UNIVERSITY OF JAFFNA, SRILANKA

BACHELOR OF PHARMACY

SECOND YEAR SECOND SEMESTER EXAMINATION – February 2018

PHACH 2224 PHARMACEUTICAL CHEMISTRY III

DATE: 08.03.2018 **TIME: 3 Hours.**

ANSWER TO ALL SIX QUESTIONS.

1.

1.1. Derive the equation for the base dissociation constant (pKb) of a weak base, B. (10 Marks)

1.2. Calculate the concentration of diprotic acid in water at pH of 6.4. (Assume that first and second ionization of this acid are complete.) (20 Marks)

1.3.

1.3.1. Find out the pH of a mixture that contains 0.45M weak acid, HA_1 and 0.25M weak acid, HA_2 at 25^0C. (Ka of $HA_1 = 5.4X10^{-5}$ and Ka of $HA_2 = 6.8X10^{-14}$) (10 Marks)

1.3.2. Find out the concentration of A_2^- of solution mentioned in 1.3.1. (10 Marks)

1.4.

1.4.1. Derive the Henderson-Hassel balch equation for weak acid, HA. (10 Marks)

1.4.2. 50ml of 0.25M ammonia solution was titrated with 0.5M $HClO_4$. Calculate the following.

1.4.2.1. Initial pH of the ammonia solution. (10 Marks)

1.4.2.2. Required volume of acid to neutralize the ammonia solution. (10 Marks)

1.4.2.3. pH of the ammonia solution after the addition of 10ml of $HClO_4$. (20 Marks)

2.

2.1. State the 'Rate law' (10 Marks)

2.2. Derive the following equations for

2.2.1. Integrated rate law for first order reaction (15 Marks)

2.2.2. Half- life of the second order reaction (10 Marks)

2.3. Half-lives of a chemical reaction were 452 seconds and 770 seconds, when initial concentrations of the reactants were 6.85M and 5.25M respectively. Find out the order of the reaction. (25 Marks)

2.4. Consider the following reaction.

$$F_2(g) + 2ClO_2(g) \longrightarrow 2FClO_2(g)$$

The above reaction was carried out with different concentrations of reactants in three different experiments at certain temperature. The measured initial rates and used concentrations of reactants are given in the table below.

Experiment	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1	1.25×10^{-3}	1.5×10^{-3}	1×10^{-5}
2	2.5×10^{-3}	1.5×10^{-3}	2×10^{-5}
3	2.5×10^{-3}	3.0×10^{-3}	4×10^{-5}

Calculate the following for this reaction.

2.4.1. Over all reaction order (20 marks)

2.4.2. Rate constant (10 marks)

2.4.3. Rate of the reaction when $[F_2] = 12.0 \times 10^{-3}$ *M* and $[ClO_2] = 6.0 \times 10^{-3}$ *M*. (10 Marks)

3.

3.1. Define the following terms used in thermodynamics.

3.1.1. Adiabatic expansion (10 Marks)

3.1.2. Isolated system (10 Marks)

3.2. State the zeroth law and first law of thermodynamics. (20 Marks)

3.3. The amount of work done during the conversion of two moles of liquid water into two moles of water vapour at 373K under 1 atm pressure was - 6.1974 kJ. Calculate the change in internal energy of this conversion. (Heat of vapourization of water is 40.82kJ/mol) (15 Marks)

3.4. The internal energy change during the isochoric decomposition of Tri nitro toluene (TNT) at 350 K is - 5.975 kJ. Decomposition of TNT is given below.

$$C_7H_5N_3O_{6(s)} + 4O_{2(g)} \longrightarrow 3/2\ N_{2(g)} + 5/2\ H_{2(g)} + 7H_2O_{(g)}$$

Calculate the enthalpy change of the the decomposition of TNT (Assume that all the gases follow the ideal gas behavior and TNT has negligible volume relative to gases. $R = 8.314\ J\ mol^{-1}K^{-1}$) (25 Marks)

3.5 Five (05) moles of an ideal gas at the temperature of 450 K and pressure of 12 atm undergoes isothermal expansion that occurs irreversibly against 3 atm external pressure. Calculate the work done by the surroundings. (20 Marks)

4.

4.1. Define the following terms.

4.1.1. Electromotive force (10 Marks)

4.1.2. Inert Electrodes (10 Marks)

4.2. List the reasons for the presence of salt bridge in galvanic cell? (15 Marks)

4.3. A galvanic cell was constructed using standard chromium and standard lead electrodes and their reduction potentials are given below.

$E^0 (Cr^{3+}/Cr) = -0.74V$ $E^0 (Pb^{2+}/Pb) = -0.14V$

4.3.1. Write the balanced equations for half- cell reactions and overall reaction. (10 Marks)

4.3.2. Write the standard short hand cell notation for this galvanic cell. (10 Marks)

4.3.3. Find out the Gibbs free energy change of this cell at 25^0C. ($F= 96500\ Cmol^{-1}$) (10 Marks)

4.3.4. Find out the equilibrium constant (K) of above mentioned reaction in 4.3.1 at 27^0C ($R = 8.314\ Jmol^{-1}K^{-1}$). (10 Marks)

4.4. Briefly explain the electrolysis of fused NaCl and aqueous NaCl solutions using carbon electrodes. (25 Marks)

5.

5.1. Define the following terms used in phase rule.

5.1.1. Phase (05 marks)

5.1.2. Component (05 marks)

5.1.3. Degree of freedom (05 marks)

5.2. Find out the number of degrees of freedom for the following systems.

5.2.1. Sulphur system (10 Marks)

5.2.2. A system in which ammonium chloride undergoes thermal decomposition. (10 Marks)

5.3. List the advantages and limitations of the phase rule. (25 marks)

5.4. Draw the temperature versus composition curve for

5.4.1. Ideal solution (10 Marks)

5.4.2. Solution with positive deviation (10 Marks)

5.5. An ideal solution contained liquids of 20g of A and 45g of B. It was boiled at 80^0C under 1 atm. Relative molecular mass of A was 20g/mol. Find out the relative molecular mass of B.

(P^0_A=1000mmHg and P^0_B= 600mmHg at 80^0C) (20 Marks)

6.

6.1. Define the terms 'solubility' and 'solubility product'. (15 Marks)

6.2. A solution contains $Mn(OH)_2$ with 0.040 M NaOH. Calculate the molar solubility of $Mn(OH)_2$ in this solution.
(Solubility product of $Mn(OH)_2$ is $1.6x10^{-13}$ mol^3dm^{-9}.) (15 Marks)

6.3. ECl and XCl_2 are dissolved together in water. Find out the equilibrium concentration of $[E^+]$, $[X^{2+}]$ and $[Cl^-]$ of this solution.
(Assumed that ECl and XCl_2 are sparingly soluble ionic substances. Solubility products of ECl and XCl_2 are $5.9X10^{-12}$ M^2 and $4.75X10^{-8}$ M^3 respectively at 300 K) (20 marks)

6.4. Briefly explain the factors that affect the rate of the reaction. (30 Marks)

6.5. Derive the Langmuir adsorption equation. (10 Marks)

6.6. List the assumptions that are required to use Langmuir adsorption isotherm. (10 Marks)

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