KATHMANDU UNIVERSITY
End Semester Examination [C]
June/July 2024

Level : B.E./B.Sc./B.Tech
Year : I
Time : 2 hrs. 30 mins.

07 JUL 2024

Course : CHEM 101
Semester : I
F. M. : 55

SECTION "B"
[5Q × 6 = 30 marks]

Attempt *ANY FIVE* questions. ***(Question No- 7 is compulsory)***

1. Complete and balance the following redox reactions. [3+3=6]
   a. $MnO_4^{2-} \longrightarrow MnO_2 + MnO_4^-$ (acid medium)
   b. $PbO_2 + Cl^- \longrightarrow ClO^- + Pb(OH)_3^-$ (basic medium)

2. Define the following terms: [2+2+2=6]
   a. Mole concept
   b. Acid base indicator
   c. System and surroundings

3. Hydrogen and nitric oxide react according to the following equation: [1.5+1.5+1.5+1.5=6]
   $2H_2(g) + 2NO(g) \longrightarrow 2H_2O(g) + N_2(g)$
   Experimentally, it was found that the rate of reaction is first order with respect to hydrogen and second order with respect to nitric oxide.
   i. Write the rate law equation for the reaction for nitric oxide and hydrogen.
   ii. What is the unit of rate constant, k?
   iii. Why are chemists interested in obtaining order of reaction and rate equations?
   iv. Define zero order reaction and find the unit of its rate constant.

4. Explain how equilibrium constant changes with temperature for exothermic and endothermic reaction. [2]
   The enthalpy changes of the following reactions at 27 °C are [1+1+1+1=4]
   i. $Na(s) + ½\ Cl_2(g) \rightarrow NaCl(s)$; $\Delta_f H = -411$ kJ/mol
   ii. $H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(l)$; $\Delta_f H = -811$ kJ/mol
   iii. $2Na(s) + S(s) + 2O_2(g) \rightarrow Na_2SO_4(s)$; $\Delta_f H = -1382$ kJ/mol
   iv. $½\ H_2(g) + ½\ Cl_2(g) \rightarrow HCl(g)$; $\Delta_f H = -92$ kJ/mol
   From the above data, calculate the heat change of reaction at constant volume (in kJ/mol) at 27 °C for the process $2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$.

5. a. For the reaction: [3]
   $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
   The proposed reaction mechanism is

   $Br_2 + M \xrightarrow{K_1} 2Br + M$
   $2Br + M \xrightarrow{K_{-1}} Br_2 + M$ } Fast equilibrium

   $Br_2 + H_2 \xrightarrow{K_2} HBr + H$ (slow)
   $H + Br_2 \xrightarrow{K_3} HBr + Br$ (fast)

   Where,"K_1, K_2, K_3 and K_4 are the rate constant respectively. Deduce the rate law for the above equation

P.T.O.

b. What are the characteristics features of primary and secondary cell? Write the cell reaction for lead storage cell and nickel-cadmium cell. What are the advantages of using Ni-Cd cell over lead storage? [1+2=3]

6. Write the differences between ideal solution and non- ideal solution. With the help of vapour pressure curve, explain that for a solution of volatile solvent and nonvolatile solute, the boiling point is elevated and its freezing point is depressed. [2.5+3.5=6]

7. a. The E^{o} for the cell Zn/Zn^{++} (0.001M) | | Ag^{+} (0.1M)/Ag is 1.56 v. Calculate the emf of the cell. Predict the feasibility of the reaction. [2.5+0.5=3]

b. Define Cp and Cv? Derive the relationship between Cp and Cv? Why is the value of Cp always greater than that of Cv? [1+2+1=4]

SECTION "C"

Attempt *ANY THREE* questions.

8. a. State and explain the second law of thermodynamics. Establish a relation for entropy change for any reversible isothermal expansion of an ideal gas. [2+2=4]

b. What do you mean by 'Enzyme Catalysis'? Discuss the mechanism for enzyme catalysis given by Michaelis-Menten equation. Also predict the kinetics with respect to substrate and enzyme. [1+3=4]

9. Write short notes on(*ANY TWO*) [4+4=8]
   a. Corrosion and ways to prevent corrosion
   b. Different concepts of 'Acids and Bases'
   c. Fuel cell
   d. Phase equilibria and its important features

10. a. Consider a solution of silver nitrate is added slowly to a mixture of solution containing 0.1 M Cl^{-} and 0.01 M CrO_4^{--} in order to carry the selective precipitation. [1+1+1+1=4]
    Answer the following questions.
    i. Define the terms solubility and solubility product.
    ii. Which salt precipitates out first and why?
    iii. Find the concentration of Ag+ ion when first and second salts just start to precipitate.
    iv. Find the concentration of anion of first precipitate when the second salt just starts to precipitate. [Ksp for AgCl : 2.8×10^{-10} and Ksp for Ag_2CrO_4 : 1.9×10^{-12}]

b. Explain cation hydrolysis with an example. [4]

11. a. How is the colour of indicator depends on concentration of H_3O^{+}? Explain the basic working principle of acid base indicators. [4]

b. The enthalpy of a reaction will change on changing temperature. Explain it. [4]

12. a. One gram of mixture of cuprous oxide (Cu_2O) and cupric oxide (CuO) was quantitatively reduced to 0.839 gm of metallic copper. Calculate the weight of CuO in the original sample. Also discuss how do you make use of the fact that copper atom is conserved, in order to solve this problem. [3+1=4]

c. What is a spontaneous process? Deduce a quantitative relation between equilibrium constant (K) and temperature (T) using thermodynamic concept.
Also give a plot of InK versus 1/T for endothermic and exothermic reactions. [1+3=4]

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Registration No.:

Date 07 JUL 2024

SECTION "A"
[20Q. × 1 = 20 marks]

Choose the most appropriate answer and **mark [X]** in the box.

1. Which of the following is independent of the temperature?
   [ ] rate constant
   [ ] rate of reaction
   [ ] equilibrium constant
   [ ] order of reaction

2. Le Chatelier's Principle states that
   [ ] A chemical system seeks the highest entropy
   [ ] A chemical system seeks the lowest enthalpy
   [ ] A chemical system will o change in order to minimize that change
   [ ] All chemical systems come to equilibrium eventually

3. NO gas is produced by the rxn $N_2(g) + O_2(g) \rightarrow 2NO(g)$, $\Delta H = 43.5$Kcal The yield of NO will be maximum at equilibrium state if
   [ ] Temperature and pressure are increased
   [ ] Temperature is decreased and catalyst is used
   [ ] pressure and temperature are reduced
   [ ] temperature is decreased and pressure is increased

4. At 25 ^{0}C the solubility product of CaF_2 is $1.7X\ 10^{-10}$ calculate its so lubility in 0.2M NaF solution. (Consider NaF is a strong electrolyte)
   [ ] 3.49×10^{-4} [ ] 1.31×10^{-5} [ ] 6.515×10^{-5} [ ] 4.25×10^{-9}

5. The pH of a 200 mL solution having 0.01moles of CH_3COOH and 0.2 moles of CH_3COONa is_____ [K_a (CH_3COOH) = $1.85X10^{-5}$]
   [ ] 6.03 [ ] 3.43 [ ] 7.97 [ ] 10.56

6. The significance of the Second Law of Thermodynamics is that for spontaneous processes
   [ ] entropy of the universe is increasing.
   [ ] entropy is the driving force of all chemical reactions.
   [ ] entropy ofan ideal solid does not change.
   [ ] absolute value for entropy can be calculated.

7. In a galvanic ceil between nicker and cobart erectrodes operating at STP
   $Ni \longrightarrow Ni^{++} + 2e^-$ $E^o = -0.25$ volt
   $Co \longrightarrow Co^{++} + 2e^-$ $E^o = -0.27$ volt
   [ ] Co is positively charged
   [ ] Ni acts as anode
   [ ] concentration of Ni^{++} increases
   [ ] Concentration of Co^{++} increases

8. Which one of the following is an example of chain branching reaction?
[ ] $O_2 + M \longrightarrow 2O\cdot$
[ ] $OH\cdot + H_2 \longrightarrow H_2O + H\cdot$
[ ] $O_2 + H\cdot \longrightarrow OH\cdot + O\cdot$
[ ] $H_2O \longrightarrow H_2O_2 + O_2$

9. Which one of the following is conjugate base of the $HCO3^-$?
[ ] HCO_3^- [ ] H_2CO_3 [ ] CO_2 [ ] CO_3^-

10. In galvanic cell, which statement is true?
[ ] oxidation occurs at cathode
[ ] chemical reaction produces the electrical energy
[ ] electrical energy produces the chemical reaction
[ ] reduction occurs at anode

Fill in the blanks with appropriate words and values.

11. Non ideal solution formed by evolution of heat shows_____ deviation from Raoult's law.

12. Molarity of 5.0 m ethanol solution (Density of solution : 0. 95 g/mL) is _____

13. The mathematical relation between osmotic pressure and concentration is _____

14. The entropy change (ΔS) at constant molar heat capacity (Cp) for'n' moles of any material from T_1 to T_2 is given by_____

15. PCl_5 with initial pressure 1.5 atm was dissociated into PCl_3 and Cl_2 at 300°C, (keeping the volume constant). The total pressure at equilibrium becomes 2.84 atm. What will be the pressure of PCl_5 at equilibrium? _____

16. By definition Gibb's free energy, G =_____

17. The enzyme catalysis reaction with low concentration of substrate has_____order.

18. If 10 gm of antimony oxide contain 2.47 gm oxygen, the empirical formula of the antimony oxide is _____ [At Wt of Sb= 121.9]

19. For a particular state transition, the heat change in reversible process is always_____ than in irreversible process.

20. According to Lewis concept, acids are_____

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SECTION "B"
[6 Q. × 5 = 30 marks]

Attempt *ANY FIVE* questions.

1. a. The proposed reaction mechanism for a reaction, $NH_4^+ + HNO_2 \longrightarrow N_2 + 2H_2O + H^+$ is

i) $HNO_2 + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + NO^+$ (fast equilibrium)

ii) $NH_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NH_3 + H^+$ (fast equilibrium)

iii) $NO^+ + NH_3 \xrightarrow{k_3} NH_3NO^+$ (slow)

iv) $NH_3NO^+ \xrightarrow{k_4} H_2O + H^+ + N_2$ (fast)

Write the expression for differential rate law & rate law equation and overall order for this reaction. [0.5+3+0.5]

b. Derive the relation between C_p and C_v for solid, liquid and gas involving reactions. [2]

2. a. For a reaction, $PCl_{5\,(g)} = PCl_{3\,(g)} + Cl_{2\,(g)}$, $K_p = 11.5$ and P_o is 3 atmospheric pressure if no PCl_5 is dissociated. Calculate the equilibrium pressure of PCl_5, PCl_3 & Cl_2 and fraction (f) of PCl_5 dissociated at equilibrium. [3]

b. Find ΔH^o at 398 K for the reaction, $CO + \frac{1}{2}O_2 \longrightarrow CO_2$. [3]

Given, $\Delta H^\circ_{298} = -67{,}640$ cal, $C_p(CO) = 6.97$, $C_p(O_2) = 7.05$ and $C_p(CO_2) = 8.96$

3. Give reasonable explanations (***ANY THREE***) [2+2+2]
   a. The osmotic pressure is colligative properties of dilute solution.
   b. The standard cell potential (ΔE°) represents the driving force of the chemical reaction.
   c. The colour of acid-base indicator in solution will depend on the concentration of H_3O^+.
   d. Heat is not a state function.

4. Differentiate between (***ANY THREE***) [2+2+2]
   a. Order of reaction and molecularity of reaction
   b. Rate constant and equilibrium constant
   c. Galvanic cell and concentration cell
   d. Ideal solution and non-ideal solution

P.T.O.

5. a. Balance the following redox reactions by ion-electron method. [2+2]

$$CuS + NO_3^- = Cu^{2+} + SO_4^{2-} + NO \quad \text{(Acidic medium)}$$

$$[Cu(NH_3)_4]^{2+} + S_2O_4^{2-} = SO_3^{2-} + Cu + NH_3 \quad \text{(Basic medium)}$$

b. Show that, $pH + pOH = 14$ [2]

6. a. How do you calculate the absolute entropy of a gaseous substance at 200°C if it melts at 0°C and evaporates at 100°C? [2]

b. A 0.596 g sample of a gaseous compound containing only boron and hydrogen occupies 484 cc at 273 K and 1-atm pressure. When the compound was ignited in excess oxygen, all its hydrogen was recovered as 1.17 g of H_2O and all the boron was present as B_2O_3. What is empirical formula, molecular formula and molecular weight of boron-hydrogen compound? [4]

7. a. The vapor pressure of a dilute aqueous solution is 23.45 mm at 25°C, whereas the vapor pressure of pure water at this temperature is 23.76 mm. Calculate the molal concentration of solute and boiling point of the solution. (K_b for water = 0.51) [3]

b. The $\Delta E^\circ = -0.32$ volt for the reaction, $Fe + Zn^{2+} = Zn + Fe^{2+}$. What is the equilibrium concentration of Fe^{2+} when a piece of iron is placed in a 1 M Zn^{2+} solution? [3]

SECTION "C"
[25 marks]

Attempt *ANY THREE* questions. **Question No. 8 is compulsory.**

8. a. Define enzyme catalysis with an example. Derive the Michaelis-menten equation for enzyme catalysis and explain its kinetics. [1+3]

b. Establish the relation, $\Delta E = \Delta E^\circ - \frac{0.059}{n} \log Q$, where notations have their usual meaning.

Also, derive the relation between equilibrium constant (K) and standard cell potential (ΔE°) at equilibrium condition. [3+2]

9. a. What is meant by cationic hydrolysis? Derive the relation between hydrolysis constant, ionic product of water and dissociation constant of weak base. [1+3]

b. Show that the work done on a system in a reversible process is less than in the corresponding irreversible process between the same two states. [4]

10. a. Derive the integrated rate law equation for second order reaction and also find its half life time. [2+1]

b. Explain the mechanism of basic buffer solution to resist the change in pH due to the addition of strong acid and base? [3]

c. How can you measure the single electrode potential experimentally? Explain with an example. [2]

11. a. State and explain the second law of thermodynamics. [1+3]
    b. State Raoult's law of dilute solution. Show how a negative deviation from raoult's law occurs in non-ideal solution made from two volatile components? [1+3]

12. Write short notes on (***ANY FOUR***) [4×2= 8]
    a. Fuel cell
    b. Chain reaction
    c. Selection of acid-base indicators
    d. Natures of chemical equilibrium
    e. Lewis acid and base
    f. Electrochemical theory of rusting of iron