

## WEST BENGAL STATE UNIVERSITY

B.Sc. Honours 2nd Semester Examination, 2023

### **CEMACOR03T-CHEMISTRY (CC3)**

#### **INORGANIC CHEMISTRY-I**

Time Allotted: 2 Hours

Full Marks: 40

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 2s and 2p orbitals and hence comment on their relative penetrating power.	3
	(b)	Find out the ground state term symbol for Co <sup>2+</sup> and Cr <sup>2+</sup> ions.	2
	(c)	Identify the possible Bohr-Sommerfeld orbits for $n = 1$ .	2
	(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?	2
	(e)	Calculate the uncertainty in position of an electron whose velocity is $3.0 \times 10^4$ cm s <sup>-1</sup> and accuracy upto 0.001%. Mass of an electron = $9.1 \times 10^{-28}$ g.	2
2.	(a)	Apply Pauli's exclusion principle to predict the maximum capacity of <i>p</i> -subshell for accommodating electrons.	2
	(b)	Why de Broglie's wave equation has no significance for a macroscopic particle?	, 1
	(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).	2
	(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.	2
	(e)	Calculate the frequency of radiation emitted when an electron jumps from the third to the first Bohr orbit. [Rydberg Constant = 109677 cm <sup>-1</sup> ].	2
	(f)	Deduce the expression for energy of a Hydrogen like atom in SI unit.	2
		i ilian — Peram montan coña descar el el cy	1
		<u>Unit-II</u>	
3.	(a)	Rationalize the electron affinity trend of C, N and O atoms:	2
		C N O	
		122 –20.3 141 (in KJ mole <sup>-1</sup> )	

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- (b) Calculate the oxidation state of Tl in TlI<sub>3</sub> and justify your answer.
- 2 (c) Atomic radii of Nb and Ta are almost identical. Comment. 2

2

2

3

3

3

2

2

3

2

3

2

1

2

- (d) The Cl-O bond length in ClO<sub>2</sub><sup>+</sup> is 141 pm while that in ClO<sub>2</sub> is 148 pm. Explain.
- 4. (a) What is meant by ionic radius? Discuss with example the Pauling's method of 1+2 determination of univalent radii applicable for isoelectronic ion pairs.
  - (b) Rationalise the trends in ionization energy in the following cases:

**Elements** В Li Be First ionisation energy (ev) 8.30 5.39 9.32

pm. Calculate Allred-Rochow (c) The F-F bond distance in F<sub>2</sub> is 141.3 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 SbF<sub>5</sub> is added to HSO<sub>3</sub>F?
  - (b) What will be the pH of the solution obtained by mixing 10 ml of 0.2 (N) KOH with 30 ml of 0.1 (N) CH<sub>3</sub>COOH?  $K_a = 2 \times 10^{-5}$ .
  - (c) Predict which way the reactions will go in the gas phase with explanation:
    - $HI + NaF \rightarrow HF + NaI$
    - (ii)  $TiF_4 + 2TiI_2 \rightarrow TiI_4 + 2TiF_2$
  - (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) CH<sub>3</sub>COOH Vs. NaOH

Explain your choice of indicators in each case.

- (b) What is the pH of  $10^{-3}$  M aqueous solution of NH<sub>4</sub>OH? Given  $K_b = 1.85 \times 10^{-5}$  M at 25°C.
- (c) Arrange BF<sub>3</sub>, BCl<sub>3</sub>, BBr<sub>3</sub>, BI<sub>3</sub> in order of their Lewis acidity with justification.
- (d) Identify the structural difference between H<sub>3</sub>PO<sub>3</sub> and H<sub>3</sub>AsO<sub>3</sub> using Pauling's rule. [Given pK<sub>a</sub> (H<sub>3</sub>PO<sub>3</sub>) ~ 2.0; pK<sub>a</sub> (H<sub>3</sub>AsO<sub>3</sub>) ~ 9.0]

#### **Unit-IV**

- 7. (a) What is comproportionation reaction? Give example.
  - (b) "Addition of phosphoric acid is essential in the titration of Fe2+ ion with dichromate" — Comment.

(Given:  $E_{\text{Cr},O_7^{2-}/\text{Cr}^{3+}}^0 = +1.33 \text{ volt}, E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = +0.77 \text{ volt},$ 

$$E^0$$
 for  $Ind_{ox}/Ind_{red} = +0.76$  V)

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- (c) Discuss the role of Zimmerman-Reinhardt reagent in the titration of Fe<sup>2+</sup> by KMnO<sub>4</sub> in HCl medium.
  - 2
- (d) Calculate the redox potential values at the following three stages of titration of 0.1 (N) Fe<sup>2+</sup> and 0.1 (N) KMnO<sub>4</sub> in 1 (N) H<sub>2</sub>SO<sub>4</sub> medium
- 3

2

3

3

- (i)  $25 \text{ ml Fe}^{2+} + 24.90 \text{ ml KMnO}_4$
- (ii)  $25 \text{ ml Fe}^{2+} + 25 \text{ ml KMnO}_4$
- (iii)  $25 \text{ ml Fe}^{2+} + 25.10 \text{ ml KMnO}_4$
- Given:  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0} = 0.77 \text{ V} \text{ and } E_{\text{MnO}_{4}^{-}/\text{Mn}^{2+}}^{0} = 1.51 \text{ V}$
- (e) What do you mean by common ion effect? In qualitative group analysis, Cu<sup>2+</sup> is precipitated as sulphide in Gr IIA but Zn<sup>2+</sup> does not Explain.
- 8. (a) What are redox indicators? Give one example with structure both in oxidised and reduced states.
  - (b)  $Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$   $E^0 = 0.36 \text{ V}$   $I_2 + 2e = 2I^ E^0 = 0.54 \text{ V}$

A solution of potassium ferricyanide cannot oxidise iodide to iodine but it can do so in presence of  $Zn^{2+}$  ion — Explain.

(c) Construct a Frost diagram for mercury in acid solution from the following Latimer diagram:

 $Hg^{2+} \xrightarrow{+0.911 \text{ V}} Hg_2^{2+} \xrightarrow{+0.796 \text{ V}} Hg$ 

Hence work out the possibility of disproportionation or comproportionation of  $Hg_2^{2+}$ .

- (d) The solubility of  $CaF_2$  in water at 18°C is  $2.04 \times 10^{-4}$  mol/lit. Calculate:
  - (i) Solubility product and
  - (ii) The solubility of CaF<sub>2</sub> in 0.01 M NaF solution.