101

Chemistry

TIME : **3** HOURS

MAXIMUM MARKS : **300**

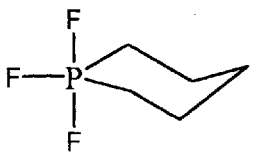
INSTRUCTIONS :

1. *All questions are **compulsory**.*
2. *Question Paper may be divided into **4 (four)** Sections from **Section-A** to **Section-D** and carry marks as under :*
   - **a.** ***Section - A** - Total **3** Questions having **two** parts, i.e. **(a) and (b)** each questions carries **12** marks × 3 Questions = Total **36** Marks.*
   - **b.** ***Section - B** - Total **3** Questions having **two** parts, i.e. **(a) and (b)** each questions carries **20** marks × 3 Questions = Total **60** Marks.*
   - **c.** ***Section - C** - Total **3** Questions having **two** parts, i.e. **(a) and (b)** each questions carries **28** marks × 3 Questions = Total **84** Marks.*
   - **d.** ***Section - D** - Total **3** Questions having **two** parts, i.e. **(a) and (b)** each questions carries **40** marks × 3 Questions = Total **120** Marks.*

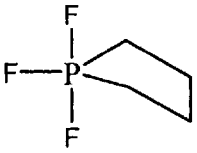
SECTION - A

(Each question is of **12** marks and each sub part **(a)** and **(b)** are of **6** marks each)

1 (a) Consider the cyclic compounds I and II. In I the rapid exchange of the fluorine atoms is inhibited just as it is in $(CH_3)_2PF_3$. However, exchange in II is very rapid. Suggest a reason.



I



II

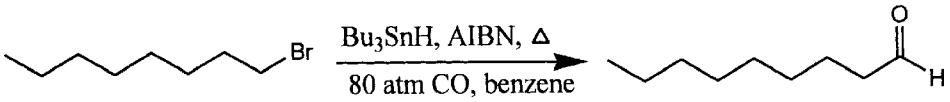
(b) The majority of clatherate compounds involve hydrogen bonding in the host cages. Discuss how the intermediate nature of the hydrogen bond (i.e., stronger than van der Waals forces, weaker than ionic forces) is related to the prevalence of hydrogen-bonded clatherates.

2 (a) The blue solution formed when an alkali metal dissolves in liquid ammonia consists of the metal cations and electrons trapped in a cavity formed by ammonia molecules. Calculate the spacing between the levels with n = 4 and n = 5 of an electron in a one-dimensional box of length 5.0 nm.

(b) The diffusion coefficient of H_2O in water is $2.26\times10^{-9}\ m^2s^{-1}$ at 25°C. How long does it take for an H_2O molecule to travel 1.0 cm from its starting point in a sample of unstirred water?

3 (a) Draw all of the stereoisomers that exist for 2,4 dimethoxycyclobutanecarboxylic acid. Identify the meso compounds, if present and assign the absolute configuration of each chiral centre.

(b) Propose a mechanism to account for formation of the aldehyde in the following reaction :



SECTION - B

(Each question is of **20** marks and each sub part **(a)** and **(b)** are of **10** marks each)

4 (a) With equations and words describe what happens : (a) when metallic potassium is dissolved in ammonia to form a dilute solution, (b) when more potassium is added to from concentrated solution, (c) when solutions (a) and (b) are evaporated carefully in vaccuo, (d) when (a) is treated with Fe_2O_3. How can (d) be considered a levelling reaction?

(b) Show how coordination of an O_2 molecule to a heme group can result in pairing of the electron on the oxygen molecule whether the bonding is (a) through a mu bond or (b) through a lone pair on one oxygen atom.

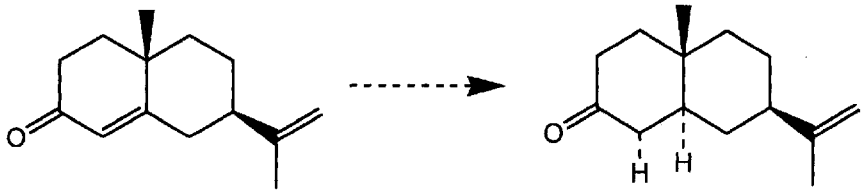
5 (a) Given the reducible representation, Γ, in C_{2v} for water molecule, determine the vibrational modes of H_2O and specify the symmetry species to which each vibrational mode belongs.

	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

	E	C_2	σ_v	σ_v'
Γ	9	−1	1	3

(b) Use the character table given in 5a to determine which of the following transitions (i) $A_1 \rightarrow A_1$ (ii) $A_1 \rightarrow A_2$ are allowed or forbidden when the change in transition moment is (i) along z-axis and (ii) in the x-y plane.

6 (a) Suggest suitable reagent and reaction conditions for the conversion of I to II and by drawing all the possible intermediates, explain in words the mechanism of the reaction.



I II

(b) Show how would you prepare (S)-2-methylcyclohexanone and (S)-3-methylhexanoic acid from any commercially available achiral reagents.

SECTION - C

(Each question is of **28** marks and each sub part **(a)** and **(b)** are of **14** marks each)

7 (a) A marine biological organism has a vanadium-containing molecule which catalyzes reactions of the type

$$Br^- + RH + H_2O_2 \rightarrow RBr + OH^- + H_2O$$

In its functional form, this molecule is EPR silent but it will undergo a one-electron reduction to give a species with an anisotropic EPR spectrum with $g_I = 1.984$, $A_I = 17.6\ mT$, $g_\perp = 1.979$, $A_\perp = 5.7\ mT$.

Infer the oxidation state of vanadium in the functional form of the molecule. Explain the structural significance of an anisotropic EPR spectrum and draw a stick diagram of the expected line positions (first-order) as a function of magnetic field for a spectrometer operating at 9.458 GHz.

$\left[{}^{51}V, 100\%,\ I = 7/2,\ \text{take}\ h/\mu = 7.145 \times 10^{-11}\ Ts\right]$

(b) For each of following half-cells, compare electrode potentials derived from (1) concentration and (2) activity data :

(i) $Sn(ClO_4)_2\left(2.00 \times 10^{-5}\ M\right)$, $Sn(ClO_4)_4\left(1.00 \times 10^{-5} M\right)/Pt.$

(ii) $Sn(ClO_4)_2\left(2.00 \times 10^{-5}\ M\right), Sn(ClO_4)_4\left(1.00 \times 10^{-5}\ M\right),$ $NaClO_4\,(0.0500M)/Pt$.

8 (a) Write the cell reactions and predict whether it is spontaneous or non-spontaneous in a cell at 298 K and also calculate the equilibrium constant of the cell reaction

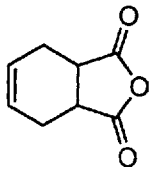
$$Zn, Zn^{2+}(1M)\ //\ I^-(1M), CuI; Cu$$

$$E^\circ\left(Zn^{2+}/Zn\right) = -0.76\ V$$

$$E^\circ(CuI, I^-, Cu) = -0.17\ V$$

(b) For a second order reaction $2A \rightarrow P$, show that $t_{1/2} \alpha 1/[A]_0$, where $t_{1/2}$ is the half life and $[A]_0$ is the initial concentration. Calculate the half life of this reaction if its rate constant is 3.33×10^{-2} dm^3 mol^{-1} s^{-1} and the initial concentration of the reactant is 0.05 mol dm^{-3}.

9 (a) Compound A, when treated with Br_2 in CH_2Cl_2, yields compound B in excellent yield. Heating compound B with sodium isopropoxide, a strong base, in a high boiling ether solvent, causes compound C to distil from the reaction mixture in good yield. Compound C is subsequently treated with maleic anhydride, and compound D is isolated. Draw the structures for compounds A, B and C and write equations showing the reaction that take place. Name compounds A, B and C.



D

(b) Draw the structure of the compound which contains C, H and O and has the following spectral data :

IR : strong absorption at 1730 cm^{-1}, broad and strong absorption between 3500 and 2500 cm^{-1}.

^1H NMR : δ 0.91 (3H, t, J = 7 Hz), 1.45 (sextet, 2H), 1.62 (2H, quintet), 2.65 (2H, t), 7.25 (2H, d, J = 7 Hz), 8.05 (2H, d, J = 7 Hz), 12.0 (1 H, s)

^{13}C NMR: δ 13.89, 22.34, 33.23, 38.80, 126.60, 128.61, 130.28, 149.49, 172.62

From High resolution mass spectrum, MW = 178.0994.

SECTION - D

(Each question is of **40** marks and each sub part **(a)** and **(b)** are of **20** marks each)

10 (a) The complex $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$ are diamagnetic and orange-yellow whereas complex $[CoF_6]^{3-}$ and $[Co(H_2O)_3F_3]$ are paramagnetic and blue. Explain qualitatively the difference in color of complexes. Also explain the difference in magnetic behaviour of the complexes using valence bond theory and crystal field theory.

(b) Specifying the suitable reaction conditions, suggest reasonable synthesis for

(i) $Mo(C_6H_6)(CO)_3$

(ii) $Mo(C_6H_6)_2$

(iii) a compound containing $[Co(C_5H_5)_2]^+$ and

(iv) $SiH_3Co(CO)_4$.

11 (a) Derive expression for Gibbs free energy of mixing, entropy of mixing, enthalpy of mixing of ideal gases. Calculate the entropy of mixing and Gibbs free energy of mixing of one mole of oxygen gas and two moles of hydrogen gas assuming that no chemical reaction occurs and the gas mixture behaves ideally at 298 K.

(b) The chromium metal crystallizes in the cubic system. The length of the unit cell edge is found to be 287 pm. The X-ray diffraction pattern of chromium shows the diffraction lines with miller indices 110, 200, 211 while 100, 111, 210 are absent. Determine the type of cubic system and calculate the atomic radius and interplanar distance of the plane (211). What would be the density of chromium in g/cm^3 ?

12 (a) Name the compounds and state the conditions under which they are formed when glucose, fructose, sucrose and maltose are treated with :

(i) Me_2CO

(ii) Ac_2O

(iii) Fehling's solution

(iv) HCN

(v) microorganisms

(b) With examples discuss mechanism of :

(i) Paal-Knorr synthesis

(ii) Ugi multicomponent reaction

(iii) Hantzsch synthesis

(iv) Heck reaction

(v) Oppenauer oxidation.