

U.G. 2nd Semester Examination - 2020

CHEMISTRY

[HONOURS]

Course Code : CEMH/CC-T-03

(Inorganic and Physical)

Full Marks : 40

Time : 2½ Hours

*The figures in the right-hand margin indicate marks.**Candidates are required to give their answers in their own words as far as practicable.*

GROUP-A

(Inorganic)

[Marks : 20]

1. Answer any **one** question: 1 × 1 = 1
- a) Give one example of each of acid buffer and basic buffer solution.
- b) What is meant by formal potential?
2. Answer any **two** questions: 2 × 2 = 4
- a) Indicate with reason the direction of the following reaction:
- $$\text{AgF}_2^- + 2\text{I}^- = \text{AgI}_2^- + 2\text{F}^-$$

- b) Arrange the following compounds in increasing order of their Lewis Acidity with proper explanation: SiF_4 , SiCl_4 , SiBr_4 and SiI_4
- c) Calculate the $E_{\text{Tl}^{3+}/\text{Tl}}^0$ from the following data: $E_{\text{Tl}^+/\text{Tl}}^0 = -0.336\text{V}$ and $E_{\text{Tl}^{3+}/\text{Tl}^+}^0 = 1.25\text{V}$.
- d) Why NH_4Cl is added along with NH_4OH during precipitation of Gr-III A metal ions?

3. Answer any **one** question: 5 × 1 = 5
- a) H_2Se is stronger acid than H_2S . Explain. SbF_5 increases that acidity as well as the conductivity of liquid HF. Explain. What happens when KHSO_4 is added to H_2SO_4 ?
2 + 2 + 1 = 5
- b) Solution of metallic Na in liquid NH_3 is highly conducting. Explain. Determine the pH of a solution obtained by mixing equal volumes of 0.015N NH_4OH and 0.15N NH_4NO_3 solutions. (K_b for NH_4OH is 1.8×10^{-5}). 2½ + 2½ = 5
- c) Find out the equivalence point potential during the titration of a 0.1M Fe^{2+} solution with 0.1M Ce^{4+} solution. Given $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.77\text{V}$ and $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.57\text{V}$. What is Z-R solution? 3 + 2 = 5
- d) The standard reduction potential of Zn^{2+}/Zn (-0.76 V) and Cu^{2+}/Cu (0.34 V) are widely different, but their simultaneous electrode

position is possible in presence of CN^- . Explain.
Give example of one redox indicator.

$$4+1=5$$

4. Answer any **one** question: $10 \times 1 = 10$

a) Reaction between CaO and P_4O_{10} in molten state is an acid-base reaction – explain. Why CH_3Hg^+ is chosen as a typical soft acid? What do you mean by levelling effect of solvent? What are super acids? Draw the acid base neutralization curve for titration between weak acid by strong base. $2+2+2+2+2=10$

b) MnO_4^- can oxidise Cl^- only in very low pH. Explain. Solutions containing Cu^{2+} readily oxidise KI to I_2 though the standard reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ (0.15V) is higher than that of $\text{I}_2/2\text{I}^-$ (0.54V). Justify. What do you mean by comproportionation reactions? Explain with example. What do you mean by Frost diagram?

$$3+3+2+2=10$$

GROUP-B

(Physical)

[Marks : 20]

5. Answer any **one** question: $1 \times 1 = 1$

a) The rate constant of a reaction has unit $\text{mol dm}^{-3} \text{s}^{-1}$. What is the order of the reaction?

b) Draw the Carnot cycle on the S-T diagram.

6. Answer any **two** questions: $2 \times 2 = 4$

a) What is the maximum possible efficiency of a heat engine that has a hot reservoir of water boiling under pressure at 125°C and a cold reservoir at 25°C ?

b) A spontaneous polymerization reaction is exothermic-Explain.

c) Specific rate constant of a reaction is 0.02 s^{-1} . What is the time for 90% reaction?

7. Answer any **one** question: $5 \times 1 = 5$

a) i) Derive Gibbs-Helmholtz equation. 3

ii) Observed rate constant of a reaction is

$$\text{given by: } K = \frac{(k_1 k_3)^{1/2}}{k_2}$$

Express the overall activation in terms of E_1, E_2, E_3 (E_i is the activation energy associated with K_i) 2

b) i) Show that in a Joule-Thomson expansion there is no change in the enthalpy of the gas. 3

- ii) A first order reaction require 16 min for 75% decomposition. What is the half-life for the process? 2

8. Answer any **one** question: $10 \times 1 = 10$

- a) i) Find the condition of equilibrium and spontaneity of a process in terms of Gibbs free energy and entropy using Clausius inequality. 4

- ii) Calculate the entropy change when Argon at 25°C and 1 atm pressure in a container of volume 500 ml is allowed to expand to 1000ml and it is heated simultaneously at 100°C ($C_v = 12.48 \text{ jmol}^{-1}\text{k}^{-1}$ for Argon at 25°C and 1 atm). 3

- iii) Decomposition of a substance A is studied at two different initial concentration a_1 and a_2 , where $a_1 = 3a_2$. If the observed half-life follow the ratio $T_2:T_1 = 2:1$, find the order of the decomposition process. 3

- b) i) The turnover number of the enzyme fumarase that catalyzes the reaction, $\text{Fumarate} + \text{H}_2\text{O} \longrightarrow \text{L-malate}$, is $2.5 \times 10^3 \text{ s}^{-1}$ and $k_m = 4.0 \times 10^{-6} \text{ mol/L}$. Calculate the rate of conversion of

fumarate to L-malate if fumarase concentration is $10 \times 10^{-6} \text{ mol/L}$ and the fumarate concentration is $2.4 \times 10^{-4} \text{ mol/L}$.

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- ii) A substance decomposes according to second order rate law. If the rate constant is $6.8 \times 10^{-4} \text{ L/mol sec}$, calculate the half-life of the substance when initial concentration is 0.05 mol/L. 3

- iii) Change in free energy (G) is more convenient index for ascertaining spontaneity of process than change in enthalpy (H), internal energy (U) or entropy (S) – Explain. 3