KATHMANDU UNIVERSITY
End Semester Examination [C]
November/December, 2023

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

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

SECTION "B"
[31 marks]

Attempt *ANY FIVE* questions. ***(Q.N. 2 is compulsory)***

1. a. The proposed reaction mechanism for the reaction

$$NH_4^+ + HNO_2 \longrightarrow N_2 + 2H_2O + H^+ \quad \text{is :}$$

$HNO_2 + H^+ \rightleftharpoons H_2O + NO^+$ (rapid equilibrium)
$NH^+_4 \rightleftharpoons NH_3 + H^+$ (rapid equilibrium)
$NO^+ + NH_3 \longrightarrow NH_3NO^+$ (slow)
$NH_3NO^+ \longrightarrow H_2O + H^+ + N_2$ (fast)

where, $K_1$, $K_{-1}$, $K_2$, $K_{-2}$, $K_3$ and $K_4$ are rate constants respectively.
Answer the following questions.

i. Which step is the rate determining step and why? [1]
ii. Write down the rate law for the overall reaction which is consistent with the above mechanism. [3]

b. The vapor pressure of benzene and toluene are 75 mm and 22 mm at 20°C. If the solution is prepared by mixing benzene and toluene with their mole fraction $X_B$=0.33 and $X_T$=0.67, then calculate composition of benzene and toluene in vapor phase in the unit of mole fraction. [2]

2. a. Consider the following reaction

$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$.

The equilibrium constant (Kp) is 11.5 at 300°C and the pressure ($P^o$) of $PCl_5$ before dissociation is 1.5 atm.
Answer the following questions.

i. Predict the effect of introduction of inert gas in the equilibrium of above reaction. [1]
ii. Calculate the equilibrium pressure of $PCl_3$. [1]
iii. Calculate the fractional amount (f) of $PCl_5$ that undergoes the dissociation. [1]
iv. What is the equilibrium pressure of $PCl_5$ if 1.5 atm. of $Cl_2$ is added to the above reaction mixture? [1]

b. What is concentration cell? Mention the application of Nernst equation. [3]

3. Give the reasonable explanations. [3×2=6]

a. The reaction rate for enzyme catalysis changes from first to zero order with respect to substrate as its concentration is increased.

b. Weaker the acid, stronger is its conjugate base and vice-versa.

c. Work done during the isothermal reversible expansion of ideal gas is less that that for irreversible process.

4. a. Define second order reaction. Deduce the integrated rate law for it and also show that half-life period for this reaction depends upon the initial concentration of the reactant. [0.5+2.5 =3]

b. Complete and balance the following redox reactions by ion-electron method. [2 × 1.5 = 3]

i. $CuS + NO_3^- = Cu^{2+} + SO_4^{2-} + NO$ (Acidic medium)

ii. $P_4 + OH^- = PH_3 + H_2PO_2^-$ (Basic medium)

5. a. Distinguish between the followings (at least two points). [3 × 1 = 3]

i. Molarity and molality

ii. Order and molecularity of a reaction

iii. Spontaneous and non-spontaneous process

b. State the First law of Thermodynamics. Show that change in internal energy is equal to the heat absorbed on carrying the reaction at constant volume. [3]

6. a. Consider that a solution of silver ion ($Ag^+$) has been added slowly to mixture of solution containing 0.1M $Cl^-$ and 0.01M $CrO_4^{--}$ concentration in order to carry out selective precipitation.
(Given Ksp for $[Ag+].[Cl^-] = 2.8 \times 10^{-10}$ ; Ksp for $[Ag+]^2.[CrO4^{--}] = 1.9 \times 10^{-12}$).

Answer the following questions

i. Define the term 'selective precipitation' and its application. [1]

ii. Which salt precipitates out at first and why? [1]

iii. Find the concentration of $Ag^+$ ion when first and second salts just start to precipitate out. [1]

b. How would you show that the elevation of boiling point depends on the molal concentration of a dilute solution containing non-volatile solute? [3]

7. a. 'If a reaction is multiplied by a factor, its equilibrium constant must be raised to a power equal to that factor in order to obtain the equilibrium constant for the new reaction'. Prove this statement with required expressions. [2]

b. The following table shows $\Delta G°_f$, $\Delta H°_f$ and $S°$ for four substances.

| | $\Delta H°_{298}$(kcal/mole) | $\Delta G°_{298}$(kcal/mole) | $S°_{298}$ (cal/mole-deg or eu) |
|---|---|---|---|
| CO | -26.42 | -32.79 | 47.3 |
| $CO_2$(g) | -94.05 | -94.24 | 51.1 |
| $H_2O$ (g) | -57.80 | -54.64 | - |
| $H_2$ (g) | - | - | 31.2 |

For the reaction $H_2O$ (g) + CO (g) = $H_2$(g) + $CO_2$ (g)

Answer the following questions.

i. Calculate the $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the above reaction. [2]
ii. What is $\Delta E°_{298}$ for the reaction? [1]
iii. Find the absolute entropy of $H_2O$(g) at 298° K. [1]

8. a. A mixture of KBr and NaBr weighing 0.56 gm was treated with aqueous Ag+ and all the bromide ion was recovered as 0.97 gm of pure AgBr. What was the fraction by weight of KBr in the original sample? (Ag = 107.868, Br = 79.904, K = 39.0983 and Na = 22.990) [3]

b. Define molar heat capacity. Why Cp is greater than Cv? [1+2=3]

## SECTION "C"

[3Q × 8 = 24 marks]

*Attempt ANY THREE questions.*

9. a. Define the term Enzyme Catalysis. Derive an equation to show the reciprocal of the reaction rate of enzyme catalysis as a linear function of the reciprocal of the substrate concentration as keeping total amount of enzyme constant, and plot it. [1+3]

b. What do you mean by hydrolysis? Deduce the relation, $K_h = K_w/K_b$, where symbols have their usual meanings. [4]

10. a. What do you mean by standard enthalpy change? Deduce the relation $\Delta H_2 - \Delta H_1 = \Delta Cp\ (T_2 - T_1)$, where notations have their usual meanings. [4]

b. Define the term 'buffer solution'. Discuss the mechanism of buffer action of acidic and basic buffer solutions. [1+3=4]

11. a. Derive the equation, $K = e^{\Delta S°/R} \times e^{-\Delta H°/RT}$, where symbols have their usual meanings. Also, correlate K with $\Delta S°$ and $\Delta H°$ in terms of molecular chaos and energy. [3+1=4]

b. Define non-ideal solution. Describe the non-ideal solution showing positive deviation from Raoult's law with suitable example. [1+3=4]

12. a. State the 3rd law of thermodynamics. Deduce the equation for the absolute entropy of any gas at temperature (T) above the boiling temperature by applying this law. [1+3=4]

b. State Le-Chatelier Principle. Discuss four factors which may contribute to increase equilibrium concentration of product for the following reactions with proper illustrations. [4]

$$N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g); \qquad \Delta H = -23.5 \text{ kcal}$$

13. Write short notes on followings (*ANY TWO*). [4+4=8]

a. Selection of suitable indicators for acid-base titrations.
b. Corrosion of iron and its preventive measures.
c. Chain reaction and polymerization of vinyl chloride.
d. Different concepts of 'acids and bases'.