

UNIVERSITY OF JAFFNA, SRILANKA

BACHLOR OF PHARMACY

SECOND YEAR SECOND SEMESTER (N/S) EXAMINATION-JAN 2013

PHACH 2201 – PHARMACEUTICAL CHEMISTRY III

Date:19.02.2013

Time: 3Hours

Answer All Six Question.

Answer Part A and Part B in a separate answer book.

Part A

1.

- 1.1 State the phase rule and explain the terms involved in it. (30 Marks)
- 1.2 Calculate the number of phase, the number of components and the number of degree of freedom in each of the following cases.
- 1.2.1 A mixture of  $\text{CaCO}_3$  (s),  $\text{CaO}$  (s) and  $\text{CO}_2$ (g) at random amount. (10 Marks)
- 1.2.1 A mixture of  $\text{CaCO}_3$  (s),  $\text{CaO}$  (s) and  $\text{CO}_2$ (g) taken at random amount but allowed to equilibrate. (10 Marks)
- 1.2.3 A saturated solution of  $\text{Na}_2\text{SO}_4$  with excess of the solid present and at equilibrium with its vapour. (10 Marks)
- 1.3 The solubility product,  $K_{sp}$ , of  $\text{Ag}_2\text{CrO}_4$  is  $9.0 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$  at  $25^\circ\text{C}$ .
- 1.3.1 Calculate the solubility of  $\text{Ag}_2\text{CrO}_4$ , in a 0.1M solution of  $\text{AgNO}_3$ . (10 Marks)
- 1.3.2 A 200 ml of  $1.5 \times 10^{-3} \text{ mol/l}$   $\text{AgNO}_3$  is mixed with 100ml of  $2.5 \times 10^{-5} \text{ mol/l}$   $\text{Na}_2\text{CrO}_4$  solution. will precipitate occur? (30 Marks)

2.

- 2.1 If concentrations are measured in  $\text{mol l}^{-1}$  and time in s, what are the units of the rate constant for the following? Explain.
- 2.1.2 First order reaction (15 marks)
- 2.1.2 Second order reaction (15 marks)
- 2.2 Show that the half life of a zero order reaction is depend and the initial concentration of the reactant. (30 marks)
- 2.3 Briefly explain the factors affecting the rate of a reaction. (40 marks)

Part B

3.

- 3.1 3.1.1 Prove that the Joule-Thompson expansion is an isoenthalpic process and define the Joule-Thompson co-efficient.
- 3.1.2 Assuming  $H=f(P,T)$  show that
- $$\mu_{JT} = -\frac{1}{C_P} \left( \frac{\partial H}{\partial P} \right)_T$$
- 3.1.3 For  $\text{CO}_2$ ,  $\mu_{JT}=1.40 \text{ Katm}^{-1}$  in the pressure range of 2-16 atm. If  $\text{CO}_2$  at  $35^\circ\text{C}$  undergoes a Joule-Thompson expansion from 16 to 2 atm, calculate the final temperature attained by the gas. (50 Marks)
- 3.2 Drive the Clapeyron equation:

$$\frac{\partial P}{\partial T} = \frac{\Delta H_{trans}}{T \Delta V_{trans}}$$

for a phase transition.

Hence derive the Clausius-Clapeyron equation :

$$\frac{\partial \ln P}{\partial T} = \frac{\Delta H_{vap}}{RT^2}$$

for a liquid-vapour equilibrium. (50 Marks)

4.

4.1 Distinguish between reversible and irreversible process. An ideal gas expands isothermally from an initial pressure  $P_1$  to final pressure  $P_2$ . Show that the maximum work is done by the gas when it expands reversibly. The pressure on 1.00 mol helium is reduced reversibly at 25°C from 10.0 atm to 1.00 atm. Calculate (i)  $q$ , (ii)  $w$ , (iii)  $\Delta H$  and (iv)  $\Delta U$ . (assume that He gas behaves ideally) (50 Marks)

4.2 Write down the criteria for spontaneity, equilibrium and non spontaneity for a process in terms of entropy.

How would you calculate the entropy changes for an isochoric temperature change, an isobaric temperature change and a reversible adiabatic process. (50 Marks)

5.

5.1 Define the following symmetry elements and explain the corresponding operation with an example.

Identity (ii) Inversion centre (iii) Rotation axis (iv) Mirror plane (V) Rotation reflection axis

(40 Marks)

5.2 Give the shape and list all the symmetry elements present in the following molecules. (20 Marks)

(i)  $\text{SO}_3$  (ii)  $\text{Ni}(\text{CO})_4$  (iii)  $\text{CH}_4$  (iv)  $\text{SF}_6$

5.3 Sketch the following planes in a three dimensional cubic structure. (20 Marks)

(i) (011) (ii) (111) (iii) (100) (iv) (311)

5.4 Find the Miller indices of the planes that intersect the crystal axes at the distances (20 Marks)

(i)  $(2a, 3b, c/2)$  (ii)  $(3a, b/2, \infty)$  (iii)  $(3a, 5b, c)$  (iv)  $(a, 2b, c)$

6.

6.1 Consider an elementary reaction of the form  $A + 2B \rightarrow C + D$

6.1.1 Write down the rate expression for this reaction

6.1.2 What is the molecularity and overall order?

6.1.3 Derive the integrated form of this rate equation; given that the initial concentration of A is  $a$  and that of B is  $2a$

6.1.4 Derive the SI unit of the rate constant. (40 Marks)

6.2 Consider the following elementary reaction  $A + A \rightarrow \text{products}$

Derive the integrated rate equation for the above reaction. Hence show that the half-life of the above reaction is inversely proportional to the initial concentration of the reactant. (35 Marks)

6.3 Briefly describe the factors affecting the rate of a chemical reaction. (25 Marks)