Signature of Invigilators

1. ....

2. ....

CHEMICAL SCIENCE
Paper III

Roll No. ☐☐☐☐☐

(In figures as in Admit Card)

Roll No. ....

....

(In words)

JY—04/3

Name of the Areas/Section (if any)......................

Time Allowed : $2\frac{1}{2}$ Hours] [Maximum Marks : 200

Instructions for the Candidates

1. Write your Roll Number in the space provided on the top of this page.
2. Write name of your Elective/Section if any.
3. Answer to short answer/essay type questions are to be written in the space provided below each question or after the questions in test booklet itself. No additional sheets are to be used.
4. Read instructions given inside carefully.
5. Last page is attached at the end of the test booklet for rough work.
6. If you write your name or put any special mark on any part of the test booklet which may disclose in any way your identity, you will render yourself liable to disqualification.
7. Use of calculator or any other Electronics Devices are prohibited.
8. There is no negative marking.
9. You should return the test booklet to the invigilator at the end of the examination and should not carry any paper outside the examination hall.

પરીક્ષાર્થીઓ માટે સૂચનાઓ :

૧. આ પૃષ્ઠના ઉપલા ભાગે આપેલી જગ્યામાં તમારી ક્રમાંક સંખ્યા (રોલ નંબર) લખો.

૨. તમે જે વિકલ્પનો ઉત્તર આપો તેનો સ્પષ્ટ નિર્દેશ કરો.

૩. ટૂંક નોંધ કે નિબંધ પ્રકારના પ્રશ્નોના ઉત્તર દરેક પ્રશ્નની નીચે આપેલી જગ્યામાં જ લખો. વધારાના કોઈ કાગળનો ઉપયોગ કરશો નહીં.

૪ અંદર આપેલી સૂચનાઓ ધ્યાનથી વાંચો.

૫. આ ઉત્તરપોથીને અંતે આપેલું પૃષ્ઠ કાચા કામ માટે છે.

૬. આ ઉત્તરપોથીમાં કયાંય પણ તમારી ઓળખ કરાવી દે એવી રીતે તમારું નામ કે કોઈ ચોકકસ નિશાની કરી હશે તો તમે આ પરીક્ષા માટે ગેરલાયક સાબીત થશો.

૭. કેલકયુલેટર અથવા ઈલેકટ્રોનિકસ સાધનો જેવાનો ઉપયોગ કરવો નહીં.

૮. નકારાત્મક ગુણાંક પદ્ધતિ નથી.

૯. પ્રશ્નપત્ર લખાઈ રહે એટલે આ ઉત્તરપોથી તમારા નિરીક્ષકને આપી દેવી. પરીક્ષાખંડની બહાર કોઈ પણ પ્રશ્નપત્ર લઈ જવું નહીં.

FOR OFFICE USE ONLY
Marks Obtained

Question Number	Marks Obtained	Question Number	Marks Obtained	Question Number	Marks Obtained
1.		20.			
2.		21.			
3.		22.			
4.		23.			
5.		24.			
6.		25.			
7.		26.			
8.		27.			
9.		28.			
10.		29.			
11.		30.			
12.		31.			
13.		32.			
14.		33.			
15.		34.			
16.		35.			
17.		36.			
18.					
19.					

Total Marks Obtained..........................
Signature of the co-ordinator..............
(Evaluation)

SEAL

CHEMICAL SCIENCE

PAPER-III

Note : (i) Question No. **1** is compulsory (**40** marks). Answer it in **800** words (8 pages).

(ii) Attempt any ten questions out of the remaining **35** questions (**16** marks each). Answer each question in maximum **300** words (3 pages)

General Physical Constants :

Speed of light C = $2.998 \times 10^{8}\ \mathrm{ms^{-1}}$

Avogadro constant N = $6.023 \times 10^{23}\ \mathrm{mol^{-1}}$

Faraday F = 96500 coulombs $\mathrm{mol^{-1}}$

Planck constant h = 6.626×10^{-34} Js

Boltzmann constant k = $1.381 \times 10^{-23}\ \mathrm{JK^{-1}}$

Gas constant R = $8.314\ \mathrm{JK^{-1}\ mol^{-1}}$ or 1.987 cal $\mathrm{K^{-1}\ mol^{-1}}$

1. (*a*) (*i*) If you are provided w.m colored solution with very low value for absorbance how will you proceed to analyse it without concentrating by the technique of the differential spectrophotometry ? OR What is called as high absorbancy and low absorbancy colorimetry ?

(*ii*) A unknown colored complex showed an molar absorpivity of 1.4×10^{4} at 430 nm with optical path of 10 mm. By differential spectrophotometry a unknown soln. with 1×10^{-2}M conc as blank is measured with transmittance of 30.2%. Indicate by how many times the scale has been expanded ?

(*b*) (*i*) The 1H nmr spectrum of $[Ru(bipy)_3]^{2+}$ gives well resolved sharp signals; whereas the corresponding $[Ru(bipy)_3]^{3+}$ displays broad and down field signals. Justify.

(*ii*) Explain why the $CHCl_3$ solution of *trans*-$[Ru(bipy)_2(PPh_3)_2]^{3+}$ displays a broad EPR signal at 298 K; whereas the same at 77 K shows an axial spectrum with two distinct 'g' values.

(*c*) Deduce the structural formulae of the compounds which are consistent with the given data

(*i*) Molecular weight 146. IR (ν cm^{-1}) 3450, 1740, 1378(s), 1040
NMR (δ, ppm)

1.28	s	6H
2.48	s	2H
3.83	s	1H (Exchange by D_2O)
4.16	q	2H
4.28	t	3H

(*ii*) A compound $C_8H_{12}O_2$ shows principal IR (ν cm^{-1})1760 and 1380. NMR shows only a singlet at (δ ppm) 1.3.

(*d*) What is the role of shielding in PMR spectrum of Ethanol ? Explain with appropriate diagram.

2. Explain briefly the following observations :-

(*a*) In the extraction chrometography the stationary phase is an extractant.

(*b*) In gas chromatographic separations the compound must be voltile and thermally stable.

(*c*) Electrochromatographic separation is based upon the exploiranoy of difference in mobility of metallic ions.

(*d*) The sample of conc. sugar and common salt can be separated by exclusion chromatography.

3. (*a*) Point out clearly difference between the following techniques :

    (1) Fluoroscence and phosphorescence Spectroscopy

    (2) Raman Spectroscopy and nephelometry

    (3) Nephelometry and turbidimetry

    (4) Flame emission and plasma emissions specroscopy.

   (*b*) An unknown compound was measured by fluorimetry with standard one microgram per ml. of sample with fluoroscence intensity of 73 units. If the unknown sample of solution has a fluoroscence intensity of 62 units, what is the concentration of the unknown solution.

4. (*a*) Explain the significance of the each term in the following Nernst Equation :

$$E = E_0 - \frac{2.303RT}{nF} \log \frac{[A]_{red}}{[A]_{oxid}}$$

   Give an example to illustrate its used in the quantitive analysis ? What is difference between Saturated Calomel Electrode (SCE) and the ion selective electrode (ISE) ?

   (*b*) Calculate the concentration of Cadmium selective electrode with method of standard addition with following data. The volume of the unknown sample was 100 ml with potential of 370 mv. After addition of one ml of 1M cadmium the potential rose to 414 ma.

5. (*a*) Define briefly the following terms :

    (*i*) resonance fluorescence

    (*ii*) Stokes shift

    (*iii*) Dark current

    (*iv*) Relaxation of radiation.

(*b*) Point out the difference between the following terms in one or two sentences only :

(*i*) Colorimeter and Photometer

(*ii*) Monochromatics–Filter and Gratings

(*iii*) Phototube and photomultiplier tubes

(*iv*) standard addition and Internal standard methods.

6. Answer briefly the following questions ?

(*a*) Show how uranium (VI) and Thorium (IV) in sulphate media can be separated by anion exchange chromatography ?

(*b*) How lanthanide series of elements are seperated by cation exchange chromatography ? Explain principles only.

(*c*) What is the difference between conductometric and amperiometric titrations in principles and in applications ?

(*d*) Pinpoint the difference between differential scanning calorimetry and thermometric titrations ?

7. (*a*) Which are the two heavier transition elements (second/third transition series) known to have natural biological functions.

(*b*) State the products of the following reactions:

(*i*) $W(CO)_6 + PhLi \rightarrow$ product

(*ii*) $PdCl_2 + 2H_2C{=}CH(CH_3) \xrightarrow{OH^-}$ Product

(*c*) Draw the Fe_4S_4 cluster present in Ferredoxin. State the oxidation state of the Fe–centres and the ground spin state.

8. Account for the following :

(*a*) Which of the following compounds has the greatest affinity for water :

P_4O_{10}, Cl_2O_7, I_2O_5

(*b*) Addition of HNO_3 to concentrated H_2SO_4 results in the formation of NO_2^+ and NO_3^- ions.

(*c*) CO_2 is a discreate molecule, whereas SiO_2 forms extended network of Si–O single bonds.

(*d*) $B_{10}C_2H_{12}$ is isostructural an isoelectronic with $B_{12}H_{12}^{2-}$.

9. (*a*) Magnesium metal burns in air to give a white ash. When this material is dissolved in water, the odor of NH_3 develops. Suggest an explanation.

(*b*) Which would you expect to be more solube in water, LiI and KI and why ?

(*c*) A solution of $BiCl_3$ in aqueous HCl yields a white precipitate when diluted with pure water. Explain.

(*d*) The bond angle of Cl_2O is less than that in ClO_2. Explain.

10. (*a*) How many geometrical isomers are possible for the complex ion $[Pd\ (NH_3)\ (NH_2OH)\ (Py)\ (NO_2)]^+$.

(b) In the reaction $[FeBr_2(PPh_3)_4]$+ Br^- $[FeBr_3(PPh_3)_3]$+PPh_3, only one isomer of the poduct is formed . Explain the geometry of the starting complex, *cis* or *trans*.

(*c*) Draw the structures of the two optical isomers of $[Mn(bpy)Br_2Cl_2]^-$ (bpy=Z, Z'–bipyridine)

(*d*) Monomeric $Mn(CO)_6$ does not exist but dimerises to stable $Mn_2(CO)_{10}$. MOnomeric $V(CO)_6$ does not form and also cannot dimerise to a stable form. Explain.

11. (*a*) Using Valence Bond approach predict whether square planar Pt(II) complexes are high–spin or low–spin.

(*b*) Calculate the CFSE of a d^6 complex having $\Delta = 30000\ cm^{-1}$ and $P = 20000\ cm^{-1}$.

(*c*) Explain why crystal field theory is not applied to main group compounds.

(*d*) Explain why Pt(II) and Pd(II) form square–planar complexes more readily than Ni(II).

12. (*a*) Deduce the value of 'n' in $Mo(CO)_n$, $H_nCo(CO)_4$, $H_nFe(CO)_4$, $[H_nCr(CO)_5]^-$

(*b*) What would be the hybridisation states of 'n' in the linear and bent modes of metal–nitrosyl complexes.

(*c*) Explain why the Co–N bond distance in the dinitrogen complex $Co(Ph_3P)_3(N_2)H$, 1.8 A° is reasonably shorter than that in the $Co–NH_3$ bond, 1.95 A°.

(*d*) Draw the structure of $(\eta^1 cp)_2Hg$ and $(\eta^5 cp)_2Hg$. The three hydrogen resonances in the ratio 1 : 2 : 2 in ^1H NMR spectrum of $(\eta^1 cp)_2Hg$ changes to a single peak down to –70°C. Explain the change in spectral behaviour with the change in temperature.

13. (*a*) An octahedral nickel complex $[Ni(L)_3]^{2+}$ (L=neutral bidentate ligand) exhibits three transitions at 500 nm (ε = 30 $M^{-1}cm^{-1}$), 450 nm (ε = 55 $M^{-1}cm^{-1}$), and 400 nm (ε = 50 $M^{-1}cm^{-1}$).Explain the origin of these transitions using Orgel diagram.

(*b*) The complex $[Cu^{II}(L)_6]^{2+}$ (L = neutral mono–dentate ligand) exhibits two closely spaced d–d transitions at 495 nm (ε = 65 $M^{-1}cm^{-1}$) and 470 nm(ε = 70 $M^{-1}cm^{-1}$). Explain.

(*c*) A low–spin Fe(III) complex, [Fe(L)3]3+ (L = strongly π – acidic bidentate ligand) displays one strong transitions at 620 nm (ε = 12,500 $M^{-1}cm^{-1}$). Suggest the origin of the transition, MLCT or LMCT and why.

14. (*a*) Lanthanides do not form complexes with the π–bonding ligands such CO and CN^-. Explain.

(*b*) The absorption maxima of the lanthanides complexes do not vary depending on the nature of the ligands. Explain.

(*c*) Calculate the magnetic moment of the complexes involving Gd^{3+} and dy^{3+}.

(*d*) Diamagnetism is an induced phenomenon. Explain.

15. (*a*) One octahedral Co(II) complex exhibits magnetic moment $\mu = 2.45$ B.M. at 298 K. Explain one spin state behaviour of the complex.

(*b*) The paramagnetic $[Ni(A\ B)_3]^{2+}$ (A B unsymmetrical neutral bidentate ligand) tansforms to a diamagnetic complex on oxidation to $[Ni(A\ B)_3]^{4+}$. Suggest an explanation.

(*c*) The dinuclear complex low-spin$[(L)_2Fe^{III}(\mu{-}O)_2Fe^{III}\ (L)_2]^{2+}$ (L = neutral bidentatc ligand) shows magnetic moment $\mu = 0.92$ B.M. at 298 K and it reduces to 0.12 B.M. at 77 K. Explain.

(*d*) Calculate the magnetic moment of $[V(O)(acac)^2]$ considering the equation μ_{L+S}.

16. (*a*) Fe(II) in deoxyhemoglobin does not fit inside the porphyrin cavity, where as the same Fe(II) is placed well inside the cavity under oxyhemoglobin mode. Suggest the mechanism.

(*b*) Synthetic Fe(II) porphyrin readily oxidises to μ–oxo dimeric species where as the same does not happen even with the oxyhemoglobin. Suggest an explanation.

(*c*) Why are transition metals such as Mn, Fe, Co and Cu present in the redox based metallo–enzymes rather than metals such as Zn, Ga or Ca.

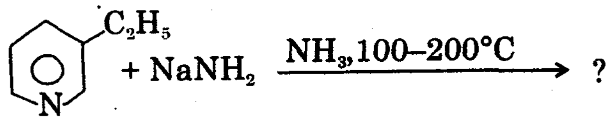
(d) Write the oxidation states of Mn which cycles in the redox reactions of photosystem–II.

17. (*a*) 3–Chlororcyclopropene shows two sets of equivalent protons. This on treatement with $SbCl_5$ yields a stable solid compound having formula $C_3H_3SbCl_6$ (1) which is soluble in solvents like nitromethane and acetonitrile, but insoluble in benzene. NMR spectrum of 1 shows three exactly equivalent protons. 3–Chlorocyclopropene reacts with $AgBF_4$ to give AgCl and a solution with an NMR spectrum identical to that of 1 . Treatment of 1 with chloride ion regenerates 3–chlorocyclopropene. Explain these reactions.

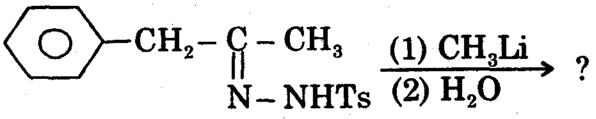
20. (*a*) Discuss the conformational analysis and resolvability of 1,2–Dimethylcyclohexane.

(*b*) Complete the following :-

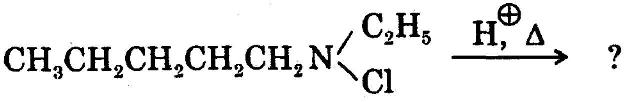
(*i*)



(*ii*)

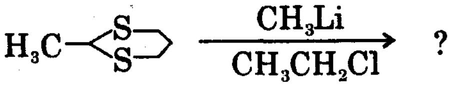


(*iii*)



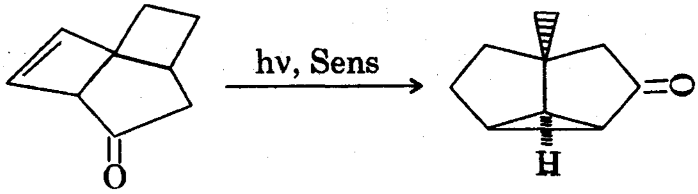
$$CH_3CH_2CH_2CH_2CH_2N\langle{}^{C_2H_5}_{Cl} \xrightarrow{H^{\oplus}, \Delta} ?$$

(*iv*)



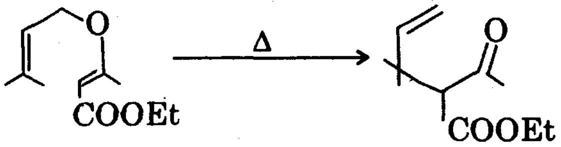
21. (*a*) (*i*) Explain the significance of ρ (rho) and σ (sigma) of Hammett equation.

(*ii*) Discuss the mechanism of the following :-

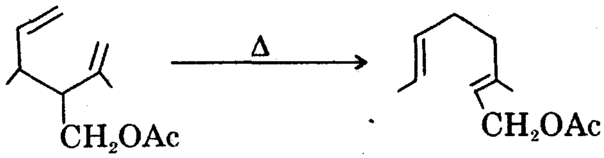


(*b*) The following steps are involved in the synthesis of Geraniol. Suggest the mechanism.

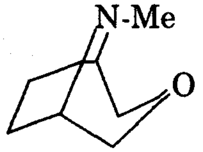
(*i*)

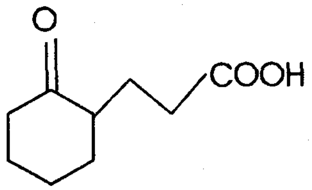


(*ii*)



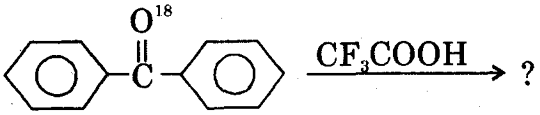
(*b*) Outline the synthesis of the following compounds

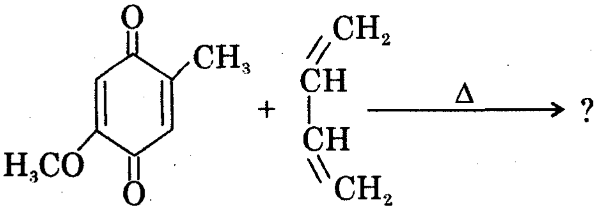
(*i*) 

(*ii*) 

18. (*a*) Based on ring current effect discuss the aromaticity of annulenes.

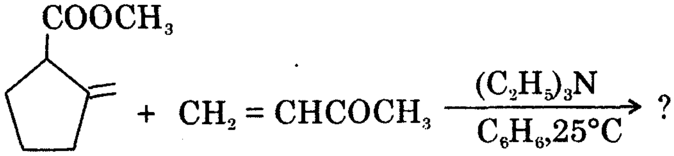
(*b*) Predict the products and suggest the mechanism of the following transformation.

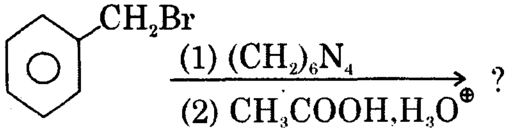
(*i*) 

(*ii*) 

19. (*a*) What is sharpless asymmetric epoxidation ? Illustrate with examples.

(*b*) Name the reactions, Predict the products and give the mechanism of the following :-

(*i*) 

(*ii*) 

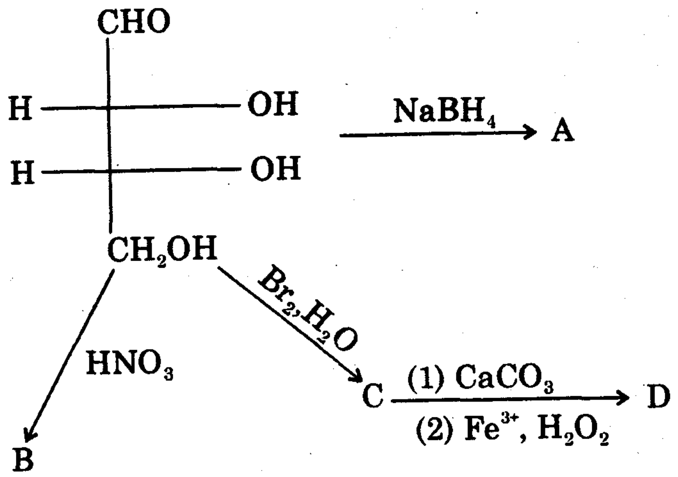
(*b*) Discuss the reactions of Quinoline with the following reagents.

(*i*) C_6H_5Li, Δ

(*ii*) HNO_3, H_2SO_4

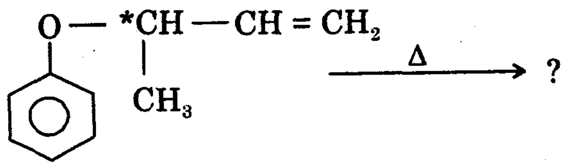
24. (*a*) Discuss the utility of Phase Transfer catalysts with special reference to Crown ethers.

(*b*) Draw the structure and discuss the stereochemistry of the Products A, B, C and D in the following :

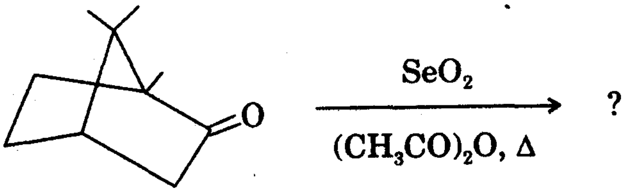


25. (*a*) Predict the products and suggest the mechanism of the following :-

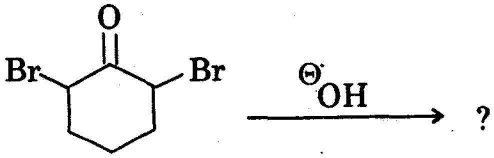
(*i*)



(*ii*)



(*iii*)



22. (*a*) Starting from 2,5–Hexanedione, how would you synthesise

(*i*) 2,5–Dimethyl Furan

(*ii*) 2,5–Dimethyl Pyrrole

(*iii*) 2,5–Dimethyl thiophene.

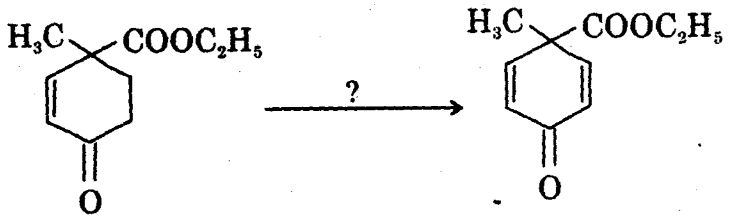
(*b*) Justify the following :-

(*i*) Pyridine is a stronger base than Pyrrole but a weaker base than aniline.

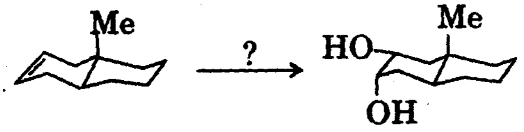
(*ii*) Bicyclo [2.2.2] octa 2,6–dione is less acidic than cyclohexadiane.

23. (*a*) Specify the appropriate reagents to bring about the following conversions.

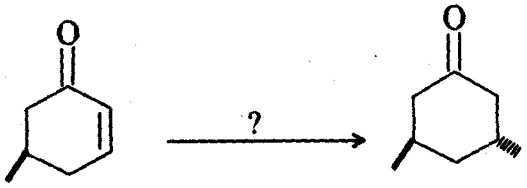
(*i*)



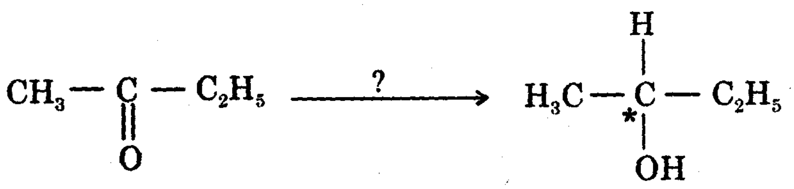
(*ii*)



(*iii*)

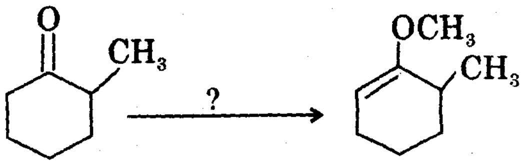


(*iv*)



$$CH_3-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow{?} H_3C-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{\overset{*}{C}}}-C_2H_5$$

(*v*)



27. (*a*) Show that expectation value of x in g.s. of Simple Harmonic Oscillator is zero.

(*b*) Assuming that π–electrons in butadiene are well described by particle in a 1–D box of length 10 a.u, show that the lowest energy transition occurs at $\frac{\pi^2}{40}$ a.u.

28. (*a*) Given that symmetry rules for vibrational transition n→n' is given by the non–zero criterion for the transition dipole integral.

$$\mu n'n = \int_{-\infty}^{\infty} \psi_{n'}(x) x \psi_n(x) dx$$

Where $\psi_n(x)$ and $\psi_{n'}(x)$ are SHO wave functions, show that the transition 0 → 1 is allowed but 0 → 2 is not.

(*b*) Show that $\left[p_x^2, x\right] = -2i\hbar p_x$

Show that $\left[p_x^2, x\right] = -2i\hbar p_x$

29. (*a*) Given that the rotational constant (B) for HCl = 10.59 cm^{-1}, calculate the spacing between rotational spectrum peaks for HCl.

(*b*) Show that the most population rotational level J_{max} is given by :

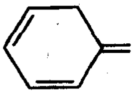
$$J_{max} = \left(\frac{kT}{2hCB}\right)^{1/2} - \frac{1}{2}$$

(*c*) Given that the character table for C_{2v} is :

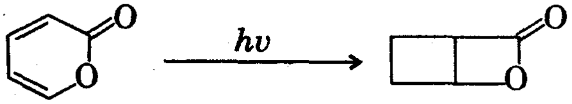
C_{2v}	E	C_2	σ_v^{XZ}	σ_v^{YZ}	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	
B_1	1	–1	1	–1	x
B_2	1	–1	–1	1	y

Show that transition between A_1 and B_1 type orbitals of H_2O is allowed and emitted radiation will be x–polarised.

(*b*) (*i*) The following isomer of toluene has been synthesised. Although much less stable than toluene it has a surprisingly long life. Explain.



(ii) Explain how α–pyrone undergoes photolytic ring closure as follows. Predict the stereochemistry of the product.



26. (*a*) Give the mass spectral fragmentation of :

(*i*) Ethyl phenylketone

(*ii*) Neopentane

(*b*) Give the structure which corresponds to the following spectral informations. Molecular formulae $C_{13}H_{18}O_2$.

IR (ν cm^{-1}) 3300–2500 (broad 1710, 1600,
1500, 1450, 1385, 1375, 1125, 1040)

NMR (δ ppm)	1.08	d	6H
	1.8	d	3H (J=7Hz)
	1.92	m	1H
	2.39	d	2H
	2.5	q	1H (J=7Hz)
	6.8	dd	2H
	7.5	dd	2H
	11.0	s	1H

Mass 206 163 161 57 45 43 (m/e)

35. (*a*) How is the anionic polymerization of styrene with potassium amide in liquid ammonia occuring ?

(*b*) What would be its kinetic of polymerization ?

(*c*) A soap ($C_{17}H_{35}COO_{Na}$) solution become a colloidal sol at the concentration of 1.2×10^{-3} M. On the average 2.4×10^{-13} colloidal particles are present in 1 mm^3. What is the average number of stearate ions in one colloidal particle (micelle)

36. (*a*) What is a cirtical mass ?

(*b*) When the nuclear reaction becomes supercritical ?

(*c*) Balance the following nuclear reaction :

$$^{232}_{90}\text{Th} + \_\_\_\_ \rightarrow {}^{240}_{96}\text{Cm} + 4\left({}^{1}_{0}n\right)$$

(*d*) A 2.0 g alloy sample was irriadated with 0.15 g standard iron having 2500 counts per second. After 3 days the sample gave 1000 counts per second. Calculate the % of iron in the alloy.

30. (*a*) Calculate the change in molar Gibbs Free Energy When an ideal gas is subjected to an isothermal compression from 1 bar to 2 bar at 298 K (RT=2.48KJ mol^{-1} at 298 K)

(*b*) . Calculate the change in internal energy ΔU of an ideal gas subjected to Carnot Cycle and show that it is zero since V is a state function.

31. (*a*) Calculate the Trasnlational Partition function for an ideal gas, confined to a cubic box of length a given that $\int\limits_0^{\infty} e^{-\alpha x^2} dx = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2}$

(*b*) What is the partition function for translational motion of a H–atom at 3000 K in a volume of 0.25 m^3. Interpret the significance of calculated partition function.

32. (*a*) Will Pb reduce Zn^{2+} ions to Zn when all concentrations are 1M ?

(*b*) Calculate the EMF of galvanic cell (using Nerst equation) at 25°C,

$Zn(s) \mid Zn^{2+}(1.00M) \mid\mid Ag^{+}(1.00M) \mid Ag(s)$

[Given $E°_{Zn} = -0.763V$ and $E°_{Ag} = +0.799V$]

(*c*) Give the cell reactions of Nickel–Cadmium battery.

33. (*a*) Show that molecules react on collosion, in which those colloiding molecules possess a certain minimum amount of energy which is effective.

(*b*) The rate constant of a reaction at 27°C and 37°C are $1.3 \times 10^{-3}\ s^{-1}$ and $2.6 \times 10^{-3} s^{-1}$, respectively. Determine the activation energy and frequency factor.

34. (*a*) How is the lowering of vapour pressure of a solution equal to the mole fraction of the non–volatile solute present in the solution ?

(*b*) Calculate the molar mass of a non–volatile solute if at 25°C, its solution containing 0.80 g per dm^3 has an 41.5 torr ($R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$)

Q. No. ....