

Indian National Chemistry Olympiad 2025

Theory (3 hours)

Total 109 marks

Time- 3 hours

Date: February 01, 2025

Instructions for students

Roll No. - -

Exam Center

- Write your Roll No. in the space provided above.
- This question booklet consists of **14** printed pages including a periodic table. Check that the booklet has all the pages. If not, report to the invigilator immediately.
- Do not write any part of your answer in this question paper.
- A copy of the Periodic Table of the Elements is provided at the end.
- Do not leave the examination room until directed to do so.

Useful Constants and Formulae

Avogadro number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

1 atm = 101325 Pa

Molar gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Density of water at 4 °C = 1000 kg m⁻³

Electronic Charge, $e = 1.602 \times 10^{-19} \text{ C}$

Mass of electron, $m_e = 9.109 \times 10^{-31} \text{ kg}$

Permittivity of vacuum, $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2/\text{Nm}^2$

Bohr radius for hydrogen atom, $a_0 = 0.53 \text{ \AA}$

$$\frac{dx^a}{dx} = ax^{a-1}$$

$$\frac{de^{ax}}{dx} = ae^{ax}$$

$$\frac{df(y)}{dx} = \frac{df(y)}{dy} \times \frac{dy}{dx}$$

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pK}_a = -\log K_a$$

Problem 1
23 marks
The golden alloy

Two or more metals can form an alloy if they have

- I. similar atomic radii, differing by less than 15%
- II. same crystal structure, and
- III. similar chemical properties or similar number of valence electrons in metals

For combinations of metals satisfying all three conditions, alloys with a single homogenous solid phase (having well defined crystal structure) are formed at all compositions. Such alloys are called continuous solid solutions. For example, alloys of Cu and Ni.

Given below is a list of metals with their size and crystal structure

Metal	Cu	Ni	Cr	K	Pb	Al	Ag	Au	Zn
Crystal Structure	fcc	fcc	bcc	bcc	fcc	fcc	fcc	fcc	hcp
Atomic radii (in Å)	1.28	1.25	1.29	2.27	1.75	1.43	1.44	1.44	1.37

1.1 For the following combinations of metals, identify if it can form a continuous solid solution.

	Yes	No
Cu & Ag		
Cr & K		
Cu & Al		
Ag & Al		

If only one or two of the conditions **I-III** are satisfied, two or more homogenous phases (each having different structure and properties) may form at different compositions. At a given composition, an alloy may exist as a single phase, or two phases may co-exist within the material. As we heat the alloy, the solid phase(s) can melt above a certain temperature and co-exist with the corresponding liquid over a temperature range and then get converted into pure liquid phase. This information of thermodynamically stable phases of different alloy compositions and at different temperatures is represented in a phase diagram.

Phase diagram of Cu and Zn alloys, commonly known as brass, is shown in **Fig. 1**. In the diagram, each area marked by solid boundaries represents a phase or a mixture. For example, regions marked by α , β , γ , etc., represent different solid phases of brass, i.e., α -brass, β -brass, etc. The regions between these two areas (not labelled) represent a mixed phase of two adjoining single phases like $\alpha + \beta$ -brass.

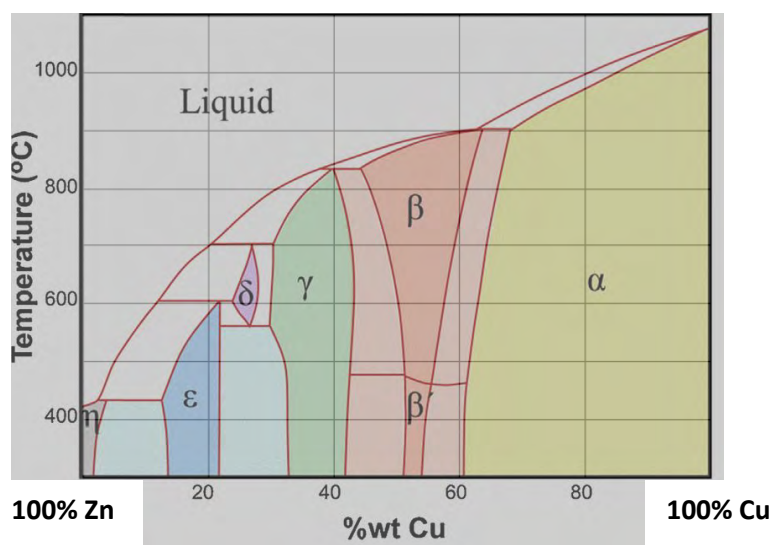


Fig 1. Phase Diagram of Cu-Zn

Adapted from: Journal of Hazardous Materials, Sep 2013, 262C:606-613

Part I: Chemical Properties of H₂O₂

2.1 When H₂O₂ is mixed with a base, it forms a new ion, A.

- i) Draw the Lewis structure of A.
- ii) Write balanced equation for the formation of A.

2.2 H₂O₂ is a weak acid (pK_a = 11.75). Determine the pH of 3% (w/w) aqueous solution of H₂O₂ (density = 1.01 g cm⁻³).

2.3 When H₂O₂ is mixed with a dilute solution of H₂SO₄, it forms solution X in which H₂O₂ is converted to species B.

- i) Draw the Lewis structure of B.
- ii) Write balanced equation for formation of B.

2.4 Write the balanced equations for the following two reactions.

- i) When solution X is mixed with another colorless solution, it resulted in a yellow-brown color solution which developed dark blue color on the addition of starch.
- ii) When solution X is mixed with a Mn-containing solution having deep violet color, it resulted in decolorization of the solution.

Part II: Recycling of Spent Catalyst

Crude petroleum and natural gas usually contain sulphur compounds which are removed industrially using catalysts containing Mo, Co, and Ni, and their oxides supported on alumina. This process is called hydrodesulfurization (HDS). After many cycles, these catalysts lose their activity due to formation of their respective sulphides and are disposed in landfills. However, metals can be recovered from these spent catalysts. For effective recovery, these materials are ground into fine powder. Extraction of metals from this powder can be done by two methods:

- **Roasting + Leaching:** The powdered catalyst is heated in an open furnace at 850 °C in presence of air. The metal sulphides get converted to oxides with 95% conversion. The oxides are then leached using H₂SO₄.
- **Direct Leaching (without roasting):** Hydrogen peroxide (30%) and sulfuric acid are used directly to dissolve the metal sulphides. Typically, 89% of the metal sulphides get dissolved in this method.

A flow diagram of the two processes is shown below.

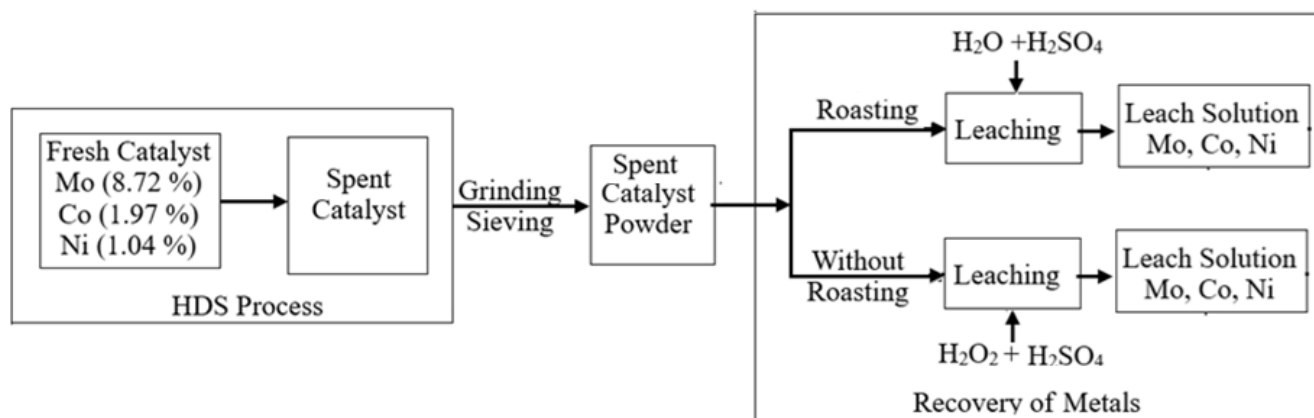


Fig. 1 Flow diagram of dissolution process of spent catalyst

Subsequently, individual metals are extracted from the leach solutions using the following process.

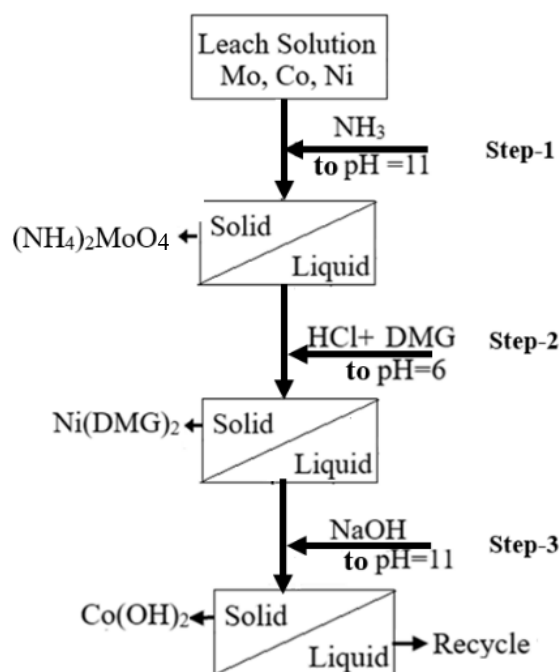


Fig. 2 Flow diagram of metal separation from leach solution

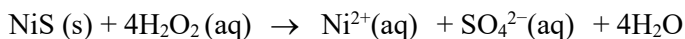
2.5 A metallurgical plant received 10 kg of spent catalyst powder (Mo = 8.72%, Co = 1.97%, Ni = 1.04%) to recover metals. As a trial, one staff tried roasting method for 1 kg of the catalyst. Molybdenum sulphide gets oxidized as per the following chemical reaction.



- Write balanced equations for the roasting of Co and Ni sulphides (where Co remains in +2 oxidation state under the roasting condition).
- Determine the volume of SO_2 released in the above process at the furnace temperature and atmospheric pressure.

2.6 Another staff dissolved 1 kg catalyst using the **direct leaching** method, by using 1 kg of 15% w/w H_2SO_4 solution and stoichiometrically equivalent amount of hydrogen peroxide (30% w/w solution). The H_2SO_4 predominantly helps dissolving metal sulphides. Note that 89% of the metals in the catalyst get dissolved.

The balanced equations for reactions during dissolution of metal sulphides are given below.



- Calculate the molality of Mo obtained in this solution.
- Identify the major species present in the final filtrate obtained at the end of Step 3 of metal extraction. (Assume that each precipitating reagent was added about 5% in excess and the metal precipitations were complete).
- The final filtrate is concentrated by boiling. Identify the compound which can be recovered in largest amount from this process.
- After concentration and separation of solids, remaining filtrate can be added back to one of the steps (1 or 2 or 3) shown in Fig 2., with a specific advantage. In the table below, **mention** this step number in Row I, and the advantage(s) in appropriate column(s) in that row. In Row II, mention disadvantage(s) if it is added in any one of the other steps.

	reduces consumption of	enhances yield of	decreases contamination in	increases contamination in
I. When added in the chosen step _____,				
II. When added in another step _____,				

2.7 The advantage of hydrogen peroxide leaching over roasting + leaching process is (mark X in box for the applicable statement(s) and for marked statements, write the appropriate substances in the blank spaces).

- It prevents formation of _____ as waste product.
- It enhances formation of _____ as a useful by-product.
- It reduces consumption of _____ as input chemicals.

Problem 3

21 Marks

Structure Elucidation of a Drug

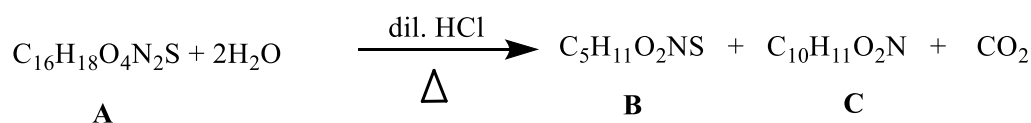
Determining the structure of an active component from natural sources (such as plants and microorganisms) which acts as a drug/medicine can help to produce it on a large scale. In this question, we will work out the structure of a drug (A) isolated from a natural source.

Analytical experiments indicate that A is a heterocyclic compound with molecular formula $C_{16}H_{18}O_4N_2S$. Compounds with free thiol (-SH) group give strong colours when treated with aqueous $FeCl_3$. A does not give color when reacted with aqueous $FeCl_3$.

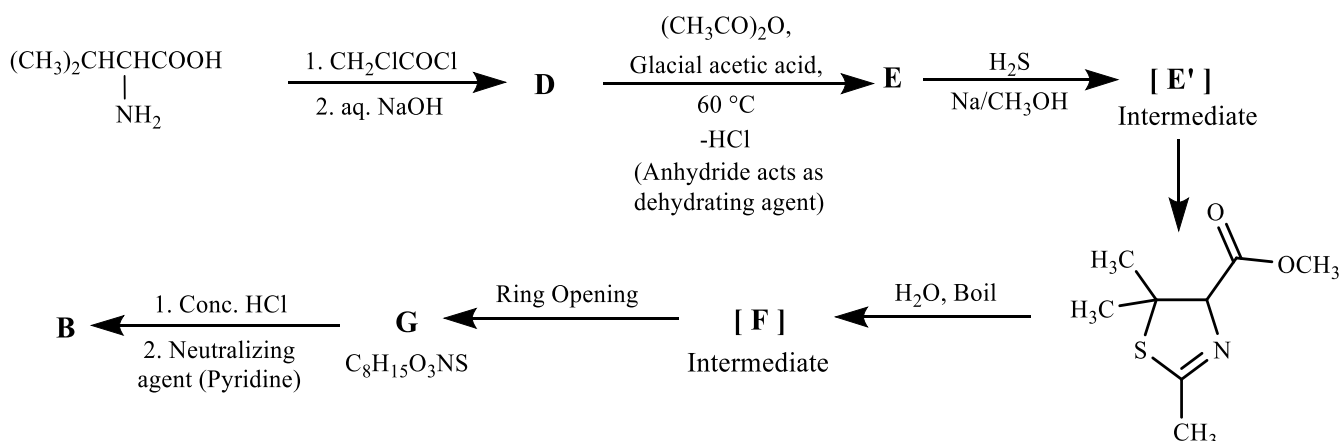
3.1 A gives effervescence with a solution of sodium bicarbonate and forms a mono-sodium salt. When A is treated with nitrous acid, no gas is evolved. From these observations, the inference that can be drawn is that molecules of A have (Mark X for the correct option(s))

- presence of -COOH and -NH₂ groups.
- presence of -COOH, phenolic -OH and absence of -NH₂ groups.
- presence of -COOH and absence of -NH₂ groups.
- presence of phenolic -OH and absence of -NH₂ groups.

On hydrolysis with hot dilute hydrochloric acid, A gives B ($C_5H_{11}O_2NS$) and C ($C_{10}H_{11}O_2N$) as shown in the following reaction.

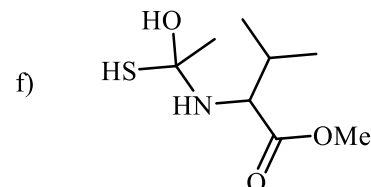
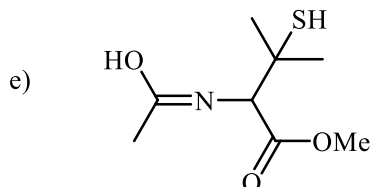
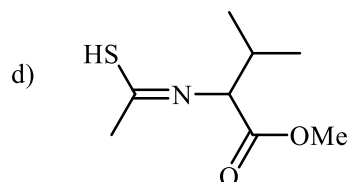
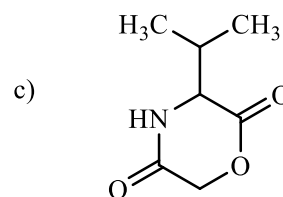
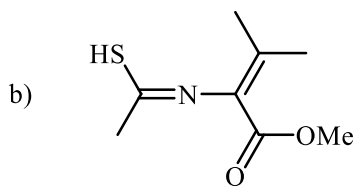
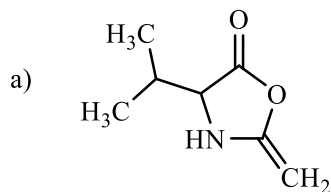


3.2 Compound B can be synthesized in the lab via the following steps.



i) Draw the structures of the major products **D** and **E**.

ii) Among the following, identify the correct structure of intermediate **E'** formed in the above reaction scheme. (Mark **X** against the correct option)



iii) Draw the structures of intermediate **F** and products **G** and **B**.

iv) pH metric titration of compound **B** showed three pK_a values 1.8, 7.9 and 10.5. Write the functional groups present in molecules of **B** corresponding to these pK_a values.

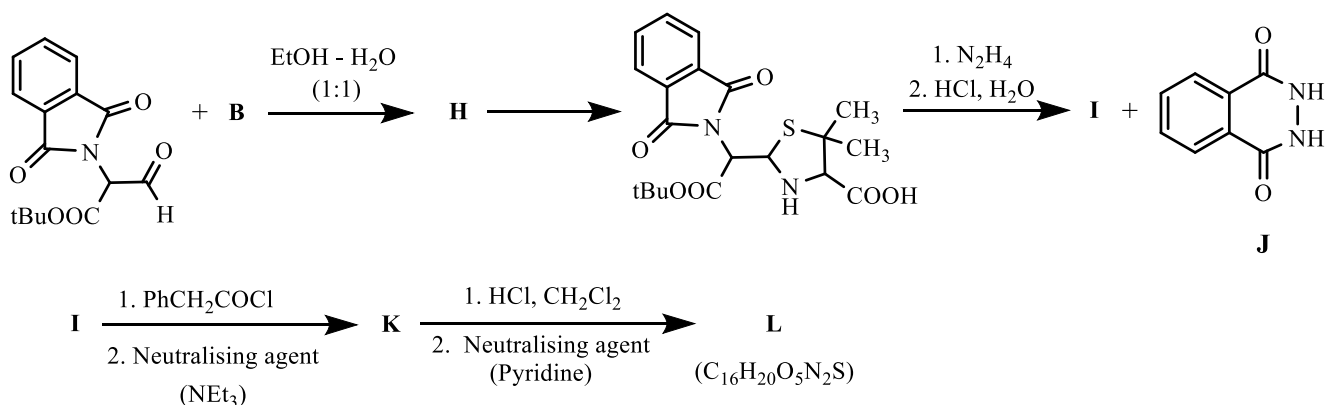
In a class, two teams of students were given compound **B** for functional group analysis. Team 1 students dissolved compound **B** in water while team 2 students dissolved it in acetone. Both teams treated their solutions of **B** with aqueous $FeCl_3$ and with nitrous acid separately. Students of one of the two teams could observe color change with aqueous $FeCl_3$ and nitrogen gas evolution with nitrous acid, while students of the other team did not obtain these two observations.

v) Identify the team that got reaction(s) with the two reagents, and the correct statement(s) from the options given below (a-e) explaining the results of Team 1 and Team 2.

- B** got hydrolyzed in water.
- B** reacted with acetone.
- B** got dissolved in water thus gave positive results for functional group analysis.
- B** did not dissolve in acetone and thus could not give results for functional group analysis.
- B** did not dissolve in water and thus could not give positive result.

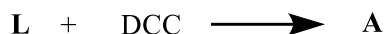
3.3 Compound **C** on heating with concentrated HCl gives phenylacetic acid and α -amino acetaldehyde. Write the structure of **C**.

3.4 Drug **A** can also be synthesized from **B** through the following route.

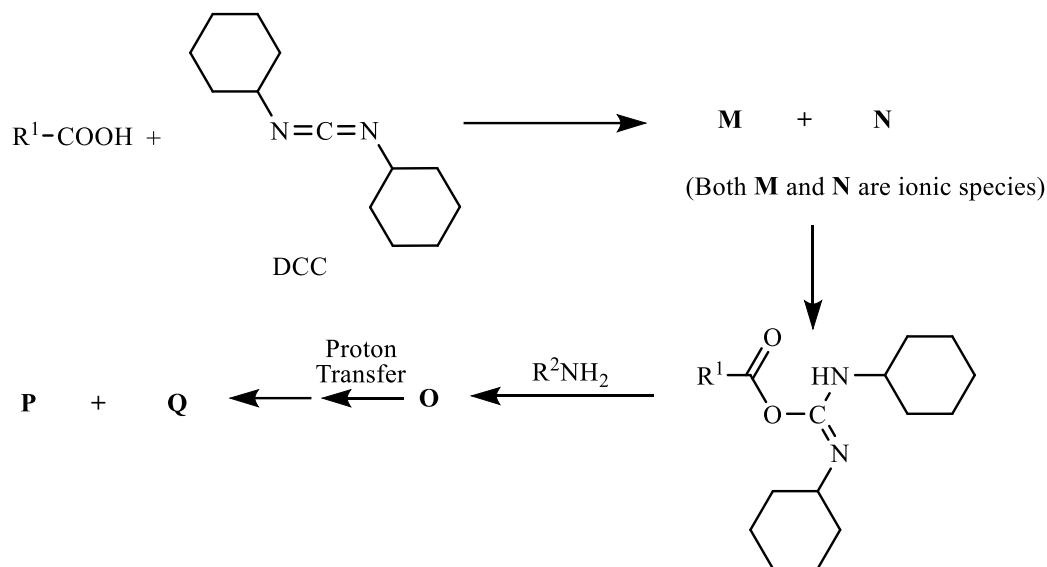


i) Draw the structures of **H**, **I**, **K** and **L**.

A can be obtained from L by reacting it with Dicyclohexylcarbodiimide (DCC).



DCC is a common reagent used to combine amino acids in peptide synthesis. The general mechanism of the above reaction with DCC is as given below.



ii) Draw the structures of M, N, O, P and Q.

iii) Draw the structure of A.

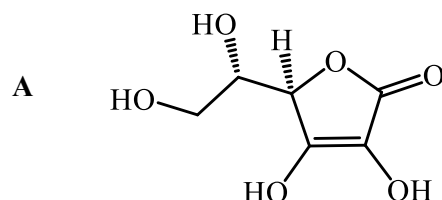
iv) An ideal drug molecule must have both polar and non-polar groups. Polar groups are required for its transport through blood while non-polar groups ensure crossing of the drug molecule through the lipid cell membrane. Redraw the structure of drug A and draw **circles** around the polar groups and draw **rectangles** around the non-polar parts of the molecule.

Problem 4

24 marks

An acid from sugar

A compound (A) named as hexuronic acid was isolated from Hungarian Paprika (*Capsicum annuum*). A is a white to very pale-yellow crystalline powder with a sharp acidic taste. It is a carbohydrate derivative with the following structure:



4.1 Draw other possible stereoisomers for A.

4.2 Molecules of A exhibit tautomerism. Draw all the tautomeric forms of A.

An experimentalist prepared 0.10 M solution of compound A and found its pH to be 2.6. Its second acid dissociation constant, pK_{a2} was found to be 11.4.

4.3 Calculate pK_{a1} of A.

4.4 Draw the structure of the predominant ionic forms of **A** with correct stereochemistry (its bioactive form) present at **i**) physiological pH 7.3 and **ii**) pH 12.0.

A reacts rapidly with diazomethane, giving derivative **B** ($C_8H_{13}O_6$). On reaction with reagent **X**, **B** gives formaldehyde as one of the products.

4.5 Give the structure of **B** and molecular formula of the reagent **X**.

B on further treatment with moist Ag_2O and CH_3I forms **C**. Action of ozone on **C** yields a neutral compound **D** which on elemental analysis gave 48.38% carbon and 6.45% hydrogen.

4.6 Derive the molecular formula of **D** and draw the structures of **C** and **D**. Show all the calculations involved in the derivation.

4.7 The reaction of moist $Ag_2O + CH_3I$ with **B** proceeds via (Mark **X** for the correct option):

- | | |
|------------------------------|-------------------------------|
| a) nucleophilic substitution | b) nucleophilic addition |
| c) electrophilic addition | d) electrophilic substitution |

4.8 In the given reaction, moist Ag_2O is acting as a (Mark **X** for the correct option):

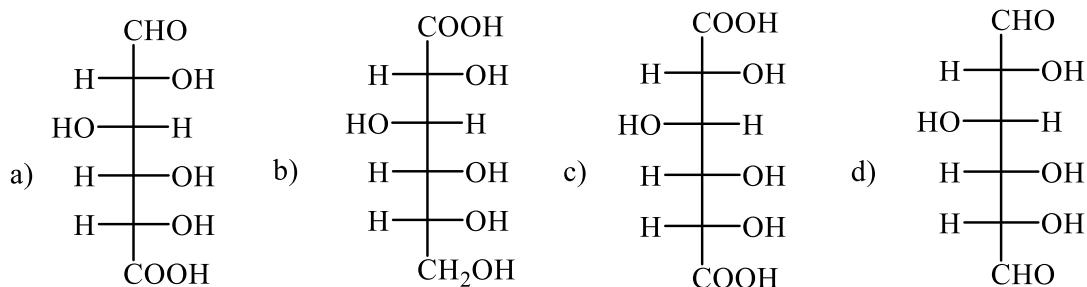
- | | | |
|--------------------------|---------------------------|---------|
| a) source of nucleophile | b) source of electrophile | c) acid |
| d) base | e) amphoteric initiator | |

A, on mild oxidation by iodine under aqueous acidic conditions gives a compound **E** ($C_6H_6O_6$). If (**A**) is oxidized using sodium hypiodite in alkaline solution, oxalic acid and a monobasic acid **F** are formed. **F** on further oxidation yields tartaric acid ($C_4H_6O_6$).

4.9 Draw the structures of **E** and **F**. If the structure(s) is/are acyclic, draw it using Fischer Projection.

A cannot be produced by humans, and hence, it must be obtained through diet. But some other species can convert D-glucose into **A** by a biochemical pathway. In this biochemical conversion, D-Glucose is first oxidized to a compound **G** having 57.70% oxygen.

4.10 Choose the correct structure of **G** from the following (Mark **X** for the correct option):



Under physiological conditions, **G** is converted to a compound **H** ($C_6H_8O_6$), which undergoes reduction to yield a compound **I**. Finally, **I** undergoes dehydrogenation to produce **A**.

4.11 Draw the structures of **H** and **I** with correct stereochemistry.

A is a powerful enhancer of non-heme iron absorption and is used in the treatment of anaemia. It reacts with Fe^{3+} ions to form an octahedral complex having a molecular formula $[C_{12}H_{16}FeO_{14}]^-$.

4.12 Draw the structure of the iron complex of **A**.

$\bullet OH$ is the most reactive of all the ROS (reactive oxygen species) and interacts with DNA causing its damage. The bioactive form of compound **A** (the form at physiological pH) reacts with $\bullet OH$ through a single electron

transfer to form **J** and **K**. On subsequent deprotonation, **J** yields a stable radical **L**, which does not cause DNA damage.

4.13 Draw the structures of **J**, **K** and **L**.

A is estimated in food substances by titrating it with ceric ammonium sulphate which acts as a one electron oxidizing agent.

4.14. Write the product in the given equation for the above titration and balance it.

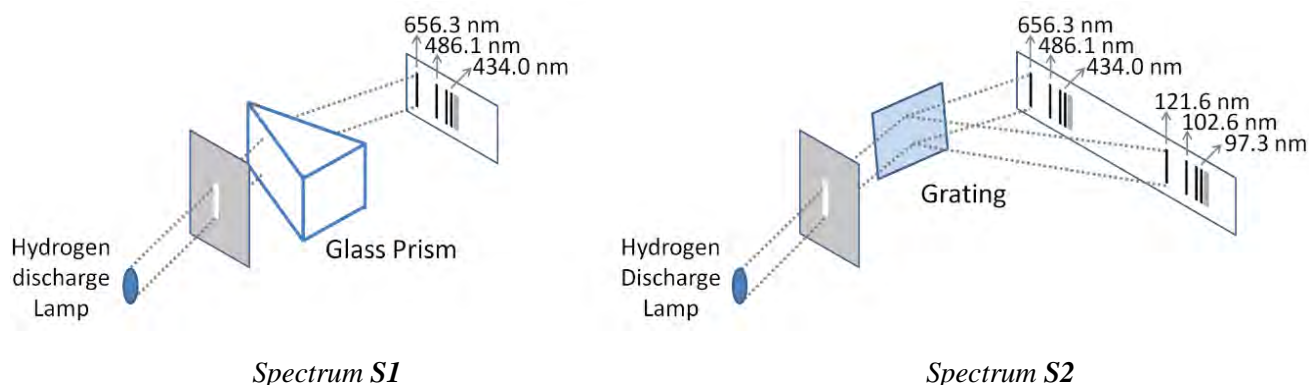


Problem 5

16 marks

The purple hydrogen

When high voltage is applied to hydrogen gas enclosed in an electric discharge tube, it gives a purple glow. In nature, such colour can be observed in light coming from some stars. Origin of this colour in hydrogen remained a mystery for long. In an experiment in the 19th century, scientists passed the light from a hydrogen discharge tube through a slit followed by a glass prism. On a screen kept behind the glass prism, multiple lines could be seen with a very bright red line followed by a blue and few closely spaced violet lines. In experiments in early 20th century when diffraction grating was used instead of glass prism, few additional lines could be detected as non-visible extensions of the spectrum as shown below.



In later experiments, several more lines at higher wavelengths were detected in the spectrum of hydrogen discharge, but no lines were detected at wavelengths lower than those seen in *spectrum S2*.

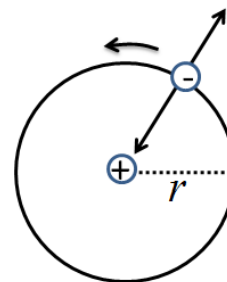
5.1 Each of these lines originated from a specific decrease in energy of hydrogen atoms as the atoms transitioned from one well-defined energy state to another. Determine the frequency of light originating from the lowest energy transition observed in *spectrum S2*.

The wavelengths obtained in the above spectra were analyzed by many mathematicians. Finally, it was recognized that the wavelengths corresponded to change in energy states of hydrogen atom, where energy of each state would be of the form $E_n = -C/n^2$, where C is a constant and n is a natural number.

5.2 i) Using the wavelength data in *S1* and *S2*, determine the value of C in Joules and in cm^{-1} . Give detailed steps followed to obtain the answers.

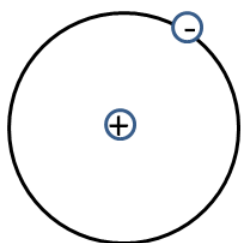
ii) Determine the n values for states, transitions between which produces light of wavelengths 102.6 nm and 434.0 nm.

According to the Bohr atomic model, electrons in an atom move in circular orbits around the nucleus (as depicted in the figure). The hydrogen atom is stable because the magnitude of the centrifugal force $\left(\frac{mv^2}{r}\right)$ and electrostatic force $\left(\frac{Ze^2}{4\pi\epsilon_0 r^2}\right)$ at distance, a_0 are equal.

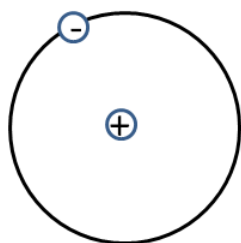


5.3 Find the magnitude of velocity of the electron in hydrogen atom and find its ratio to the speed of light.

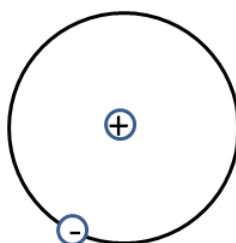
Imagine that we can capture snapshots of the electron orbiting in the circular path. Four representative snapshots among several are illustrated below:



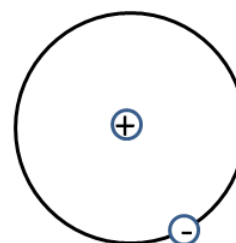
Snapshot 1



Snapshot 2

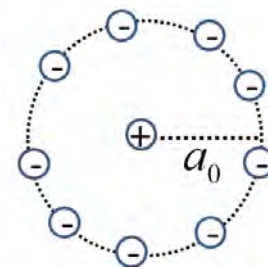


Snapshot 3

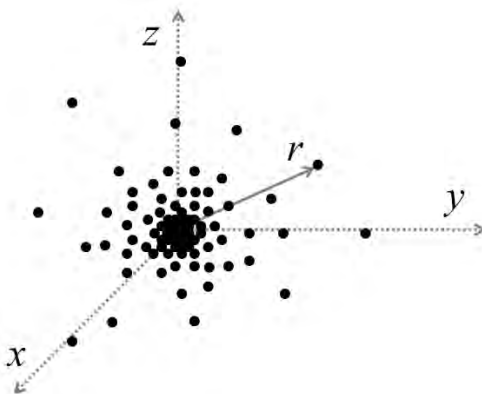


Snapshot 4

Alternatively, several snapshots can be collectively represented in a single figure as given on the right-hand side image. This figure shows that the probability of finding the electron on the orbit of radius $r = a_0$ is 100% (according to the Bohr model).



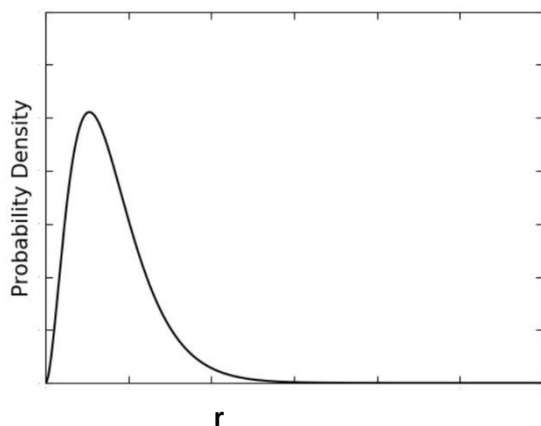
On the contrary, different experiments collectively exhibit the following superimposed snapshots for the position of the electron in a hydrogen atom. Here, the nucleus is located at the origin and position of the electron (shown by dots) can be anywhere around the nucleus; however, there are regions where the electron is found more frequently than the other regions.



Quantum mechanical model provides a possible explanation for the above experimental realization using a mathematical function, called the *probability density function*. The probability density of the electron in hydrogen atom or hydrogen like atoms/ions (with atomic number Z) in lowest energy state at a distance r obtained from quantum mechanical model, can be expressed as:

$$f(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2\frac{Zr}{a_0}}$$

This function for hydrogen is plotted in the following figure:

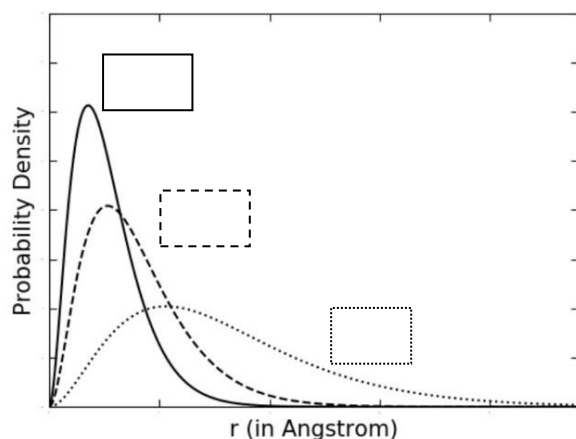


5.4 Find the most probable value of r (the distance from the origin where the probability density of finding the electron is maximum) for a hydrogen atom.

5.5 Based on the most probable value of r , possible true statements among the following is/are (Mark **X** for the correct option(s)):

- Bohr model predicted locations of electron which are impossible in reality.
- In quantum mechanical model, circular motion is not possible, only linear motion is possible.
- In quantum mechanical model, electron motion is not possible.
- In quantum mechanical model, electron in lowest energy state can be found at a distance $r = 8a_0$.

5.6 Curves representing the ground state probability density functions of electron in H atom, He^+ ion and Li^{2+} ion are given in diagram below. Identify which curve corresponds to which specie.



Assume that a specially designed hydrogen discharge lamp **DL** creates excited hydrogen atoms in $n = 2$ state only. Electronically excited atoms finally transition back to the ground state by emitting photons with appropriate frequency. One can monitor the emission intensity, I at any given time, t , using a photosensitive detector.

Assume that at time $t = 0$ (i.e., when the excited hydrogen atoms were generated), the emission intensity was I_0 . Change of emission intensity as a function of time can be expressed by the following rate equation:

$$-\frac{dI}{dt} = kI ; \text{ where, } k = 10^8 \text{ s}^{-1} \text{ for } n = 2 \rightarrow n = 1 \text{ transition and depends on the electron distribution}$$

in the initial and final states.

5.7 Find the time at which the intensity of discharge lamp drops to 10% of the initial intensity after it is switched off.

5.8 Identify the colour of emission of this discharge lamp **DL**.

IUPAC Periodic Table of the Elements

1 H hydrogen [1.0078, 1.0082]	2 He helium 4.0026											17 F fluorine 18.998	18 Ne neon 20.180	
3 Li lithium [6.938, 6.997]	4 Be beryllium 9.0122											9 O oxygen [15.999, 16.000]	10 N nitrogen [14.006, 14.008]	
11 Na sodium [22.990, 23.004, 24.307]	12 Mg magnesium [24.304, 24.307]											8 S sulfur [32.059, 32.076]	16 P phosphorus [30.974, 30.974]	
19 K potassium [39.098, 39.098]	20 Ca calcium [40.078(4), 40.078(4)]											7 N nitrogen [14.006, 14.008]	15 As arsenic [74.922, 74.922]	
37 Rb rubidium [85.468, 85.468]	38 Sr strontium [87.62, 87.62]											6 C carbon [12.011, 12.011]	14 Si silicon [28.085, 28.086]	
55 Cs caesium [132.91, 132.91]	56 Ba barium [137.33, 137.33]											5 B boron [10.81, 10.821]	13 Al aluminium [26.982, 26.982]	
87 Fr francium	88 Ra radium											13 Al aluminium [26.982, 26.982]	14 Si silicon [28.085, 28.086]	
57 La lanthanum	58 Ce cerium	59 Pr praseodymium	60 Nd neodymium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb terbium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
89-103 actinoids	89 Ac actinium	90 Th thorium	91 Pa protactinium	92 U uranium	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
21 Sc scandium	22 Ti titanium	23 V vanadium	24 Cr chromium	25 Mn manganese	26 Fe iron	27 Co cobalt	28 Ni nickel	29 Cu copper	30 Zn zinc	31 Ga gallium	32 Ge germanium	33 As arsenic	34 Se selenium	35 Br bromine
39 Y yttrium	40 Zr zirconium	41 Nb niobium	42 Mo molybdenum	43 Tc technetium	44 Ru ruthenium	45 Rh rhodium	46 Pd palladium	47 Ag silver	48 Cd cadmium	49 In indium	50 Sn tin	51 Sb antimony	52 Te tellurium	53 I iodine
57-71 lanthanoids	72 Hf hafnium	73 Ta tantalum	74 W tungsten	75 Re rhenium	76 Os osmium	77 Ir iridium	78 Pt platinum	79 Au gold	80 Hg mercury	81 Tl thallium	82 Pb lead	83 Bi bismuth	84 Po polonium	85 At astatine
89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hasmium	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

Key:
 atomic number
Symbol
 name
 conventional atomic weight
 standard atomic weight



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