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**AG—153—2018**  
**FACULTY OF SCIENCE**  
**M.Sc. (Third Semester) EXAMINATION**  
**NOVEMBER/DECEMBER, 2018**  
**(CBCS Pattern)**

**PHYSICAL CHEMISTRY**

Paper XVII(533/3)

(Chemical Dynamics)

**(Friday, 30-11-2018)**

**Time : 2.00 p.m. to 5.00 p.m.**

*Time—Three Hours*

*Maximum Marks—75*

*N.B. :— (i) Attempt All questions.*

*(ii) Use of log table and calculator is allowed.*

*(iii) Solve Q. 5 (A), MCQ in one attempt only.*

1. Solve any *three* : 15

(a) Explain in brief surface rate of effusion.

(b) Explain in brief kinetics of consecutive reaction.

(c) Calculate A and rate constant for the reaction :



If the collision diameter is  $3.0 \times 10^{-10}$  m and it is assumed that activation energy is zero for the above reaction.

(d) Write a note on autocatalysis.

(e) What are main characteristics of Arrhenius equation ?

2. Solve any *three* : 15

(a) Write a note on ion interaction.

(b) Explain in brief temp. dependence of Hit and trial method.

P.T.O.

- (c) If the activation energy of a reaction is 90.8 kJ/mol, calculate the fraction of molecules at 600°C which have enough energy to react to form products.
- (d) Show the variation of rate reaction with pressure and the three explosion limits.
- (e) Give an expression for collision theory of unimolecular reaction. How does the order vary with concentration of reacting molecule ?

3. (a) Derive :

7

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

Or

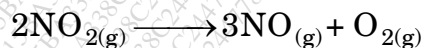
Derive :

$$\ln \frac{x_{eq}}{x_{eq} - x} = k_f \frac{[A]_0}{x_{eq}} \cdot t$$

- (b) What do you meant by Oscillatory reaction ? Explain Lotka Volterra mechanism of an oscillatory reaction.

Or

Calculate  $\Delta H^*$ ,  $\Delta G^*$  and  $\Delta S^*$  for the second order reaction :



at 500 K [given :  $A = 2 \times 10^9 \text{ sec}^{-1}$ ,  $Ea = 111 \text{ kJ/mol.}$ ]

4. (a) Derive Frying equation.

7

Or

Show that  $t_{3/4} = (2^{n-1} + 1) t_{1/2}$ , where  $n$  is order of reaction. Use this in the reaction of pyrolysis of  $\text{CH}_3\text{—CHO}$  to determine 'n'.

So  $t_{1/2} = 420 \text{ sec.}$   $t_{3/4} = 1220 \text{ sec}$  in a particular kinetics run.

- (b) Explain in brief methods used to determine the rate laws. 8

Or

Explain in brief collision theory of reaction rate.

5. (a) Select the correct alternative from the following : 5

- (i) The rate constant for the reaction depends upon each of the following except :

- (a) Solvent for reaction
- (b) Temperature
- (c) Concentration of reactant
- (d) Nature of reactant

- (ii) For a reaction  $A \rightarrow P$  a graph of  $[A]$  Vs time is found to be a straight line what is the order of reaction ?

- (a) Zero
- (b) First
- (c) Second
- (d) Third

- (iii) Which of the following does *not* affect the rate of chemical reaction ?

- (a) Enthalpy
- (b) Temperature
- (c) Surface area
- (d) Concentration of reactant

- (iv) Arsenic oxide acts in the contact process as :

- (a) Catalyst
- (b) Promotor
- (c) Poison
- (d) Enzyme

P.T.O.

- (v) An example of acid base catalysis is .....
- (a) Inversion of cane sugar
  - (b) Keto enol tautomerism
  - (c) Decomposition of Nitramine
  - (d) All of the above
- (b) Write short notes on (any *two*) : 10
- (i) Diffusion probabilities
  - (ii) Chemical chaos
  - (iii) Explosion.