2018

2nd Semester

CHEMISTRY

PAPER—C3T

(Honours)

Full Marks: 40

Time: 2 Hours

The figures in the right-hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

Group-A

1. Answer any five questions:

 5×2

(a) SnCl₂ is reducing while PbCl₂ is neither recucing nor oxidising. — Explain.

(Turn Over

- (b) Show that de Broglie's hypothesis applied to an electron moving in a circular orbit leads to Bohr's Postulate of quantisation of angular momentum.
- (c) Find out the pH of 10⁻⁸M HCl solution.
 - (d) From the following Latimer diagram, Calculate the reduction potential of ClO₄⁻ HClO

$$\text{ClO}_4^{-} \, {}^{+1.20}_4 \, \, \text{ClO}_3^{-} \, {}^{+1.18}_4 \, \, \text{ClO}_2^{-} \, {}^{+1.70}_4 \, \, \text{HClO} \, {}^{+1.63}_4 \, \, \text{Cl}_2 \, {}^{+1.36}_4 \, \, \text{Cl}_1^{-}_4 \, \, \text{HClO}_3^{-}_4 \, {}^{+1.18}_4 \, \, \text{ClO}_3^{-}_4 \, {}^{+1.18}_4 \, \, \text{ClO}_3^{-}_4 \, {}^{+1.70}_4 \, \, \text{HClO}_3^{-}_4 \, {}^{+1.70}_4 \, \, \text{HClO}_3^{-}_4 \, {}^{+1.36}_4 \, \, \text{Cl}_2^{-}_4 \, {}^{+1.36}_4 \, \, \text{Cl}_3^{-}_4 \, {}^{+1.36}_4 \, {}^{+1.36}_4 \, {}^{+1.36}_4 \, \, \text{Cl}_3^{-}_4 \, {}^{+1.36}_4 \, {}^{+1.36}_4 \, {}^{+1.36}$$

- (e) Me_3P acts as a stronger base than Me_3N in their reaction with B_2H_6 Explain.
- (f) Calculate the screening constant (σ) for the 3d electron of iron (26).
 - (g) The kinetic energy of an electron is 5.76×10^{-15} J. Calculate the wavelength associated with the electron (Given mass of an electron = 9.1×10^{-31} kg; $h = 6.626 \times 10^{-34}$ JS).

(h) State the role of H_3PO_4 in the estimation of iron by $Cr_2O_7^{2-}$ in presence of diphenyl amine indicator.

Group-B

Answer any four questions.

 4×5

2. (a) For the hydrogen spectrum show that Lyman series occurs between 912 Å and 1216 Å and Balmer series occurs between 3647 Å and 6564 Å.

$$(R = 1.0968 \times 10^7 \text{ m}^{-1})$$

- (b) Comment on the relative ionic radii of O^{2-} , F^- and Na^+ .
- 3. (a) Draw a Frost Diagram for Hg in acid solution from the given Latimer Diagram

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

comment on the tendency of any of the species to undergo disproportionation.

- (b) What is acidity function? How does it behave in dilute aqueous solution? (2+1)+2
- 4. (a) Calculate the eletronegativity of chlorine in Mulliken's scale and hence find out the electronegativity of the same element in Pauling's Scale.

(Given electron affinity of Cl = 4.0 ev per atom; Ionisation energy of Cl = 13.0 ev per atom)

- (b) The solubility of a sparingly soluble salt in water increases in presence of added salt without common ion — Explain.
 3+2
- 5. (a) What are Eigen functions? What are their characteristics?
 - (b) Arrange BF_3 , BCl_3 , BBr_3 and BI_3 in order of their Lewis acidity with justification. 3+2
 - (a) The equilibrium constant of the disportionation reaction $2Cu^{+1}$ (aq.) \rightleftharpoons Cu + Cu^{+2} (aq.) at 298 K is 1.66×10^6 M⁻¹. If the standard reduction potential

of Cu^{+2}/Cu system is 0.337 volt, Calculate the standard reduction potential of Cu^{+1}/Cu system.

- (b) Deduce ground state term symbol for atom having atomic number 22.
- 7. (a) How pH of an aqueous solution of KF will be affected if solid HgO is added?
 - (b) How Cu⁺² can be estimated in presence of Fe⁺³ iodometrically?

Given that
$$E_{Fe^{+3}/Fe^{+2}}^0 = +0.77V$$
; $E_{\frac{1}{2}I_2-I^-}^0 = +0.54V$.

2 + 3

Group-C

Answer any one question.

 1×10

8. (a) What is radial distribution function? Show diagramatically the variation of radial distribution function with 'r' for the 3s, 3p and 3d orbitals in a hydrogen atom.

- (b) Although In and Tl occur in the same group of the periodic table, In show +3 oxidation state in most of its compounds, however, Tl is +1. Explain.
- (c) Draw the acid-base neutralisation curve for
 - (i) Strong acid by strong base
 - (ii) Weak acid by weak base.
- (d) H₃BO₃ is a very weak acid (pk_a = 9.2), but in presence of any cis 1, 2 diol it behaves as strong acid. Explain.
 (1+3)+2+2+2
- (a) What is quantum mechanical interpretation of an orbital?
 - (b) $CaO + P_4O_{10} \xrightarrow{\Delta}$? Predict the product and hence explain the reaction by Lux-Flood concept.
- (c) Calculate the first ionization energy of oxygen using Slater's rule.

(d) Consider two redox couples as follows:

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of

$$Ox_1 + 2e \rightleftharpoons Red_1 (E^0 = E_1^0)$$

 $Ox_2 + 2e \rightleftharpoons Red_2 (E^0 = E_2^0)$

What should be the minimum difference between $E_1^{\ 0}$ and $E_2^{\ 0}$ in order to have 90% complete reaction between the two systems at equilibrium at 25°C?

(e) Ionisation energy of nitrogen is higher than that of 1+2+3+2+2 oxygen—Explain.