
(c) Using Slater's rules calculate the effective nuclear charge for the following electrons:
(i) 4 s electron in Cu atom ( $\mathrm{Z}=29$ ), (ii) a 3d electron in Cu atom.
(d) A solution of potassium ferricyanide cannot oxidise iodide to iodine but it can do so in presence of zinc ion—Explain. [Given $\mathrm{E}^{0}($ volts $): \mathrm{Fe}(\mathrm{CN})_{6}{ }^{3-} / \mathrm{Fe}(\mathrm{CN})_{6}{ }^{4-}=+0.36 \mathrm{~V}$ and $\left.1 / 2 \mathrm{I}_{2} / \mathrm{I}^{-}=+0.54 \mathrm{~V}\right]$
(e) State Heisenberg's uncertainty principle and discuss its significance.
2. (a) Draw the vector orientation of the $\mathrm{m}_{1}$ values corresponding to $l=3$ in magnetic field. 3
(b) Arrange $\mathrm{BF}_{3}, \mathrm{BCl}_{3}$ and $\mathrm{BBr}_{3}$ in the increasing order of their acidity with justification. 2
(c) The interionic distance in RbBr is 342 pm . Use Pauling's method to calculate the radii of $\mathrm{Rb}^{+}$and $\mathrm{Br}^{-}$(Atomic no of Rb is 37).
(d) Construct the Frost diagram from the following Latimer diagram for ' Hg ' in acid solution.


Comment on the tendency of any of the species to undergo disproportionation.
(e) Deduce the ground state term symbol for $\mathrm{Ni}^{2+}$ ion (atomic no. of Ni is 28).
3. (a) Calculate the equilibrium constant for the reaction of $\mathrm{KMnO}_{4}$ and $\mathrm{Fe}^{2+}$ in acid medium. [Given $\mathrm{E}^{0}$ (volts) : $\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}=+0.77 \mathrm{~V} \& \mathrm{MnO}_{4}^{-} / \mathrm{Mn}^{2+}=+1.51 \mathrm{~V}$ ]
(b) Electron affinity of $\mathrm{Mn}^{3+}$ is greater than that of $\mathrm{Fe}^{3+}$ - explain.
(c) Sketch the radial distribution function for the $3 \mathrm{~s}, 3 \mathrm{p}$ and 3d hydrogenic orbitals. Which orbital electron has the greater probability to be closer to the nucleus?
(d) How many radial nodes and nodal planes do 3p, 3d and 4f orbitals each have?
(e) Draw the structures of chloric acid $\left(\mathrm{HClO}_{3}\right)$ and chlorous acid $\left(\mathrm{HClO}_{2}\right)$ and predict their $\mathrm{pK}_{\mathrm{a}}$ values using Pauling's rules.
4. (a) The solubility product $\left(\mathrm{K}_{\mathrm{sp}}\right)$ of $\mathrm{MgF}_{2}$ is $7 \times 10^{-4}$. Find its solubility in water and in 0.01(M) NaF solution.
(b) What are superacids? Indicate the parameter used to have a quantitative measure of superacid strength.
(c) Account for the decrease in first ionisation energy between P and S .
(d) Show that Bohr's postulates of quantisation of angular momentum for an electron can be derived by the application of de-Broglie's hypothesis.
(e) Balance the equation by ion electron method:
$\mathrm{NaNO}_{3}+\mathrm{Zn}+\mathrm{NaOH} \rightarrow \mathrm{NH}_{3}+\mathrm{Na}_{2} \mathrm{ZnO}_{2}+\mathrm{H}_{2} \mathrm{O}$

## Group - B

Answer any one question :
5. (a) Predict the wavelengths of the first two lines in the Paschen series.
(b) Draw the acid base titration curve of weak acid by strong base. Name the suitable indicator used in this titration.
(c) ' $\mathrm{SnCl}_{2}$ is reducing while $\mathrm{PbCl}_{2}$ is neither reducing nor oxidizing' - explain.
(d) Define comproportionation reaction with example. 2
6. (a) Draw the Sommerfeld's orbit for $\mathrm{n}=4$. 2
(b) Predict the direction of the following reaction (left or right) in gas phase with explanation.
(i) $\mathrm{TiF}_{4}+2 \mathrm{TiI}_{2} \rightarrow \mathrm{TiI}_{4}+2 \mathrm{TiF} 2$
(ii) $\mathrm{HI}+\mathrm{NaF} \rightarrow \mathrm{HF}+\mathrm{NaI}$
(c) Establish the working potential of BDS indicator $\left(\mathrm{E}^{0}=0.83 \mathrm{~V}\right.$ at $\left.1(\mathrm{M}) \mathrm{H}^{+}\right) \quad 2.5$
(d) Explain the basis of electronegativity as described by Allred-Rockhow scale. 2.5

## PRACTICAL (Marks: 20)

Paper: C 3P

Answer any one question :

1. Discuss the principle, methodology and calculation for the quantitative estimation of Fe (III) Mn (II) mixture using potassium permanganate giving all the chemical reactions involved. 20
2. (a) Describe titrimetric method for estimation of iron(III) using potassium dichromate.
(b) What is the role of $\mathrm{H}_{3} \mathrm{PO}_{4}$ and $\mathrm{NH}_{4} \mathrm{HF}_{2}$ in the above titration.
3. Discuss the principle, methodology and calculation for the estimation of free alkali present in different soaps/detergents.
