

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.  $\text{MnO}_4^{2-} \longrightarrow \text{MnO}_2 + \text{MnO}_4^-$  (acid medium)  
b.  $\text{PbO}_2 + \text{Cl}^- \longrightarrow \text{ClO}^- + \text{Pb(OH)}_3^-$  (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]  
 $2\text{H}_2(\text{g}) + 2\text{NO}(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$   
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.  $\text{Na}(\text{s}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$ ;  $\Delta_f H = -411 \text{ kJ/mol}$   
ii.  $\text{H}_2(\text{g}) + \text{S}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{l})$ ;  $\Delta_f H = -811 \text{ kJ/mol}$   
iii.  $2\text{Na}(\text{s}) + \text{S}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{Na}_2\text{SO}_4(\text{s})$ ;  $\Delta_f H = -1382 \text{ kJ/mol}$   
iv.  $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$ ;  $\Delta_f H = -92 \text{ kJ/mol}$   
From the above data, calculate the heat change of reaction at constant volume (in kJ/mol) at 27 °C for the process  $2\text{NaCl}(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Na}_2\text{SO}_4(\text{s}) + 2\text{HCl}(\text{g})$ .

5. a. For the reaction: [3]  
 $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g})$   
The proposed reaction mechanism is  
$$\left. \begin{array}{l} \text{Br}_2 + \text{M} \xrightarrow{K_1} 2\text{Br} + \text{M} \\ 2\text{Br} + \text{M} \xrightarrow{K_{-1}} \text{Br}_2 + \text{M} \end{array} \right\} \text{Fast equilibrium}$$
  
$$\begin{array}{l} \text{Br}_2 + \text{H}_2 \xrightarrow{K_2} \text{HBr} + \text{H} \text{ (slow)} \\ \text{H} + \text{Br}_2 \xrightarrow{K_3} \text{HBr} + \text{Br} \text{ (fast)} \end{array}$$

Where, "K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> and K<sub>4</sub> are the rate constant respectively. Deduce the rate law for the above equation

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- 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  $E^\circ$  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  $C_p$  and  $C_v$ ? Derive the relationship between  $C_p$  and  $C_v$ ? Why is the value of  $C_p$  always greater than that of  $C_v$ ? [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]
- Corrosion and ways to prevent corrosion
  - Different concepts of 'Acids and Bases'
  - Fuel cell
  - 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  $0.01 M CrO_4^{2-}$  in order to carry the selective precipitation. [1+1+1+1=4]  
Answer the following questions.
- Define the terms solubility and solubility product.
  - Which salt precipitates out first and why?
  - Find the concentration of  $Ag^+$  ion when first and second salts just start to precipitate.
  - Find the concentration of anion of first precipitate when the second salt just starts to precipitate. [ $K_{sp}$  for  $AgCl : 2.8 \times 10^{-10}$  and  $K_{sp}$  for  $Ag_2CrO_4 : 1.9 \times 10^{-12}$ ]
- 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 ( $\text{Cu}_2\text{O}$ ) and cupric oxide ( $\text{CuO}$ ) was quantitatively reduced to 0.839 gm of metallic copper. Calculate the weight of  $\text{CuO}$  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  $\ln K$  versus  $1/T$  for endothermic and exothermic reactions. [1+3=4]





8. Which one of the following is an example of chain branching reaction?

- $O_2 + M \longrightarrow 2O\cdot$   
  $OH\cdot + H_2 \longrightarrow H_2O + H\cdot$   
  $O_2 + H\cdot \longrightarrow OH + O\cdot$   
  $H_2O \longrightarrow H_2O_2 + O_2$

9. Which one of the following is conjugate base of the  $HCO_3^-$ ?

- $HCO_3^-$                         $H_2CO_3$                         $CO_2$                         $CO_3^{2-}$

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 ( $\Delta S$ ) at constant molar heat capacity ( $C_p$ ) 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  $300^\circ C$ , (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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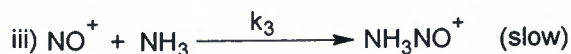
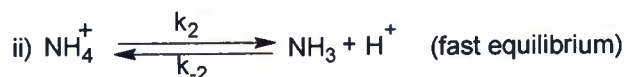
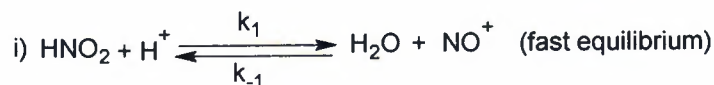
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SECTION "B"  
[6 Q. × 5 = 30 marks]

Attempt ANY FIVE questions.

1. a. The proposed reaction mechanism for a reaction,  $\text{NH}_4^+ + \text{HNO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{H}^+$  is



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,  $\text{PCl}_5(\text{g}) = \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ ,  $K_p = 11.5$  and  $P_0$  is 3 atmospheric pressure if no  $\text{PCl}_5$  is dissociated. Calculate the equilibrium pressure of  $\text{PCl}_5$ ,  $\text{PCl}_3$  &  $\text{Cl}_2$  and fraction (f) of  $\text{PCl}_5$  dissociated at equilibrium. [3]
- b. Find  $\Delta H^\circ$  at 398 K for the reaction,  $\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$ . [3]
- Given,  $\Delta H_{298}^\circ = -67,640$  cal,  $C_p(\text{CO}) = 6.97$ ,  $C_p(\text{O}_2) = 7.05$  and  $C_p(\text{CO}_2) = 8.96$

3. Give reasonable explanations (ANY THREE) [2+2+2]
- The osmotic pressure is colligative properties of dilute solution.
  - The standard cell potential ( $\Delta E^\circ$ ) represents the driving force of the chemical reaction.
  - The colour of acid-base indicator in solution will depend on the concentration of  $\text{H}_3\text{O}^+$ .
  - Heat is not a state function.
4. Differentiate between (ANY THREE) [2+2+2]
- Order of reaction and molecularity of reaction
  - Rate constant and equilibrium constant
  - Galvanic cell and concentration cell
  - Ideal solution and non-ideal solution

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

$$\text{CuS} + \text{NO}_3^- = \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{NO} \quad (\text{Acidic medium})$$

$$[\text{Cu}(\text{NH}_3)_4]^{2+} + \text{S}_2\text{O}_4^{2-} = \text{SO}_3^{2-} + \text{Cu} + \text{NH}_3 \quad (\text{Basic medium})$$
- b. Show that,  $\text{pH} + \text{pOH} = 14$  [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<sub>2</sub>O and all the boron was present as B<sub>2</sub>O<sub>3</sub>. 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<sub>b</sub> for water = 0.51) [3]  
 b. The  $\Delta E^\circ = -0.32$  volt for the reaction,  $\text{Fe} + \text{Zn}^{2+} = \text{Zn} + \text{Fe}^{2+}$ . What is the equilibrium concentration of Fe<sup>2+</sup> when a piece of iron is placed in a 1 M Zn<sup>2+</sup> 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 ( $\Delta E^\circ$ ) 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

