MANIPAL UNIVERSITY

Reg. No.										

Deemed- to -be -University under Section 3 of the UGC Act, 1956

DEPARTMENT OF SCIENCES, I SEMESTER M.Sc. (CHEMISTRY)
END SEMESTER EXAMINATIONS, Nov/Dec 2017

PHYSICAL CHEMISTRY I [CHM 4105]

(REVISED CREDIT SYSTEM-2017)

Time: 3 Hours Date: 21/11/2017 MAX. MARKS: 50

Note: (i) Answer all FIVE FULL questions

(ii) Draw diagrams, and write equations wherever necessary

1. A. (i) With suitable graphical representation, explain the concentration variation profile of a consecutive reaction. What is meant by induction time in consecutive reaction?
(ii) Half-life for disintegration of radium is 1590 years. Calculate the rate constant in sec^{-1}. How many years will be taken for the disintegration of 80 %?

B. Derive the rate expression for the branched chain reactions. Deduce the conditions for explosion. **[4+6]**

2. A. (i) With suitable equations and examples show that different types of adsorptions from the solutions can be predicted with the help of Gibbs adsorption isotherm.
(ii) What is Hammett equation? How is it used to arrive at linear Gibbs free energy relationship?

B. What are Arrhenius and van't Hoff complexes in homogeneous catalysis? Under protolytic condition, apply steady state treatment and derive an expression for rate of acid base catalysis. **[4 +6]**

3. A (i) Two second order reactions have identical pre-exponential factors and activation energies differing by 20.0 kJ mol^{-1}. Assuming that the activation energies are temperature independent calculate the ratio of their rate constants at (a) 273 K and (b) 1273 K.
(ii) Calculate the thickness of the ionic atmosphere in a 0.01 M and 0.001 M KBr solution at 25° C. Comment on the results. Given dielectric constant of water is 78.5.

B. Write explanatory note on the following:
(i) Effect of dielectric constant and ionic strength on reactions in solutions.
(ii) Stern model for electrical interface. **[4+6]**

P.T.

4.A. (i) Deduce the integrated form of Clausius – Clapeyron equation as applied to solid ↔ liquid equilibrium.

(ii) Draw and explain with a suitable example the phase diagram for a system of two salts and water of the type crystallization of pure components only

B. What are fundamental property relations? Mention its significance. Deduce Maxwell's relationships from fundamental property relationship.

[4+6]

5. A. (i) Define the term fugacity. Mention its physical significance.

(ii) Calculate the ΔG of the following reaction and predict whether it would be feasible at standard state or not.

$\frac{1}{2} H_2$ (g) + $\frac{1}{2} I_2$ (g) $\rightarrow$ HI (g) where S of H_2, I_2 and HI are 131.2, 114.3 and 207.3 Joules /mole. Given $\Delta H = 26.1$ kJ/mole.

B. Deduce Gibbs- Duhem equation from chemical potential concept. Give its significance. [4+6]

****