MANIPAL UNIVERSITY

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DEPARTMENT OF SCIENCES, I SEMESTER M.Sc. (CHEMISTRY)
END SEMESTER EXAMINATIONS, December, 2017

PHYSICAL CHEMISTRY I [CHM 4105]

(REVISED CREDIT SYSTEM-2017)

Time: 3 Hours Date: 23.12.2017 MAX. MARKS: 50

Note: (i) Answer **all FIVE FULL** questions

(ii) Draw diagrams, and write equations wherever necessary

1 A **(i)** Write the mechanism, and mathematical expression for kinetics of formation of hydrogen bromide from hydrogen and bromine, and show that reaction follows fractional order.

(ii) A reaction is 50% complete in 10 minutes. It is allowed to proceed another 5 minutes. How much of the reaction would be complete at the end of these 15 minutes, if the reaction follows zero order kinetics?

B. State and explain steady state principle. Demonstrate the use of this principle in evaluation of the kinetics and mechanism of pyrolysis of ethane. **[4+ 6]**

2. A **(i)** With appropriate mathematical equations and graphical representation, prove that Freundlich adsorption isotherm is a special case of Langmuir adsorption isotherm.

(ii) Explain the effect of temperature and pH on the enzyme catalysis.

B. How are the protolytic and prototropic mechanisms of acid-base catalysis different? By applying Arrhenius treatment derive mathematical expression for rate of specific acid catalysis. **[4+ 6]**

3. A **(i)** A reaction is 25 % complete in 25 minutes. If it follows first order kinetics, what would be the concentration at the end of another 50 minutes? The initial concentration is 2×10^{4} mol dm^{-3}

(ii) State the Nernst heat theorem. Give its significance.

B Write an explanatory note on the following:

(i) Thermodynamic formulation of CTST

(ii) Wein effect and Debye- Falkenhagen effect **[4+6]**

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4. A. **(i)** The latent heat of vaporization of benzene at its boiling point (80 °C) is 7,413 cal mol^{-1}. What is the vapour pressure of benzene at 27° C?

(ii) What is plait point in a 3 component phase diagram? Explain with a suitable example.

B. Discuss the Bjerrum theory of ion association in electrolytic solutions. List the outcomes of the theory **[4+6]**

5. A. **(i)** Construct a phase diagram for acetic acid –chloroform-water system and apply the phase rule to it.

(ii) The free energy change ΔG accompanying a given process is – 65.77 kJ at 25°C and −63.68 kJ at 35°C. Calculate the change in enthalpy for the process at 30° C.

B. Discuss the thermodynamic treatment of electrified interfaces leading to the derivation of the Lippmann equation.

[4+6]

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