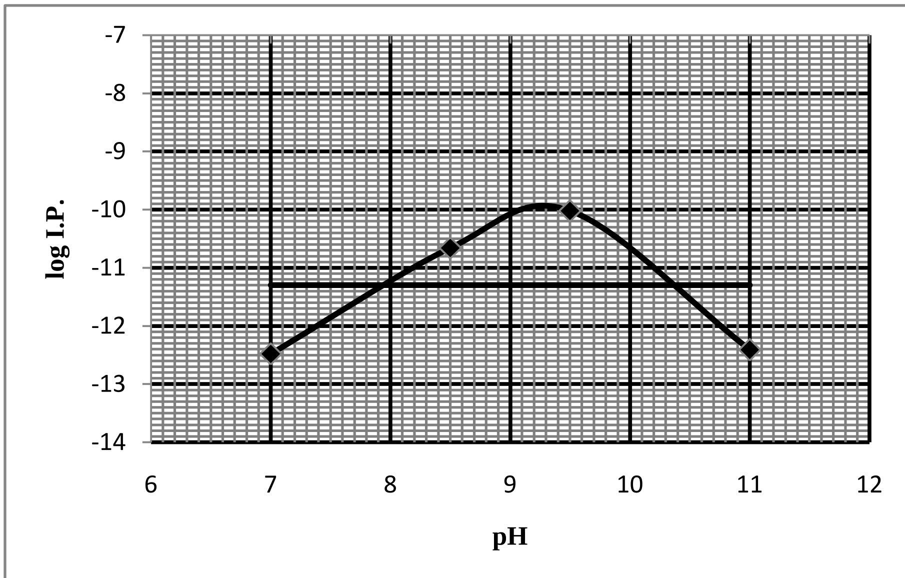
5.6 % Mg^{2+} = 71.56% **(2 marks)**

5.7 **(i)** At pH 7, I.P. = 3.24×10^{-13}

At pH 11, I.P. = 3.85×10^{-13}

(4 marks)

(ii)



pH Range: 7.9- 10.4

(2.5 marks)

5.9 **c)** **X** **(1 mark)**

5.10 **Effect**

a)	iii
b)	iii
c)	iii
d)	i

(2 marks)