MANIPAL
ACADEMY of HIGHER EDUCATION
(Deemed to be University under Section 3 of the UGC Act, 1956)

Reg. No.										

DEPARTMENT OF SCIENCES, I SEMESTER M.Sc (CHEMISTRY)
END SEMESTER EXAMINATIONS, NOVEMBER 2018

PHYSICAL CHEMISTRY I [CHM- 4105]
(REVISED CREDIT SYSTEM-2017)

Time: 3 Hours Date: 23rd Nov 2018 MAX. MARKS: 50

Note: (i) Answer **ALL** questions
(ii) Draw diagrams, and write equations wherever necessary

1A. **(i)** Starting from Hammett equation, arrive at linear Gibbs energy relationships. What is the limitation of Hammett equation?

(ii) A first order reaction is 50% completed in 30 min at 300 K and in 10 min at 320 K. Calculate the reaction rate constant at 300 K and energy of activation of the reaction.

B. Compare the assumptions of Langmuir and B.E.T adsorption isotherm. Write B.E.T adsorption isotherm and explain its use in the determination of surface area of the catalyst. **[4 + 6]**

2A **(i)** Explain the use of potential energy diagram in understanding CTST

(ii) A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of catalyst at the same rate, temperature required is 400 K. Calculate the activation energy of the reaction if the temperature lowers the activation barrier by 20 kJ mol^{-1}.

B. Write the reaction scheme and mechanism for gas phase combustion of hydrogen. Derive rate expression, and explain reason for various explosion limits.

[4 +6]

3A **(i)** Write short notes on

(a) Kinetics of enzyme catalysis under varying substrate concentration

(b) Kinetic salt effect, and its application

B. **(i)** Derive Gibb's Helmholtz equation and mention its applications.

(ii) Calculate ΔH, ΔS, and ΔG when 1 mole of water is vaporized at 100° C and 1 atm. pressure. The latent heat of vaporization of water is 540 cal. g^{-1}. **[5+5]**

4A **(i)** Draw and explain the phase diagram of Na_2SO_4– NaCl–H_2O system at 15° C.

(ii) What is meant by activity coefficient of an electrolyte? Calculate ionic strength, mean ionic activity coefficient and the mean ionic molality for a 0.02 molal aqueous solution of $ZnCl_2$.

B. **(i)** Describe the determination of the surface excess of the Cl^- ions in Hg–HCl interface.

(ii) State and explain the third law of thermodynamics. How can it be verified experimentally? **[4+6]**

5A. **(i)** Derive an equation to calculate fugacity at low pressures. Mention the physical significance of fugacity.

(ii) Justify the following statements:

a) Clapeyron –Clausius equation cannot be obtained in the integrated form for solid- liquid equilibrium.

b) Internal energy of the system is an intensive property whereas heat capacity is an extensive property.

B. What are the important postulates of Debye– Huckel Ionic cloud model? Show that each central ion is enveloped by a cloud of equal and opposite charge. **[4+6]**

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