Registration No : | | | | | | | | | | |

Total Number of Pages : 02

M.Sc.I
FCYC802

8th Semester Regular Examination 2017-18
PHYSICAL CHEMISTRY - VI
BRANCH : M.Sc.I(AC)
Time : 3 Hours
Max Marks : 70
Q.CODE : C183

Answer Question No.1 which is compulsory and any five from the rest.
The figures in the right-hand margin indicate marks.

Q1 **Answer the following questions :** **(2 x 10)**

a) What are complex reactions? Mention the disturbing factors in the complex reactions.
b) Explain the diffusion limited reactions.
c) Discuss the consecutive reactions and show which step is known as the principle of bottle neck in reaction kinetics.
d) What are fast reactions? Name at least one method to study the fast reactions.
e) What are meant by primary and secondary salt effects?
f) What are surface active agents? Name two surface active agents.
g) Write Nernst-Einstein's equation and define each term involved therein.
h) Distinguish between fluorescence and phosphoresce.
i) Explain CMC.
j) What is quantum yield?

Q2 a) Deduce the rate expression for the reaction between two ions in solution based on double sphere model. **(5)**

b) For primary salt effect show that $\log K = \log K_0 + 1.108\, Z_A Z_B\, I^{1/2}$, where the symbols have their usual meaning. **(5)**

Q3 Show from the activated complex theory that the rate expression (γ) for a bimolecular reaction comprising (A+B) is given by $\gamma = [\dot{K}\frac{RT}{Nh}][A][B]$, and hence show that $K_2 = \frac{RT}{Nh} \exp\left[-\frac{\Delta H\#}{RT}\right] \exp\left[\frac{\Delta S\#}{R}\right]$ **(10)**

Q4 **Write notes on :** **(4+6)**

a) Frank Condon principle.
b) Law of photo chemical equivalence.

Q5 Discuss the influence of ionic strength in explaining the primary and secondary salt effects on the reaction rates in solution. How do you explain the negative and zero salt effects for the acid catalyzed reactions in solution? **(8+2)**

Q6 **a)** Write all the chain reactions for $H_2+Br_2 \rightarrow 2HBr$ and show that **(5)**

$$\frac{d[HBr]}{dt} = \frac{2k_2(\frac{k1}{k5})^{1/2}[Br2]^{\frac{1}{2}}[H2]}{1+(\frac{k4}{k3})\frac{[HBr]}{[Br2]}}$$

b) The Lindemann mechanism for a unimolecular reaction is given below **(5)**

$$A + A \underset{k_{-1}}{\overset{k_1}{\longrightarrow}} A^* + A$$

$$A^* \overset{k_2}{\rightarrow} P$$

Show that $\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_{-1}[A] + k_2}$

Q7 **a)** Derive Bronsted- Bjerrum equation on the basis of activated complex theory of reactions in solution. **(7)**

b) Calculate the ionic strength of a solution containing 0.5M Na_2SO_4 and 0.1M K_3PO_4 at 25^0C. **(3)**

Q8 **Write notes on :** **(6+4)**

a) Kinetics Isotope effects.

b) Rate expression for the first order reaction opposed by a first order reaction.