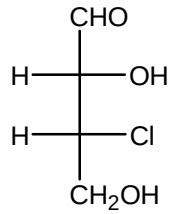
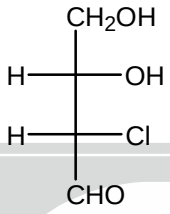
PAPER : IIT-JAM 2007

CHEMISTRY-CY

NOTE: Attempt ALL the **44 questions.** Questions 1-30 **(Objective questions)** carry ***three*** marks each and questions 31-44 **(Subjective questions)** carry ***fifteen*** marks each.

1. The compound, which
(i) Reacts rapidly with acetyl chloride
(ii) Does not react with 2, 4-dinitrophenylhydrazine and
(iii) Does not form a yellow precipitate with excess of iodine in aqueous alkali is
(a) Acetone (b) Diethyl ether (c) 2-methyl-2-propanol (d) Ethanol

2. **(1)** 

(2) 

The given compounds 1 and 2 are
(a) Identical (b) Diastereomeric (c) Enantiomeric (d) Constitutionally isomeric.

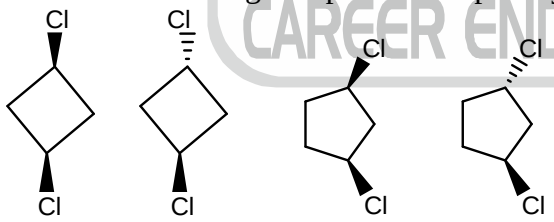
3. The correct order of dipole moments (μ) of the following compounds is:

1. $CH_3CH_2CH_2CHO$ 2. $CH_3CH=CHCHO$ 3. $CH_3CH_2CH=CH_2$

(a) $\mu_1 > \mu_2 > \mu_3$ (b) $\mu_2 > \mu_3 > \mu_1$ (c) $\mu_3 > \mu_1 > \mu_2$ (d) $\mu_2 > \mu_1 > \mu_3$

4. Which one of the following compounds gives positive test for both nitrogen and halogen with its Lassaigne's extract?
(a) $CH_3NH_2.HCl$ (b) $NH_2OH.HCl$ (c) NH_4Cl (d) $H_2NNH_2.HCl$

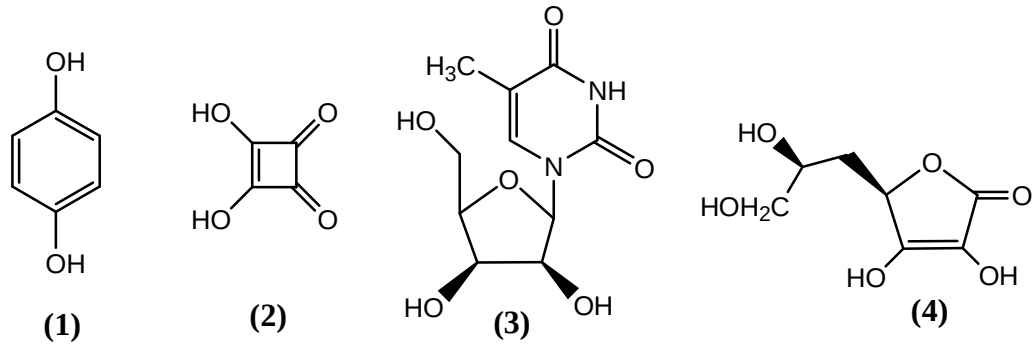
5. Which one of the following compounds is optically active?



(1) **(2)** **(3)** **(4)**

(a) 1 (b) 2 (c) 3 (d) 4

6. The compounds that react with aqueous $NaHCO_3$ to release CO_2 are



(1) **(2)** **(3)** **(4)**

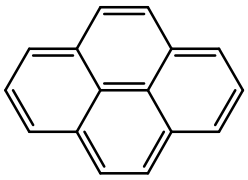
(a) 1 and 3 (b) 2 and 4 (c) 2 and 3 (d) 1 and 4

7. The complementary strand of DNA for the following single stranded DNA sequence, 5'–A–T–C–A–T–G–C–3' is:

(a) 5'–A–T–C–A–T–G–C–3' (b) 5'–T–A–G–T–A–C–G–3'

(c) 5'–G–C–A–T–G–A–T–3' (d) 5'–C–G–T–A–C–T–A–3'

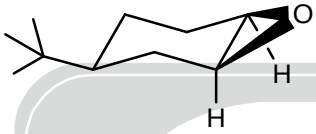
8. The value of 'n' for the following molecule according to Huckel's rule is:



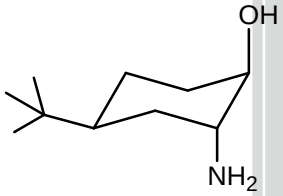
(a) 16 (b) 4 (c) 3 (d) 14

9. Which one of the following compounds reacts with nitrous acid to give the product [P]?

[P] =

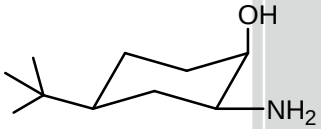


(a)

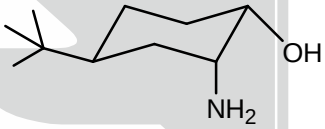


(b)

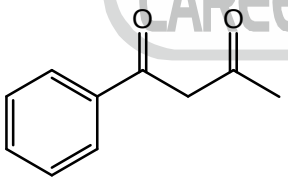
(c)



(d)

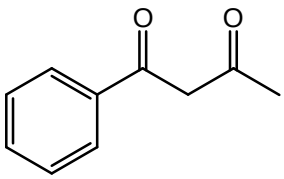


10. The main product obtained in the following reaction is:

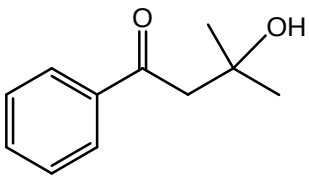


$\xrightarrow[2.\ H^+/H_2O]{1.\ MeMgBr/dry\ ether}$ [?]

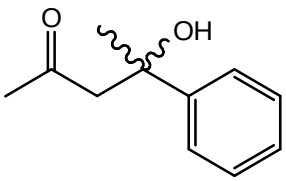
(a)



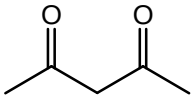
(b)



(c)



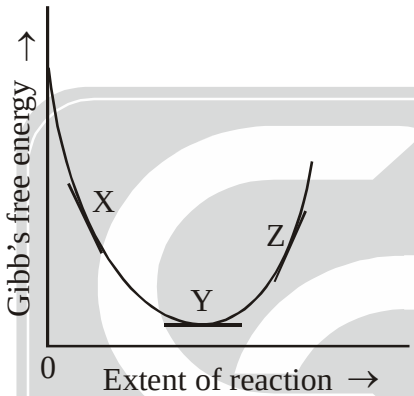
(d)



11. For a reaction with rate equation $-dC/dt = kC^2$, C_0 and C are the concentrations of the reactant at time 0 and t respectively. If 10 minutes were required for C_0 to become $C_0/2$, the time required for C_0 to become $C_0/4$ is:
(a) 10 min (b) 20 min (c) 30 min (d) 40 min.

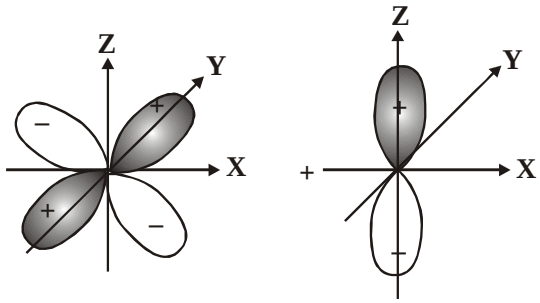
12. For a cyclic process performed by an ideal gas, changes in some thermodynamic functions are zero. Indicate the set in which all the functions are zero.
(a) $w, \Delta E, \Delta H, \Delta G$ (b) $q, \Delta S, \Delta H, \Delta A$ (c) $q, \Delta E, \Delta S, \Delta G$ (d) $\Delta E, \Delta S, \Delta H, \Delta A$

13. The plot of Gibb's free energy G and the extent of a reaction ξ is given below for the reaction $A \rightleftharpoons B$. If μ_A and μ_B are the chemical potentials of A and B respectively, the **INCORRECT** statement is:



(a) At point X, $\mu_A > \mu_B$
(b) At point Y, $\Delta G = 0$
(c) At point Z, $\mu_A > \mu_B$
(d) At equilibrium, the composition of the reaction mixture can be identified.

14. The overlap between the atomic orbitals sketched below is:



(a) Positive (b) Negative (c) Zero (d) No overlap

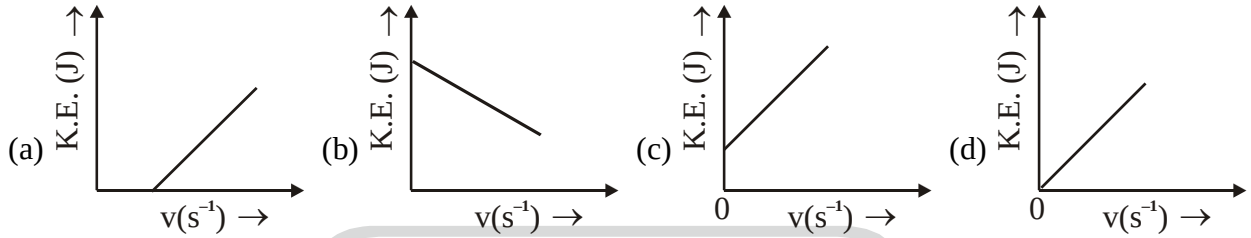
15. The pH of a 1.0×10^{-3} M solution of a weak acid HA is 4.0. The acid dissociation constant K_a is:
(a) 1.0×10^{-3} (b) 1.0×10^{-4} (c) 1.0×10^{-5} (d) 2.0×10^{-5}.

16. The normalisation constant 'A' for the wavefunction $\psi(\phi) = Ae^{(im\phi)}$ where $0 \le \phi \le 2\pi$ is:

(a) $\frac{1}{\sqrt{2\pi}}$ (b) $\sqrt{2\pi}$ (c) 2π (d) $\frac{1}{\sqrt{2}}$

17. The standard potential of a Daniel cell is +1.10 V and the equilibrium constant for the cell reaction is 1.5×10^{37}. It can be concluded that
(a) Zinc oxidises copper
(b) Displacement of copper by zinc goes to near completion.
(c) Copper oxidises zinc
(d) Displacement of zinc by copper goes to completion.

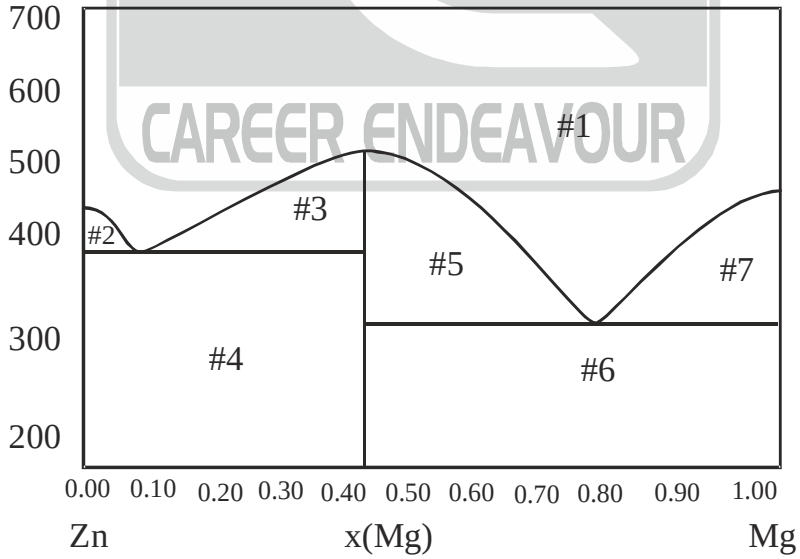
18. Which one of the following figures, showing kinetic energy of the ejected electron versus the frequency (v) of the incident photon, represents the Einstein's photoelectric effect?



19. An aqueous solution containing 0.01 M $FeCl_3$ and 0.06 M $HClO_4$ has the same ionic strength as a solution of
(a) 0.09 M NaCl (b) 0.04 M Na_2SO_4 (c) 0.06 M $CuSO_4$ (d) 0.03 M H_3PO_4.

20. Which one of the following species is the conjugate base of HO^- ?
(a) H_2O (b) O^{2-} (c) O_2^- (d) O_2^{2-}

21. The solid-liquid phase diagram for the Mg-Zn system is shown in the figure below where the vertical line at X(Mg) = 0.33 represents the formation of a congruent melting compound $MgZn_2$. The figure is divided into seven regions depending upon the physical state of the system. The composition of the region #6 represents.



(a) Single phase of a solution of Mg and Zn
(b) Two phase region between the solid Zn and solid $MgZn_2$.
(c) Two phase region between the liquid and solid $MgZn_2$.
(d) Two phase region between solid Mg and solid $MgZn_2$.

22. In the extraction of metals from their ores, which one of the following reduction methods can bring about a non-spontaneous reduction?
(a) Electrolytic reduction (b) Reduction by carbon
(c) Reduction by another metal (d) Reduction by hydrogen.

23. The correct order of the ionic radii is:

(a) $In^{3+} > Sn^{4+} > Sr^{2+} > Rb^{+}$ (b) $Sn^{4+} > In^{3+} > Sr^{2+} > Rb^{+}$

(c) $Rb^{+} > In^{3+} > Sr^{2+} > Sn^{4+}$ (d) $Rb^{+} > Sr^{2+} > In^{3+} > Sn^{4+}$

24. The correct valence shell electronic configuration of the element with atomic number 22 is

(a) $[Ar]4s^2 3d^2$ (b) $[Ar]3d^4$ (c) $[Ar]3d^2 4s^2$ (d) $[Ar]4s^2 4p^2$

25. The ligand with only sigma (σ) bonding character is:

(a) CN^{-} (b) CH_3^{-} (c) CO (d) NO

26. Which one of the following species is **NOT** isoelectronic with CO?

(a) N_2 (b) CN^{-} (c) NO^{+} (d) O_2^{+}

27. During wittig reaction, a phosphorus yield gets converted to

(a) R_3P (b) $R_3P=0$ (c) $R_3P^{+}HOH^{-}$ (d) R_2P-PR_2

28. Which of the following reactions does NOT give H_3PO_4?

(a) $Ca_3(PO_4)_2 + H_2SO_4 \longrightarrow$ (b) $P_4O_6 + H_2O \longrightarrow$

(c) $PCl_5 + H_2O \longrightarrow$ (d) $P_4S_{10} + H_2O \longrightarrow$

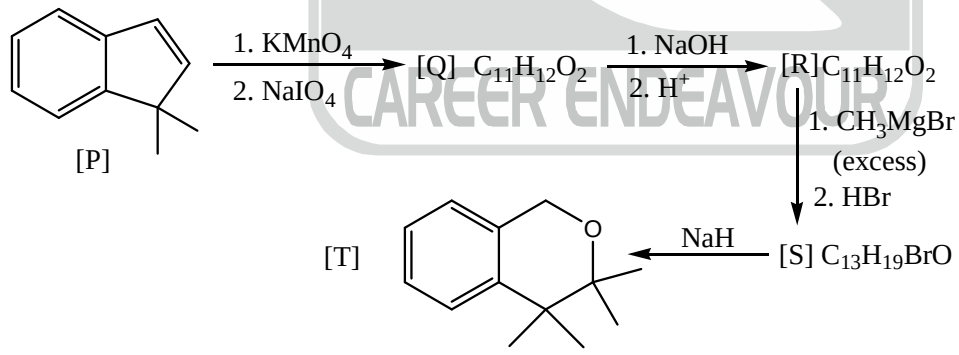
29. The ionic radii of Ca^{2+} and F^{-} are 100 pm and 133 pm respectively. The coordination number of Ca^{2+} in the ionic solid will be

(a) 8 (b) 6 (c) 4 (d) 2

30. The shape of CH_3^{-} ion is:

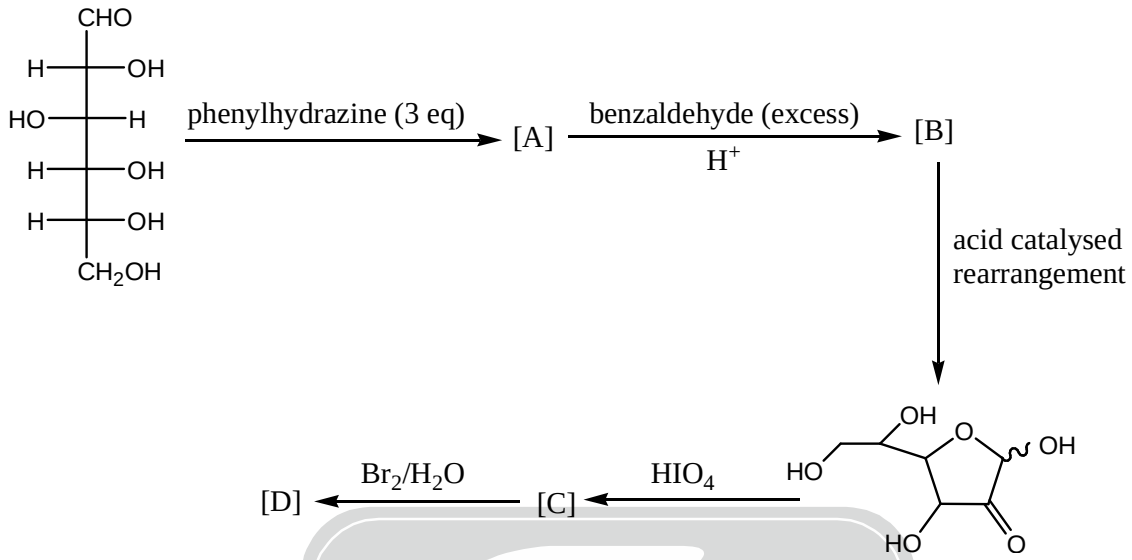
(a) trigonal planar (b) tetrahedral (c) trigonal pyramidal (d) linear.

31. **[15]**



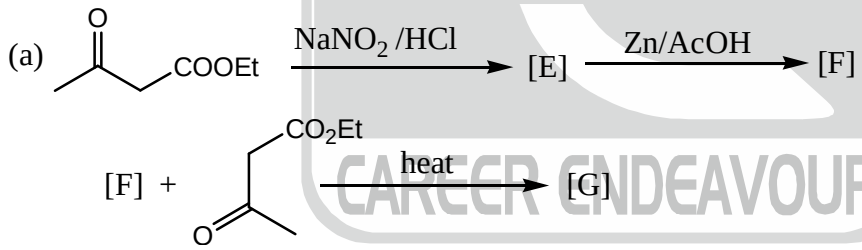
Identify the structures of the intermediate compouds Q, R and S. Show the transformation for each step

32. (a) For the following scheme of transforamations, draw the structures of A, B, C and D. **[9]**



(b) Complete hydrolysis of a pentapeptide with 6 N HCl at 110°C in a sealed tube gave 2 equivalents of glycine, one equivalent each of tyrosine, leucine and phenylalanine. Reaction of the pentapeptide with Sanger's reagent (2, 4-dinitrofluorobenzene, DNFB) and subsequent hydrolysis gave the DNFB derivative of tyrosine. Chymotrypsin cleavages of this peptide yielded tyrosine, leucine and a tripeptide. Deduce the sequence of the pentapeptide. **[6]**

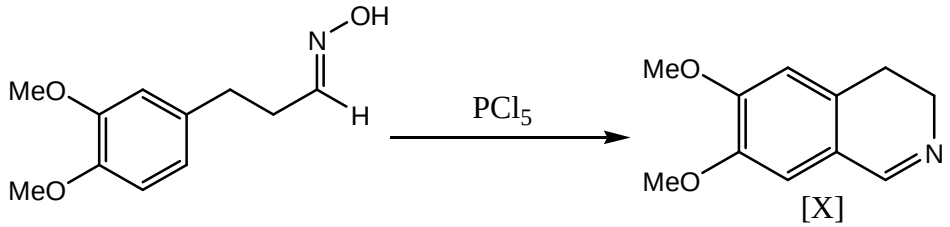
33. Complete the following reactions with appropriate structures for E, F, G, H and I.



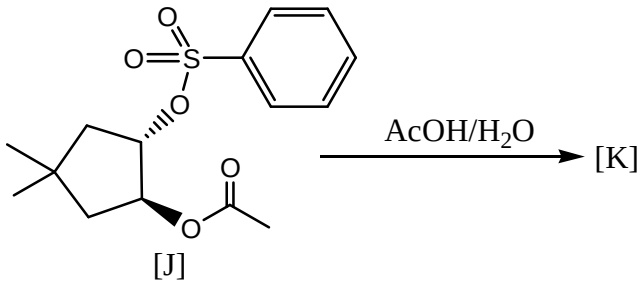
[9]

[6]

34. (a) Account for the following transformation with an appropriate mechanism. Give the structure of the Hoffmann exhaustive methylation product of 1, 2-dihydro derivative of [X]. **[9]**



(b) The optically pure ester [J] is hydrolysed in aqueous acetic acid to form a racemic mixture of cis-4, 4-dimethyl-2-acetoxycyclopentanol [K]. Give a mechanistic explanation to account for the formation of [K] and the observed change in the optical activity. **[6]**



[J]

35. (a) M is a first row transition metal. MCl_2 on treatment with aqueous ammonia gives a blue coloured solution of complex N. A solution of MCl_2 also gives a bright red prcipitate of complex O with ethanolic dimethylglyoxime. **[9]**

(i) Identify M and draw the structure of O.

(ii) Determine the hybridisation of M in complex N.

(iii) Identify the paramagnetic complex.

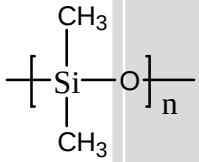
(b) $\left[Cr\left(H_2O\right)_6\right]^{3+}$ gave an absorption at 208 kJ/mol which corresponds to Δ_0. Calculate the crystal field stabilisation energy of this complex in kJ/mol. **[6]**

36. (a) Consider the ethers $H_3SiOSiH_3$ and H_3COCH_3. **[9]**

(i) Which ether has more lewis base character?

(ii) Which angle [Si–O–Si and C–O–C] is greater? Justify your answer.

(b) Starting from SiO_2, show how the following polymer is prepared industrially? **[6]**



37. (a) A solution of metal ion $\left(M^{2+}\right)$ when treated with H_2S gas gives a black precipitate A. Precipitate A dissolved in hot concentrated nitric acid to give B along with elemental sulfur. The metal ion solution also gives a white precipitate C with an excess of KI. Write the chemical formulae of A, B, and C **[9]**

(b) Why are potassium permanganate solutions unstable in the presence of Mn^{2+} ions? In the quantitative estimation of iron present in iron ores dissolved in dilute HCl, titrations with dichromate are preferred over titrations with permanganate. Rationalise. **[6]**

38. (a) Al_2Cl_6 and Al_2Me_6 are dimeric in gas phase. Draw their structures. Which compound has more Lewis acid character? Explain. **[9]**

(b) Arrange the halides $SnCl_2, PbCl_2, SiCl_2$ in increasing order of their stability. Give reasons for your answer. **[6]**

39. (a) Acidification of an aqueous solution of yellow sodium chromate gives an orange coloured A. A saturated solution of A on treatment with concentrated H_2SO_4 gives a bright orange solid B. Compound A in the presence of concentrated H_2SO_4 reacts with anion C to give a deep red coloured liquid. Identify A, B and C. **[9]**

(b) $^{215}_{84}Po$ undergoes an α emission to give element X followed by a β emission to give element Y.

(i) Write the valence shell electronic configuration of Y. **[6]**

(ii) Indicate the groups of the periodic table to which X and Y belong.

40. (a) When an ideal monoatomic gas is expanded from 1.5 bar, 24.8 L and 298 K into an evacuated container, the final volume becomes 49.6 L. Calculate ΔH, ΔS and ΔG for the process. **[9]**

(b) The Maxwell distribution function for the distribution of speeds of molecules in gaseous systems is given by

$$f(c) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 \exp\left(\frac{-mc^2}{2kT}\right)$$

Show that the most probable speed, $c_{mps} = \left(\frac{2kT}{m}\right)^{1/2}$ **[6]**

41. (a) At 600 K and 200 bar, a 1:3 (molar ratio) mixture of A_2 and B_2 react to form an equilibrium mixture containing $x_{AB_3} = 0.60$. Assuming ideal gas behaviour, calculate K_p for the reaction

$$A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$$ **[9]**

(b) A 50 mL 0.05 M solution of Fe(II) is titrated with 0.05 M solution of Ce(IV) in the presence of dilute H_2SO_4 at 25ºC. Calculate the equivalence point potential and the equilibrium constant K in terms of log K. **[6]**

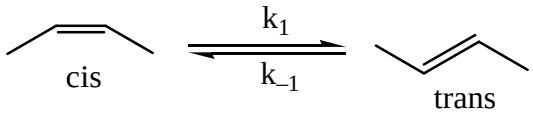
$$\left[E^0_{\left(Fe^{3+}/Fe^{2+}\right)} = +0.75\ V,\ E^0_{\left(Ce^{4+}/Ce^{3+}\right)} = +1.45V\right]$$

42. (a) The vapour pressure of D_2O at 20 ºC is 745 mm Hg. When 15 g of a non-volatile compound is dissolved in 200 g of D_2O, the pressure changes to 730 mm Hg. Assuming the applicability of Raoult's law, calculate the molecular weight of the compound. **[9]**

(b) An enzyme following Michaelis-Menten kinetics was found to have highest activity at 37ºC and pH 7.0. If the maximum velocity V_{max} for this enzyme was 2.4×10^{-4} mol L^{-1} s^{-1} with an initial enzyme concentration $[E]_0 = 2.4$ nM, calculate the turnover frequency. **[6]**

43. (a) Consider the 4π electrons in cyclobutadiene to be free particles in a 2-dimensional square box of length 2Å. Calculate the wavelength of the electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Also write down the normalised wavefunctions for the occupied degenerate states. **[9]**

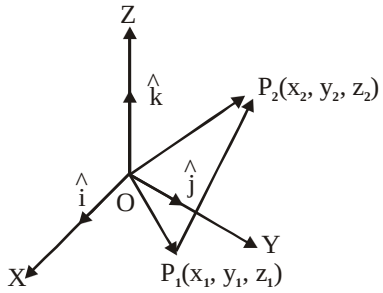
(b) The reaction



[6]

is first order in both directions. At 25ºC, the equilibrium constant (K) of this reaction is 0.40. If 0.115 mol.
dm^{-3} of cis-isomer is allowed to equilibrate, calculate the equilibrium concentration of each isomer.

44. (a) With i, j and k as the unit vectors along, X, Y, Z axes, express the vector, $\overrightarrow{P_1P_2}$ in the given figure in terms of the coordinate of P_1 and P_2. Also determine the dot products of the unit vectors, i, j, k.



[9]

(b) Deduce whether the matrices A and B commute or not. **[6]**

$$A = \begin{pmatrix} 2 & 1 \\ 0 & 1 \end{pmatrix} \qquad B = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}$$