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 EXAMINATION, FEBRUARY 2022

PHYSICAL CHEMISTRY I [CHM 5103]

(REVISED CREDIT SYSTEM-2020)

CBCS Scheme

Time: 2 Hours Date: 11.2.22 MAX. MARKS: 40

Note: (i) Answer **ANY FOUR OUT OF FIVE** questions

(ii) Draw diagrams, and write equations wherever necessary

1.A Distinguish between Arrhenius and van't Hoff intermediate in acid base catalysis. Derive mathematical expression for rate constant for general acid catalysis. CO2

1.B Explain the following with appropriate reasoning

(a) Lindemann-Christieasen mechanism for gas phase reactions needs modification

(b) Gibbs adsorption isotherm is useful to distinguish between positive and negative adsorption CO2

(c) Solvation has profound influence on reaction rate of solution phase reaction

1.C Hydrolysis of ethyl acetate by NaOH using equal concentrations of reactants was studied by titrating 25mL of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction. CO2

Time (mts)	2	5	15	25
Acid used (ml)	16.00	10	6	4.

[5 +3+2]

2.A Define composite reaction. What are different types of composite reactions? Derive mathematical expression for variation of concentration of each species for reaction of type $A \rightarrow X \rightarrow Z$. Explain with suitable graphical representation CO2

2.B Explain the following with appropriate reasoning

(a) Overall rate of formation of HBr from H_2 and Br_2 follows fractional order kinetics and addition of the product usually brings down the rate of reaction CO2

(b) Rate of enzyme catalysis reaches maximum at certain optimum pH

(c) Final product during thermal decomposition of acetaldehyde depends upon termination reaction

2.C A bottle of milk stored at 30 °C sours in 36hrs, stored in a refrigerator at 5 °C sours after 144hrs. Assuming the rate constant to be inversely related to the souring time, estimate the activation energy of the chemical reaction involved in the souring process. (R =8.314 J K^{-1} mol^{-1}) CO2

[5 +3+2]

3.A Explain in detail mechanism of gas phase combustion of hydrogen gas. Derive rate expression for formation of water. Arrive at the conditions for 1st and 2nd explosion limits. CO2

CO1 **3.B** Explain the structure of electrified interface using Helmholtz –Perrin model. What are the conclusions drawn from it.

CO1 **3.C** **(i)**Calculate the thickness of the ionic atmosphere in a 0.01M KBr solution. Given dielectric constant of water is 78.5 at 25°C.

(ii) Give reason: Electrocapillary curves obtained with Lippmann electrometer are not usually parabolic. **[5 +3+2]**

CO1 **4.A** Show that $\log \gamma_{\pm} = -A Z+ Z- \sqrt{\mu}$ on the basis of Debye-Huckel theory.

CO4 **4.B** Draw and discuss the phase diagram for a three-component system consisting of NaCl - $NaNO_3$- H_2O.

CO3 **4.C** **(i)**The vapour pressure of water at 95 °C is found to be 634 mm. What would be the vapour pressure at a temperature of 100 °C? The molar heat of vaporization of water in this range of temperature may be taken as 40,593 J mol^{-1}.

CO3 **(ii)** Justify: Clapeyron –Clausius equation cannot be obtained in the integrated form for solid- liquid equilibrium. **[5 +3+2]**

CO3 **5.A** State and explain third law of thermodynamics. Explain how the absolute entropy of a substance can be determined with the help of the third law of thermodynamics.

CO3 **5.B** What is meant by Chemical potential? Discuss the variation of chemical potential with temperature and pressure.

5.C Justify the following statements:

CO1 **(i)** In aqueous media ion association in pairs rarely occurs for uni-univalent electrolyte.

(ii) Mercury-solution interface possesses unique advantages in understanding the structure of electrical double layer. **[5 +3+2]**

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