III-33306

CHEMISTRY SCIENCE PAPER - III

Time Allowed : 2 1/2 Hours **Maximum Marks :** 200

Note :

i) Attempt Question No 1 and Fourteen other questions.

ii) Log table is enclosed.

1. Attempt any three of the following : [6]

(A) Deduce the structure of a compound based on the following data :

Molecular formula	:	$C_{12}H_{16}O$
I. R.	:	1710,1603,758, 688 cm^{-1}
M. S. (m/z)	:	176 (M^+), 119 (strong), 77, 43
P. M. R. (δ)	:	1.41 (6H,S), 1.95 (3H,S), 2.74 (2H, S), 7.23 (5H,S)

(B) Assign structure to the compound based on the following data : [6]

Molecular formula	:	$C_5H_8O_2$
I. R.	:	3300 - 2700 (broad), 1715, 1638 cm^{-1}
M. S.	:	100 (M^+), 55, 45, 41
P. M. R. ( )	:	2.52 (m, 20 mm), 5.15 (dd, J = 10 and 1.5 Hz, 5 mm) 5.25 (dd, J = 16 and 1.5 Hz, 5 mm), 5.86 (m, 5 mm), 11.50 (bs, 5 mm, exchangeble with D_2O)

(C) Cyclopentadienyl radical shows six lines in esr spectrum line in esr spectrum. Explain and comment on their intensities. [6]

(D) Explain following observation in Mossbauer spectra. [6]

Compound	d mm/s	DE_Q mm/S
i) $FeCl_2.6H_2O$	1.03	1.58
ii) $FeBr_2.6NH_3$	1.04	0.0

(E) Calculate the wavelength (in mm) corresponding to the lowest excitation in $(CH_3)_2N^+ = CH - (CH=CH_2) - N(CH_3)_2$ using the free-electron approximation model. (Given C - C & C - N bond lengths 1.4 A^o) [6]

(F) If the fundamental vibrational frequency of $35Cl_2$ is 564.9 cm^{-1}, what is its force constant (in Nm^{-1}) ?. [6]

Q.2 (A) Comment on the following observations.

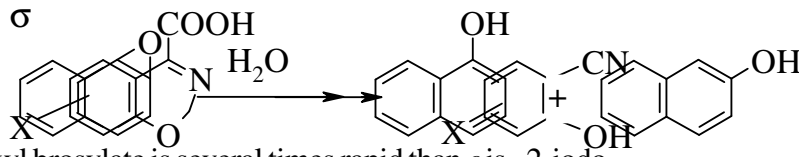
a) In the following decarboxylation reaction rho is 1.37 in H_2O but 2.40 in HMPA. [2]

b) σ M – oph = 0.25 but p – oph = - 0.03 [2]

c) The rho value for the alkaline hydrolysis of substituted methyl benzoates is 2.39 and the rate for unsubstituted ester is 2 x 10^{-4} mol^{-1} sec^{-1}. Evaluate rate for km – NO_2 and km – CH_3 esters. How much faster m – NO_2 ester will hydrolyse than m – CH_3 ester ? [3]

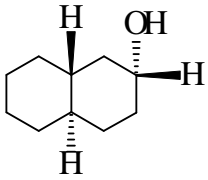
(B) Account for the following facts. [6]

a)

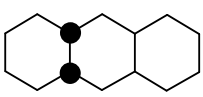


b) Solvoysis of *trans*-2-iodo cyclohexyl brosylate is several times rapid than *c* is –2-iodo cyclohexyl brosylate.

Q.3. (A) Draw the conformational structure of the equatorial isomer of trans-2-decalol and assign R/S configuration to the chiral centres. [4]

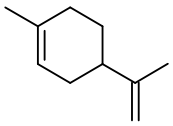


(B) Draw the conformational structures of *cis-anti-cis* perhydroanthracene and state why is it optically inactive. [3]



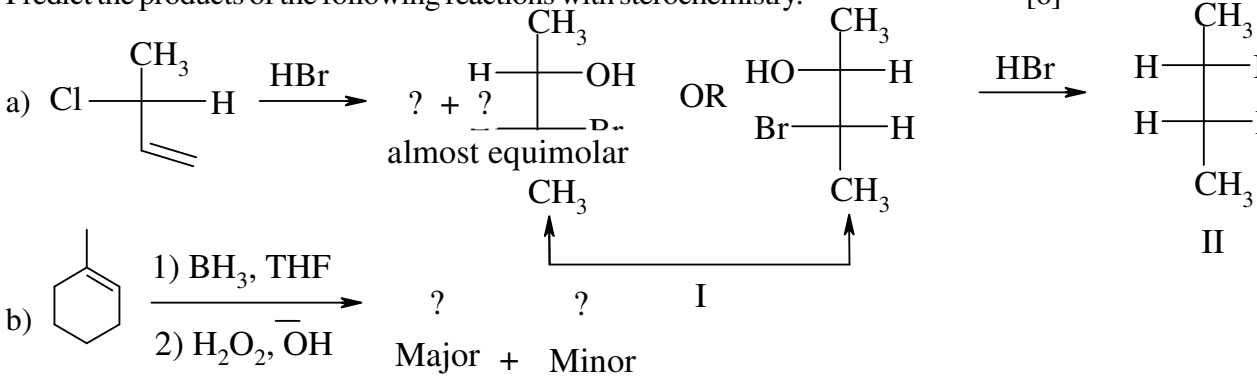
(C) Treatment of (±) – erythro-3-bromo-2-butanol I with HBr gave only the meso-2, 3 – dibromobutane II and no trace of the dI –2, 3-dibromobutane was obtained. Explain with mechanism & sterochemistry. [6]

Q.4. (A) Limonene X is a natural odour principle found in most citrus fruits. Plan a synthesis of Limonene starting from 2-methyl-1, 3-butadiene using Diels Alder reaction as a key step. [7]



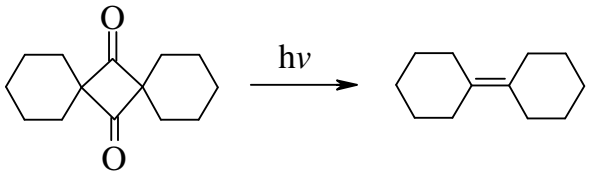
X

(B) Predict the products of the following reactions with sterochemistry. [6]

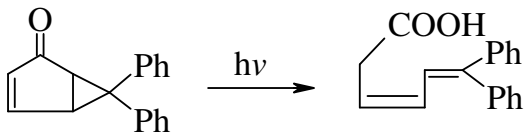


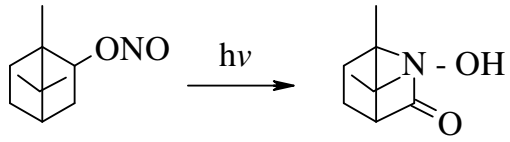
Q.5. Indicate the type of reaction and mechanism involved in each step of the following transformations [13]

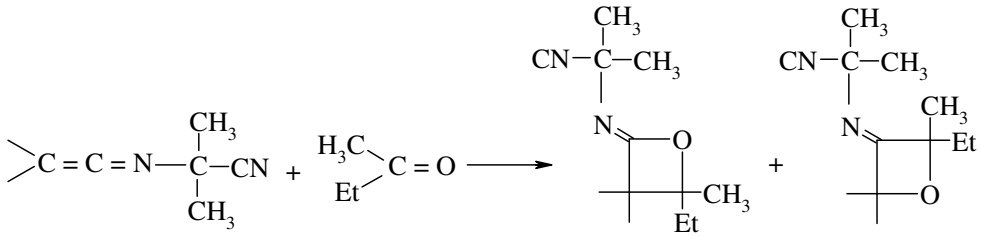
(A)

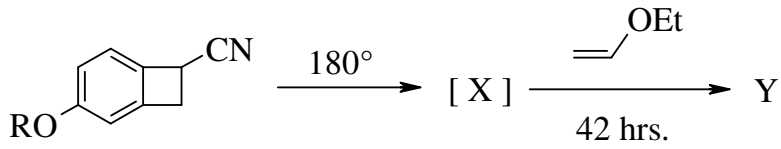


(B)



(C) 

(D) 

Q.6. 

[13]

(A) Write the structure of X

(B) What is the name of the first reaction and the process involved.

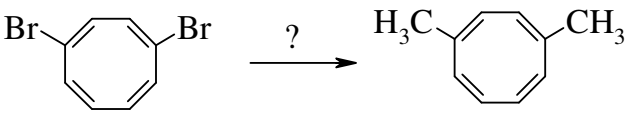
(C) Identify the second reaction.

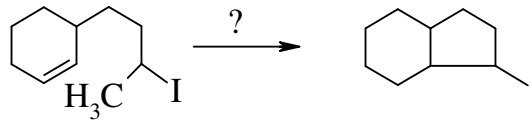
(D) Whether the second reaction is a normal electron demand or inverse electron demand reaction and why ?

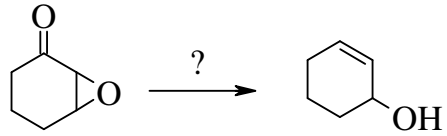
(E) How many isomers are possible for product Y ?

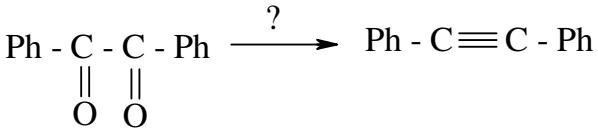
(F) What is the relationship between the isomers ?

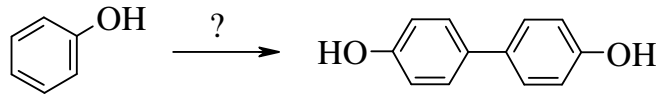
Q.7. (A) Indicate appropriate reagents for the following. [6]

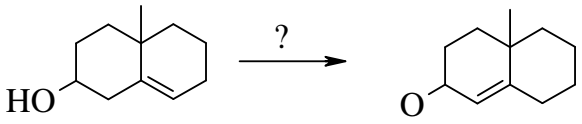
(i) 

(ii) 

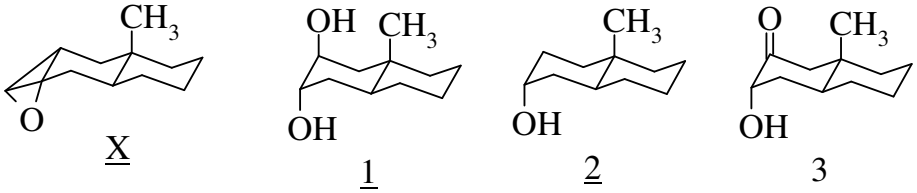
(iii) 

(iv) 

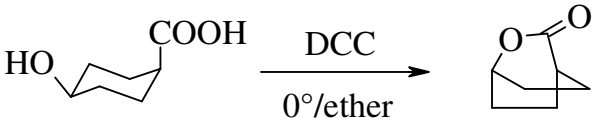
(v) 

(iv) 

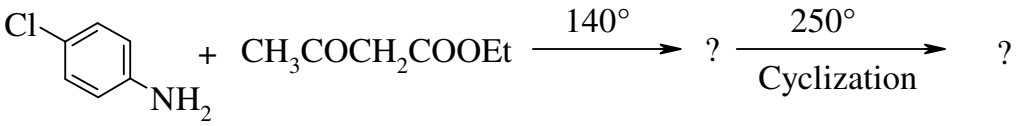
(B) Write reagents to convert 'X' into 1,2 and 3 separately. [4]

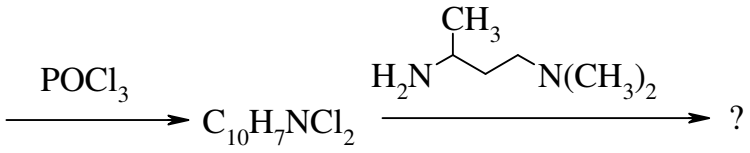


(C) The following lactonigation is very facile explain with mechanism. [3]



Q.8. (A) Complete the following scheme. [6]

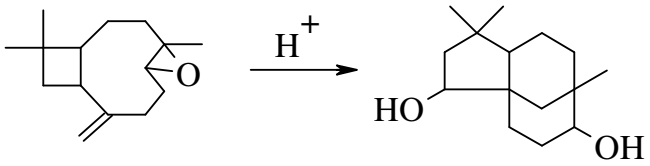




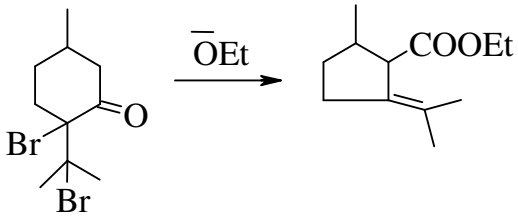
(B) Treatment of 4-bromopyridine with $NaNH_2/liqNH_3$ gives two isomeric products $C_5H_6N_2$ but reaction with NAOMe gives a single product C_6H_7ON. What are the products ? Why is there a difference ? [7]

Q.9. Propose the mechanisms for the following conversions and name the reaction involved. [3]

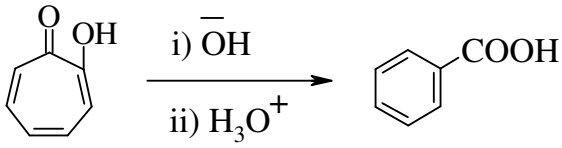
(A)



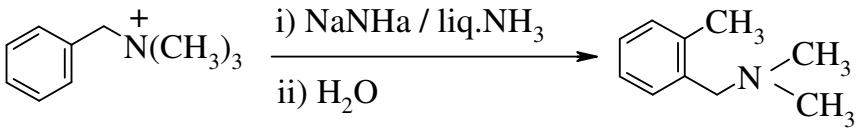
(B)



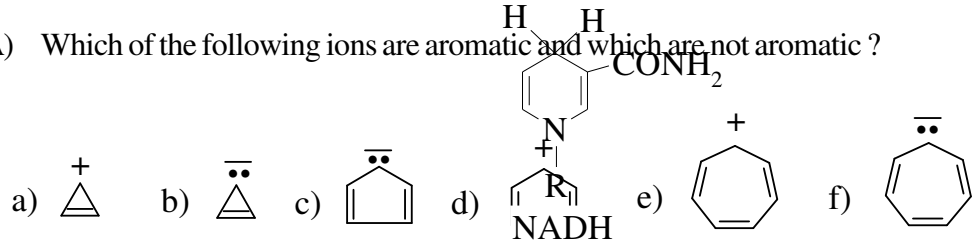
(C)



(D)



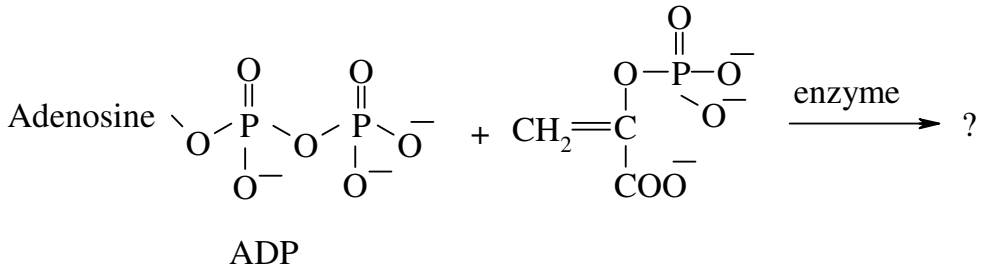
Q.10. (A) Which of the following ions are aromatic and which are not aromatic ? [3]



(B) Why pyridine is a stronger base than pyrrole ? [3]

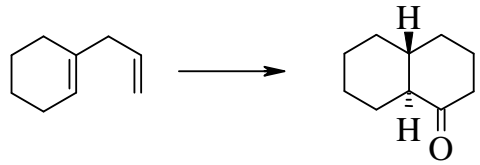
(C) NADH is nature's reducing agent. Explain the reduction of pyruvic acid by NADH. [3]

(D) What is the role of phosphoenolpyruvate in the conversion of ADP to ATP ? [4]

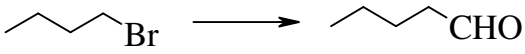


Q.11. (A) How the following can be effected ? Identify the steps involved. [10]

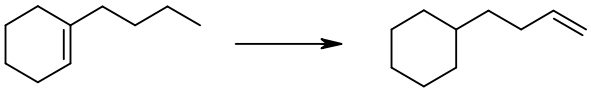
a)



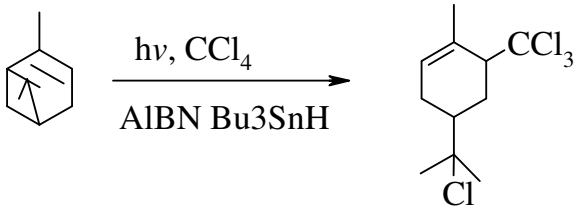
b)



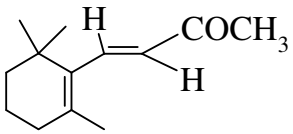
c)



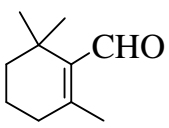
(B) Explain the following reaction. [3]



Q.12. Study the following structure and answer the following question.



(A) How would you prepare it from ? [2]



(B) Calculate the λ_{max} [4]

(C) Comment on the coupling constant of olefinic protons and the stereochemistry of the double bond. [3]

(D) What will be the product of ozonolysis under reductive conditions ? [2]

(E) How can it be converted into ? [2]

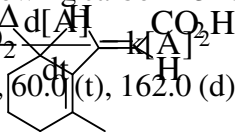
Q.13. (A) Derive the structure of a compound based on the following data : [8]

Molecular formula	:	$C_{11} H_{11} N$
U. V.	:	272 nm ($\in$ '18000)
I. R.	:	2212, 1604, 845, 814 cm^{-1}
P. M. R. (d)	:	1.03 (3H, t, J = 7Hz), 2.60 (2H, q, J = 7 Hz), 5.60 (1H, d, J = 16) 7.21 (2H, d, J = 8.5 Hz), 7.43 (2H, d, J = 8.5 Hz), 7.72 (1H,d, J = 16 Hz)

(B) Deduce the structure based on the following carbon-13 N. M. R. data [5]

Molecular formula	:	$C_3 H_6 O_2$
Carbon -13 (d)	:	13.0 (q), 60.0 (t), 162.0 (d)

$$-\frac{d[A]}{dt} = k[A]^2$$



14. (A) Match the entries in column A from those given below. [7]

	Column A	Column B
i)	Second order reactions	……..
ii)	entropy	……..
iii)	Joule-Thompson experiment	……..
iv)	Specific heats of solids	……..
v)	Troutons rule	……..
vi)	Patterson synthesis	……..
vii)	Raman active vibrations	……..

Column B

i)	Huckel	ii) H_{vap}/T
iii)	Electron diffraction	iv) Polarizability
v)	Adiabatic demagnetization	vi) Lindemann
vii)		viii) Debye
ix)	F = C – P + 2	x) S = k *ln* W

B) Write down the transformation matrices for the following symmetry operations : C_2, E, σ_v and $_v^1$. Explain with a suitable diagram. [6]

Q.15. (A) Evaluate the commutator [$_x$, $_z$]. State the significance of this result. [7]

(B) In case of particle in 3-D box how many energy levels lie below the state having energy $27h^2/8\ ma^2$ (a defines the box length). Explain your answer. [6]

16. (A) What are the hybrid orbitals ? Explain the mutual orientation of these orbitals in sp, sp^2 and sp^3 hybrid orbitals. Sketch quantitatively these orbitals. Give one example in each case. [8]

(B) Using Huckel theory obtain the MO energies for ethylene. [8]

Q.17. (A) Set up the differential rate law for each of the following types of reversible reactions : [6]

i) First order opposed by second order.

ii) First order opposed by first order.

iii) Second order opposed by second order.

$$\left(T_1^2 - 3T_1 + 2\right) x^2$$

(B) Sketch the radial wave function, its square and the radial probability distributions for the 4p and 4d hydrogenic orbitals. Comments on the number of radial nodes. [7]

Q.18. (A) If the transnational operator is given as $_a f(x) = f(x+a)$ [6]

Is $_a$ a linear operator ?

Evaluate

(B) Prove that eigenvalues of a hermitian operator are real. [7]

Q.19. (A) Show that in the mathematical equation of Boltzmann distribution law ($Ni = No \bullet e^{-tb}$), the parameter p is equal to 1/kT. [6]

(B) Write down the expression for transnational partition function for a monoatomic gas. Calculate the transnational partition function for a hydrogen molecule ($^1H_2$) confined to a 100 cm^3 vessel at 25^0c. [7]

Q.20. (A) The ΔH_{vap} of CH_4 is 9.27 kJ/mole. Calculate its boiling point. [6]

(B) Show that :

i)

ii)

Q.21. (A) The NO molecule can exist in two different possible structures and exists as dimer at absolute zero. What will be its entropy at absolute zero. [6]

(B) Estimate the percentage of ionic character of the HCl molecule. The dipole moment of HCl is 1.08D and the equilibrium bond length is 127.5 pm (electronic charge is 1.602 x 10^{-19}C). [7]

Q.22. (A) The chloride can be oxidised to chlorine in an acid solution by permangante ion : [6]

$2MnO_4^- + 10\ Cl^- + 16H^+ \quad 2\ Mn^{2+} + 5Cl_2 + 8H_2O$

Show that this reaction is spontaneous. Calculate DG^0 and K for this reaction. The half-reactions are given :

$Cl_2 + 2e \quad 2Cl^- \qquad E^0 = 1.359$ V.

$MnO_4^- + 8H^+ + 5e \quad Mn^{2+} + 4H_2O \qquad E^0 = 1.51$ V.

(B) Draw and explain Pourbeaux for corrosion. [7]

Q.23. (A) Differentiate between adsorption and absorption. What do you mean by "sorption" ? [6]

(B) If a gas adsorbed in monolayer the surface of a solid, then show that the symbols have their usual significance. How does it lead to Freundlich isotherm ? [7]

Q.24. (A) From the following reaction sequences show that the Onsager reciprocal relation $L_{12} = L_{21}$ is obeyed. [7]

(B) Obtain an expression for entropy change when simultaneous flow of heat and diffusion occurs irreversibly over a body. [6]

Q.25. (A) What is meant by Q value of nuclear reactions ? How is it calculated ? Calculate the Q value for the reaction : [7]

$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{98}_{42}Mo + ^{136}_{54}Xe$

(given : 1amu = 931.5 MeV, Exact masses of neutron, uranium, molybdnium and xenon are 1.009, 235.044, 97.905 and 135.917 respectively)

(B) Explain why polymeric materials have more than one molecular weight, while non-polymeric materials show only one molecular weight. Distinguish molecular weights of a polymer and explain the use of osmotic pressure method for determination of virial coefficient and molecular weight. [6]

Q.26. (A) Calculate r^+/r^- for a cubic site. [6]

(B) Why do alkali metal halides, generally form schottky defect ? [4]

(C) Show diagrammatically that in an HCP arrangement of atoms, the coordination number of an atom is 12. [3]

Q.27. (A) Explain why NaO_2, KO_2, RbO_2 and CsO_2 are deeply coloured [6]

(B) What are Nido-Boranes and Arachno-Boranes ? Give an example for each case. [4]

(C) Describe Graphite –Potassium intercalation reaction. Why Graphite-Sodium reactions are not known ? [3]

Q.28. (A) Give reasons for the products obtained in the following hydrolysis reactions - [5]

$NCl_3 + 4H_2O \rightarrow NH_4OH + 3HOCl$

$PCl_3 + 3H_2O \quad H_3PO_3 + 3HCl$

$AsCl_3 + 3H_2O \quad H_3ASO_3 + 3HCl$

$SbCl_3 + H_2O \quad SbO^+ + 3Cl^- + 2H^+$

$BiCl_3 + H_2O \quad BiO^+ + 3Cl^- + 2H^+$

(B) Explain why PCl_3 on heating gives PCl_3 and Cl_2. [4]

(C) Describe the structures of SO^{2-}_4 and $S_2O^{2-}_3$ [4]

Q.29. (A) Describe structure and bonding of I_2O_5 and indicate its importance in the reaction $I_2O_5 + 5CO \quad I_2 + 5CO_2$. [6]

(B) Draw structures of the following molecules showing the position of lone pair of electrons
i) XeO_2F_2
ii) $XeOF_4$ [4]

(C) Explain structure of I^-_3 ion. [3]

Q.30. (A) Write the formula of the mononuclear carbonyls formed by V, Cr, Fe and Ni. Which of these satisfy the noble gas formalism. [8]

(B) $[Os_3(CO)_{12}]$ does not show any infrared absorption below 2000 cm^{-1} while $[Fe_2(CO)_9]$ exhibits infrared bands at 1840, 2020 and 2090 cm^{-1}. Based in this, predict the possible structures of both the complexes. [5]

Q.31. (A) Explain with special reference to Ni^{2+} complexes how increasing tetragonal distortion in octahedral geometry results in square. Illustrate your answer with suitable energy diagram. [5]

(B) If a complexing metal ion of the first transition series has d^n configuration, for what values of n, can the , magnetic properties alone distinguish strong and weak field ligand complexes in octahedral coordination ? [4]

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(C) Explain different types of magnetic behaviours with the help of magnetic susceptibility-temperatures plots. [4]

Q.32. (A) Given that the 10Dq values for $[Ni(bipy)_3]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ are 12,650 cm^{-1} and 10,800 cm^{-1} respectively, predict the values of 10 Dq for $[Ni(bipy)_2(NH_3)_2]^{2+}$ and $[Ni(Bipy)(NH_3)_4]^{2+}$ using the rule of average environment proposed by J regnson. [5]

(B) Name the different types of electronic transitions probable for transition metal complexes. How would you differentiate between them ? [5]

(C) Explain giving reason why a solution of potassium dichromate is orange in colour. [3]

Q.33. (A) Classify the following complexes into labile and inert giving reasons :
$[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$ (highspin), $[Cr(CN)_6]^{4-}$. [4]

(B) Electron transfer between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ is much faster than between $[CO(NH_3)_6]^{3+}$ and $[CO(NH_3)_6]^{2+}$. Explain. [3]

(C) Work out ground state spectroscopic term symbols for V^{4+}, Cr^{3+}, pr^{3+}.
At. No. : V = 23, Cr = 24, Pr = 59. [6]

Q.34. (A) Explain the following observations of Magnetic Moments for lanthanide compounds containing following ions. [6]

M^{3+}	μ_{expt} (B.M.)
i) Nd^{3+}	3.5 – 3.6
ii) Er^{3+}	9.4 – 9.6
iii) Pr^{3+}	3.4 – 3.6

Given At. No. Nd = 60, Er = 68, Pr = 59

(B) Write briefly on electronic spectral behaviour of the lanthanide and actinide complexes. How does this behaviour from that of transition metal complexes ? [7]

Q.35. (A) Define following terms in chromatography : [6]

i) WCOT and SCOT columns

ii) Gel filtration

(B) Explain following relation in size exclusion chromatography. [3]

$V = V_m + K. V_s$.

Q.36. (A) Enlist types of interferences in AAS and discuss any one. [4]

(B) Define : DTA and DSC [4]

(C) A TG plot of 2.89 mg of $MgSO_4.7H_2O$ shows single step at onset temperature ~ 378 K corresponding to formation of $MgSO_4.H_2O$. The mass loss in the step was 0.59mg. Determine percentage of $MgSO_4.7H_2O$ in the sample.
Given At. Wt. of : Mg = 24.312, S = 32.064, O = 15.999, H = 1.008. [5]

Q.37 (A) Match the entries in column A from those given below in column B [5]

	Column A	Column B
i)	Blue copper	……..……..
ii)	Hemerythrin	……..……..
iii)	Chlorophyll	……..……..
iv)	Cobalamin	……..……..
v)	Nitrogenase	……..……..

Entries for Column B :

i) photoredox
ii) electron carrier
iii) Oxygen carrier
iv) Molybdenum
v) liver extract

(B) What are the functions of hemoglobin and myoglobin ? What are the similarities and differences in their structures ? [8]