WEST BENGAL STATE UNIVERSITY
B.Sc. Honours 2nd Semester Examination, 2023

## CEMACOR03T-CHEMISTRY (CC3)

InORganic CHEMISTRY-I
Full Marks: 40
Time Allotted: 2 Hours

> The figures in the margin indicate full marks.
> Candidates should answer in their own words and adhere to the word limit as practicable.
> All symbols are of usual significance.

## Answer any four questions taking one from each unit

## Unit-I

1. (a) Compare the radial distribution plots for $2 s$ and $2 p$ orbitals and hence comment on 3 their relative penetrating power.
(b) Find out the ground state term symbol for $\mathrm{Co}^{2+}$ and $\mathrm{Cr}^{2+}$ ions.
(c) Identify the possible Bohr-Sommerfeld orbits for $n=1$.
(d) In an atom the angular momentum of an electron is $\sqrt{6} h / 2 \pi$. What will be the minimum value of the principal quantum number of the electron?
(e) Calculate the uncertainty in position of an electron whose velocity is $3.0 \times 10^{4} \mathrm{~cm} \mathrm{~s}^{-1}$ and accuracy upto $0.001 \%$. Mass of an electron $=9.1 \times 10^{-28} \mathrm{~g}$.
2. (a) Apply Pauli's exclusion principle to predict the maximum capacity of $p$-subshell for accommodating electrons.
(b) Why de Broglie's wave equation has no significance for a macroscopic particle?
(c) Show that the de-Broglie wavelength of the electron in the first Bohr orbit of the hydrogen atom is $2 \pi a_{0}$ (where $a_{0}=$ First Bohr radius).
(d) "Though the $(n+1)$ rule to determine the order of energy of different subshells is useful in most cases, there are some exceptions" - Justify the statement with an example.
(e) Calculate the frequency of radiation emitted when an electron jumps from the third to the first Bohr orbit. [Rydberg Constant $=109677 \mathrm{~cm}^{-1}$ ].
(f) Deduce the expression for energy of a Hydrogen like atom in SI unit.

## Unit-II

3. (a) Rationalize the electron affinity trend of $\mathrm{C}, \mathrm{N}$ and O atoms:

| C | N | O |  |
| :---: | :---: | :---: | :---: |
| 122 | -20.3 | 141 | (in KJ mole |

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(b) Calculate the oxidation state of Tl in $\mathrm{TlI}_{3}$ and justify your answer
(c) Atomic radii of Nb and Ta are almost identical. Comment.
(d) The $\mathrm{Cl}-\mathrm{O}$ bond length in $\mathrm{ClO}_{2}^{+}$is 141 pm while that in $\mathrm{ClO}_{2}$ is 148 pm Laplain.
4. (a) What is meant by ionic radius? Discuss with example the Pauling methed of determination of univalent radii applicable for isoelectronic ion pairs,
(b) Rationalise the trends in ionization energy in the following cases:

| Elements | Li | Be | B |
| :--- | :--- | :--- | :--- |
| First ionisation energy (ev) | 5.39 | 9.32 | $\mathbf{8 . 3 0}$ |

(c) The F-F bond distance in $\mathrm{F}_{2}$ is 141.3 pm . Calculate Allred-Rochow electronegativity of fluorine using Slater's rule.

## Unit-III

5. (a) What is Hammett acidity function, $H_{0}$ ? How can you define super-acid on its basis?

What happens when $\mathrm{SbF}_{5}$ is added to $\mathrm{HSO}_{3} \mathrm{~F}$ ?
(b) What will be the pH of the solution obtained by mixing 10 ml of $0.2(\mathrm{~N}) \mathrm{KOH}$ with 30 ml of $0.1(\mathrm{~N}) \mathrm{CH}_{3} \mathrm{COOH} ? \mathrm{~K}_{\mathrm{a}}=2 \times 10^{-5}$.
(c) Predict which way the reactions will go in the gas phase with explanation:
(i) $\mathrm{HI}+\mathrm{NaF} \rightarrow \mathrm{HF}+\mathrm{NaI}$
(ii) $\mathrm{TiF}_{4}+2 \mathrm{TiI}_{2} \rightarrow \mathrm{TiI}_{4}+2 \mathrm{TiF}_{2}$
(d) When 0.05 mole of NaOH was added to one litre of a buffer solution, its pH changed from 5.70 to 5.85 . Find the buffer capacity.
6. (a) Draw the acid-base neutralization curves for the titration of
(i) HCl Vs. NaOH
(ii) $\mathrm{CH}_{3} \mathrm{COOH}$ Vs. NaOH

Explain your choice of indicators in each case.
(b) What is the pH of $10^{-3} \mathrm{M}$ aqueous solution of $\mathrm{NH}_{4} \mathrm{OH}$ ? Given $\mathrm{K}_{\mathrm{b}}=1.85 \times 10^{-5} \mathrm{M}$ at $25^{\circ} \mathrm{C}$.
(c) Arrange $\mathrm{BF}_{3}, \mathrm{BCl}_{3}, \mathrm{BBr}_{3}, \mathrm{BI}_{3}$ in order of their Lewis acidity with justification.
(d) Identify the structural difference between $\mathrm{H}_{3} \mathrm{PO}_{3}$ and $\mathrm{H}_{3} \mathrm{AsO}_{3}$ using Pauling's rulc.
[Given $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{H}_{3} \mathrm{PO}_{3}\right) \sim 2.0 ; \mathrm{pK}_{\mathrm{a}}\left(\mathrm{H}_{3} \mathrm{AsO}_{3}\right) \sim 9.0$ ]

## Unit-IV

7. (a) What is comproportionation reaction? Give example.
(b) "Addition of phosphoric acid is essential in the titration of Fe " wn with dichromate" - Comment.
(Given: $E_{\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathrm{Cr}^{3+}}^{0}=+1.33$ volt, $E_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{0}=+0.77$ volt,

$$
\left.E^{0} \text { for } \operatorname{Ind}_{\mathrm{ox}} / \operatorname{Ind}_{\mathrm{red}}=+0.76 \mathrm{~V}\right)
$$

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(c) Discuss the role of Zimmerman-Reinhardt reagent in the titration of $\mathrm{Fe}^{2+}$ by $\mathrm{KMnO}_{4}$ in HCl medium.
(d) Calculate the redox potential values at the following three stages of titration of $0.1(\mathrm{~N}) \mathrm{Fe}^{2+}$ and $0.1(\mathrm{~N}) \mathrm{KMnO}_{4}$ in $1(\mathrm{~N}) \mathrm{H}_{2} \mathrm{SO}_{4}$ medium
(i) $25 \mathrm{ml} \mathrm{Fe}^{2+}+24.90 \mathrm{ml} \mathrm{KMnO}_{4}$
(ii) $25 \mathrm{ml} \mathrm{Fe}^{2+}+25 \mathrm{ml} \mathrm{KMnO}_{4}$
(iii) 25 ml Fe 2+ $+25.10 \mathrm{ml} \mathrm{KMnO}_{4}$

Given: $E_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{0}=0.77 \mathrm{~V}$ and $E_{\mathrm{MnO}_{4} / \mathrm{Mn}^{2+}}^{0}=1.51 \mathrm{~V}$
(e) What do you mean by common ion effect? In qualitative group analysis, $\mathrm{Cu}^{2+}$ is precipitated as sulphide in Gr IIA but $\mathrm{Zn}^{2+}$ does not - Explain.
8. (a) What are redox indicators? Give one example with structure both in oxidised and reduced states.
(b)

$$
\begin{array}{ll}
\mathrm{Fe}(\mathrm{CN})_{6}^{3-}+e=\mathrm{Fe}(\mathrm{CN})_{6}^{4-} & E^{0}=0.36 \mathrm{~V} \\
\mathrm{I}_{2}+2 e=2 \mathrm{I}^{-} & E^{0}=0.54 \mathrm{~V}
\end{array}
$$

A solution of potassium ferricyanide cannot oxidise iodide to iodine but it can do so in presence of $\mathrm{Zn}^{2+}$ ion - Explain.
(c) Construct a Frost diagram for mercury in acid solution from the following Latimer diagram:

$$
\mathrm{Hg}^{2+} \xrightarrow{+0.911 \mathrm{~V}} \mathrm{Hg}_{2}^{2+} \xrightarrow{+0.796 \mathrm{~V}} \mathrm{Hg}
$$

Hence work out the possibility of disproportionation or comproportionation of $\mathrm{Hg}_{2}^{2+}$.
(d) The solubility of $\mathrm{CaF}_{2}$ in water at $18^{\circ} \mathrm{C}$ is $2.04 \times 10^{-4} \mathrm{~mol} / \mathrm{lit}$.

Calculate:
(i) Solubility product and
(ii) The solubility of $\mathrm{CaF}_{2}$ in 0.01 M NaF solution.
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