Chemical Sciences Paper II



(b) Sketch the ${}^{31}P$ NMR spectral pattern for the following compound [consider only ${}^{2}J(PP)$].

CI	
	63
(c) Sketch all isomers of $PF_3(CH_3)_2$ assuming a trigonal bipyramidal	· · · /
geometry in each case.	(6)
4. (a) What is the origin of the blue colour in Prussian Blue? Comment on	4.0
the effect of (i) oxidant and (ii) reductant on its colour.	
	(/)
(b) Give an example of a diamagnetic transition metal hydride complex.	V.
How is the presence of metal bound hydride detected by	
spectroscopic methods.	(6)
THF, H ₂	(0)
(c) Nu($\Gamma \Gamma \Gamma_{3/3}$ \longrightarrow A Draw the structure of A above, showing the step schemistry	
Draw the structure of A above, showing the stereochemistry.	(2)
5. (a) The complex ion $[Co(tren)NH_3Cl]^{2+}$ (tren = N(CH ₂ CH ₂ NH ₂) ₃) exists	as
red and purple isomers. Draw the structures of these two forms.	(A)
	(4)
(b) Red isomer undergoes hydrolysis much more rapidly compared to	
the purple one Explain.	$\langle 2 \rangle$
(c) Match the items in Column I with those in Column II	(3)
(c) Watch the rents in column 1 with those in column it.	
Column I Column II	
A. Siderophores 1. Co	
B. Chlorophyll 2. Fe	
C. Superoxide dismutase 3. Mg	
D. Vitamin B_{12} 4. Cu-Zn	
(a) Sketch the structure of the his(dimethylglyoximato)nickel(II) compl	(8) xe
used in the gravimetric estimation of nickel(II). Why is a large exces	s of
dimethyglyoxime solution avoided in this estimation?	-
	(7)
(b) Two isomers of $[PtCl_2(PEt_3)_2]$ have ${}^{1}J({}^{195}Pt-P)$ values of 3500 Hz an	d
2400 Hz respectively. Assign the coupling constants to the isomers,	
giving reason.	

(4)

(5)

(c) $^{23}_{11}$ Na is a stable nucleus. Predict which of the following unstable nuclei decay by β^{-} or β^{+} emission.

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(i) {}^{23}_{10}Ne (ii) {}^{23}_{12}Mg (iii) {}^{22}_{11}Na (iv) {}^{24}_{11}Na
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- 7. (a) Write equations for reduction of oxygen at dropping mercury electrode, when the medium is alkaline.
 - (b) Sketch the curve for amperometric titration of $0.01M \text{ Pb}(\text{NO}_3)_2$ with 0.05 M K₂Cr₂O₇ at -1.0V (vs SCE), the potential at which both the species are electroactive.
 - (c) Match items in column I with those of II.

. Derivative Thermogravimetry
2. Differential Scanning Calorimetry
3. Quanturi yield
-
4. Migration current
5. Diffusion current
6. Mercury
7. Graphite furnace

- 8. (a) Write equations for the preparation of:
 - (i) S_4N_4 from SCl₂(liq.)
 - P_4S_{10} from white phosphorus

(b) Sketch the structures of S_4N_4 and P_4S_{10}

- (4)
- (c) A one-electron paramagnetic copper complex can have two charge distributions:-

 $Cu^{II}-L$ or $Cu^{I}-L^{\bullet\oplus}$ (L= organic ligand)

How they can be distinguished by ESR spectroscopy?

(7)

- 9. (a) Draw generally accepted structure of active site of the enzyme involved in nitrogen fixation. Indicate the site on which nitrogen first binds.
 - (b) Bent metallocenes have general formulation $[(\eta^5-C_5H_5)_2ML_X]$. Write two examples choosing appropriate 'M', having different values of 'x'.
 - (c) Examples of carbonylate anions are many more than those of metal carbonyl cations. Explain.
- (a) KMnO₄ shows an intense pink colour, while KReO₄ is colourless. Explain.
 - (b) Copper(I) iodide is a stable species, while coppe(II) iodide does not exist. Explain.
 - (c) H^+ is a hard acid while H^- is a soft base. Explain,
- 11. (a) Identify $\mathbf{A} \mathbf{D}$ in the following catalytic cycle with their structures



(6)

(4)

(6)



(b) Draw the molecular structures of the following compounds in solid state

(i)
$$Ti(\eta^{1}-Cp)_{2}(\eta^{5}-Cp)_{2}$$
 (ii) $U(\eta^{5}-Cp)_{4}$ (iii) $Sm(\eta^{5}-Cp^{*})_{3}$ (7)

- 12. (a) What property/properties of lanthanide β-diketonate complex make(s) them useful as shift reagents in NMR spectroscopy?
 - (b) Write the products in the following reactions.

(i)
$$I_2O_5 \xrightarrow{CO} \to$$

i)
$$\operatorname{Cl}_2 \xrightarrow{\operatorname{ngo}} \rightarrow$$

(iii) NaClO₃
$$\xrightarrow{SO_2 + H_2SO_4}$$

iv)
$$F_2 \xrightarrow{2\% \text{ NaOH Solution}} \rightarrow$$

(8)

(3)

- (c) ¹⁰B used in nuclear reactors participates in two reactions. One reaction yields ⁷Li and another product X. The other reaction yields ³T and X. Identify X and write two balanced nuclear reactions.
- 13. (a) For the complexation reaction

 $[\operatorname{Ni}(\operatorname{en})_{2}(\operatorname{H}_{2}\operatorname{O})_{2}]^{2^{+}}(\operatorname{aq}) + \operatorname{tren}(\operatorname{aq}) \rightarrow [\operatorname{Ni}(\operatorname{tren})(\operatorname{H}_{2}\operatorname{O})_{2}]^{2^{+}}(\operatorname{aq}) + 2\operatorname{en}(\operatorname{aq})$ (A) the log β value is 1.88. Explain this value giving structure of A. [tren = N(CH_{2}CH_{2}NH_{2})_{3}]

- (b) What change in the position of iron in hemoglobin occurs upon binding to oxygen and why?
- (c) Identify isolobal pairs from the following CH₃, CH₂, CH, Cr(CO)₄, Mn(CO)₅, and Co(CO)₅
- 14. a) The spacing between the first and second lines in the rotational spectrum of a diatomic molecule with an equilibrium bond length of 1 Å is 40 cm⁻¹. The spacing between the 9th and 10th lines is 36 cm⁻¹. Calculate the extension of the bond due to the centrifugal distortion.

(7)

(8)

(6)

(4)

b) Calculate the vibrational quantum number at the dissociation limit for a diatomic molecule (given the anharmonicity constant as 0.05).

15. a) The character table of the point group D_3 is given below:

	- 1 - A					
-	6 6	D_3	VE.	2C ₃	3C ₂	
10.		A ₁	1	1	1	
a		A ₂	1	1	-1	z
	11	Е	2	-1	0	(x,y)
	,					

Show that the row A_2 is orthogonal to the row E.

(4)

b) Given the reducible representation, Γ , in D₃

$$\begin{array}{c|cccc} E & 2C_3 & 3C_2 \\ \hline \Gamma & 7 & 1 & 1 \end{array}$$

Determine its irreducible components.

- c) Use the above character table to determine whether the $A_1 \rightarrow A_2$ transition is allowed when the change in transition moment is (i) along z axis and (ii) in the x-y plane.
- 16. a) Show that all Bragg reflections of a primitive cubic crystal have the same intensity.
 - b) Plot the Fermi factor f(E) versus energy E, for a free electron metal at T = 0 K and T > 0 K.
 - c) The temperature variation of the high-temperature magnetic susceptibility, χ , of three solids is shown below. Identify the ferromagnet, paramagnet and antiferromagnet.



17. a) For a particle in a one-dimensional (x) box of length *a*, where the potential is given by

$$V(\mathbf{x}) = \infty \qquad \mathbf{x} < 0, \mathbf{x} > a$$
$$V(\mathbf{x}) = 0 \qquad 0 \le \mathbf{x} \le a$$

write the vavefunctions (without derivation) for all states for the full region of x. State if the wavefunctions are even or odd (*i.e.* have parity symmetry). State the boundary conditions involved in the derivation.

(4+1+3)

(7)

(4)

b) Discuss the parity of the wavefunctions if, in the above problem, the origin is shifted to the centre of the box, *i.e.* the potential V(x) is

$$V(x) = \infty$$
 $x < -a/2, x > a/2$
 $V(x) = 0$ $-a/2 \le x \le a/2$

Write the wavefunctions in this case.

(7)

- 18. a) Find the inverse of the matrix $\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$
- b) How do the states ψ , ψ^* , $-i\psi$, and $e^{i\alpha}\psi$ differ with respect to observable properties and why?
- 19. a) Show that $\langle x \rangle = 0$ for systems that respect parity as a constant of motion.

b) Evaluate the commutator $[L_x^2, L_z]$

20. a) Two variables x_i and y_i are related by $y_i = 3 - 2x_i$. Show that the covariance of x and y, defined by $c(x, y) = \langle xy \rangle - \langle x \rangle \langle y \rangle$ is equal to $-2\Delta x^2$, where $\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2$.

- b) For a polydisperse polymer solution, use basic definitions to show that $\langle M_w \rangle = \langle M_n^2 \rangle / \langle M_n \rangle$.
- 21. a) Calculate the mean ionic activity coefficient of 0.01 mol L⁻¹ NaCl aqueous solution at 298 K (A = 0.509 for an aqueous solution at 298 K).
 (8)
 - b) Write the cell reactions and predict whether it is spontaneous or non-spontaneous in a cell at 298 K.
 Cd(s)|Cd²⁺(aq)|| Fe²⁺(aq)|Fe(s)

Given:
$$E^{0}(Cd^{2+}/Cd) = -0.403 V$$
 and $E^{0}(Fe^{2+}/Fe) = -0.447 V$

- 22. a) For a second order reaction $2A \rightarrow P$, show that $t_{1/2} \propto 1/[A]_0$ where $t_{1/2}$ is the half-life and $[A]_0$ is the initial concentration.
 - (10)

(7)

(8)

(10)

(5)

b) The equilibrium constant (K) for the elementary reaction at 1000 K $C_2H_6(g) \longrightarrow 2 \text{ CH}_3(g)$ is $1.30 \times 10^{-13} \text{ mol } \text{L}^{-1}$ and the rate constant for the forward reaction (k₁) is $1.57 \times 10^{-3} \text{ s}^{-1}$. Write the rate law and calculate the rate constant for the reverse reaction (k₁)

(5)

- 23. a) 3.64 g of compound A (molar mass 150) is dissolved in 180 g of benzene and the vapour pressure of this solution is 756 torr at the boiling point of benzene. Calculate the molar mass of A in benzene and explain the discrepancy, if any [assume dilute solution].
- b) First two quantum states of an atom A (${}^{3}P_{0}$ and ${}^{3}P_{1}$) are separated by 300 cm⁻¹. Calculate the electronic partition function at 1000 K for this system (h/1000k_b = 4.8×10^{-14} s).
- 24. a) Calculate the entropy of mixing and Gibbs free energy of mixing of 5 moles of component A and 5 moles of component B at 27 °C.
 - b) Show that, if an engine takes up heat Q from a sink at a temperature T_2 and gives to a source at a temperature T_1 without any work, the process would violate the principle $\Delta S(\text{universe}) \ge 0$.

25. a) During an adiabatic reversible expansion $(a \rightarrow b)$, 1 mole of a monatomic ideal gas undergoes a decrease of temperature from 400 K to 100 K. If the initial volume is 32.8 L, calculate the final volume.

reversible expansion $(a \rightarrow c)$ and (ii) an isochoric reversible process $(c \rightarrow b)$. Calculate the entropy change in each process and the total entropy change in going from $a \rightarrow b$. (5+5+1)

b) Transformation $a \rightarrow b$ can also be achieved by undergoing (i) an isothermal

(a) Draw a correlation diagram for **disrotatory** opening of a cyclobutene to buta-13-diene. Predict the outcome of the reaction in the ground state.

(10)

(5)

(8)

(5)

(4)

(b) Predict the products **A** and **B** in the following reactions, and suggest mechanism of their formation.

 $[A] \stackrel{\Delta}{\longleftarrow} \stackrel{hv}{\longleftarrow} [B]$

27 (a) Predict the products **A** and **B** (with correct stereochemistry) in the following reaction, and suggest a mechanism of formation of **B**.

(6)

$$\bigcup_{OAc}^{O} + \bigcup_{A} \xrightarrow{hv} [A] \xrightarrow{aq. KOH} [B]$$

(b)

Triplet sensitized irradiation of compound **C** gives **D**. Suggest a mechanism.



(c) Suggest a plausible mechanism for the following transformation



28 (a) In the following transformation, predict the structures (with appropriate stereochemistry) of compounds A and B.

(6)

(6)

Me_____CHO ____MeMgBr _____[A] ____Nat ____[B]

- (b) Explain the origin of ster oselectivity in the formation of **A** with Cram chelate or Felkin-Anh model. (4)
- (c) Predict the absolute configuration of the newly formed stereocentre and state whether the compound **B** will be optically active or not.
 - (5)
- 29 (a) Write the structures of the compounds **A-C** and the reagent **D** in the reaction sequence given below.

(10)

30 (a) The k_H/k_D of base catalysed elimination reaction given below in H_2O and D_2O was found to be 0.13. Write suitable mechanism consistent with this observation.



32 (a) Write the structure of the compounds **A** and **C**, and suggest suitable mechanism for their conversion to the products **B** and **D**, respectively.



(b) Identify the compound **E** and suggest a suitable mechanism for its conversion to compound **F**.

(5)



