## 4 SEM TDC CHM M 1

2023

( May/June )

## **CHEMISTRY**

(Major)

Course: 401

## ( Physical Chemistry )

Full Marks: 48
Pass Marks: 14

Time: 2 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct option:

 $1 \times 4 = 4$ 

- (a) What is the necessary condition for a reaction to be spontaneous at all temperatures?
  - (i)  $\Delta S$  should be negative and  $\Delta H$  should be positive
  - (ii)  $\Delta S$  should be positive and  $\Delta H$  should be negative
  - (iii)  $\Delta S$  and  $\Delta H$  should be positive
  - (iv)  $\Delta S$  and  $\Delta H$  should be negative

- (b) Which of the following laws states that, "when a system is at absolute zero temperature, its entropy is equal to zero"?
  - (i) Zeroth law of thermodynamics
  - (ii) First law of thermodynamics
  - (iii) Second law of thermodynamics
  - (iv) Third law of thermodynamics
- Hydrogen electrode which is the reference electrode can be used as which of the following?
  - (i) Anode only
  - (ii) Cathode only
  - (iii) Anode or cathode
  - (iv) Salt bridge
- A type of battery which can be charged, discharged into a load and then recharged many times is called
  - (i) rechargeable battery
  - (ii) secondary battery
  - (iii) primary battery
  - (iv) Both (i) and (ii)

- 2. Answer the following questions:
  - (a) State and explain Nernst heat theorem.
  - Write the relationship between molar conductance and specific conductance. Write their SI units.
  - Write a short note Debveon Falkenhagen effect.
  - Write the differences between electrolytic cell and galvanic cell.
  - What do you mean by anomalous transference number?
  - The specific conductivity of 0.01 N solution of KCl 298-K is at 0.0014114 S cm<sup>-1</sup>. If the resistance of the solution is  $725 \Omega$ , then find the cell constant.
- 3. Answer any two of the following questions:  $4 \times 2 = 8$ 
  - Derive an expression for the entropy change for isothermal mixing of ideal gases.
  - Discuss the criteria for spontaneity of a reaction in the light of Gibbs-Helmholtz equation.
  - Discuss how the absolute entropy of a pure substance can be determined using the third law of thermodynamics.

 $2 \times 6 = 12$ 

- **4.** Answer any *three* of the following questions:  $4\times3=12$ 
  - (a) The molar conductances at infinite dilution of HCl, NaCl and NaZ (sodium crotonate) are  $4.25 \times 10^{-2}$ ,  $1.25 \times 10^{-2}$  and  $8.0 \times 10^{-3}$  S m<sup>2</sup> mol<sup>-1</sup> respectively. Calculate the molar conductance of crotonic acid (HZ) at infinite dilution. The specific conductance of a 0.001 M aqueous solution of crotonic acid (HZ) at  $25 \,^{\circ}$ C is  $3.8 \times 10^{-3}$  S m<sup>-1</sup>. Find the degree of dissociation of crotonic acid at  $25 \,^{\circ}$ C.
  - (b) What is transport number? State the Hittorf's rule. How is this rule related to transport number of an ion? 1+1+2=4
  - (c) Write short notes on any two of the following: 2×2=4
    - (i) Asymmetric effect
    - (ii) Wien effect
    - (iii) Walden's rules
  - (d) Write the principle of conductometric titration. Mention the advantages of conductometric titrations. 2+2=4

- **5.** Answer any *two* of the following questions:  $6 \times 2 = 12$ 
  - (a) What are concentration cells? Derive an expression for the e.m.f. of a concentration cell without transference.

    2+4=6
  - (b) Describe how the pH of a solution can be determined with the help of glass electrode.
  - (c) (i) Deduce the Nernst equation for cell potential.
    - (ii) Calculate the e.m.f. of the following cell. Given that the standard potentials of Ag/Ag<sup>+</sup> and Zn/Zn<sup>2+</sup> half cells are +0.80 V and -0.76 V respectively:

 $Zn |Zn^{2+}(0.001 M)| Ag^{+}(0.1 M) |Ag$ 

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6

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3