DOON UNIVERSITY, DEHRADUN

End Semester Examination

Academic Year 2023-24(odd Semester)

School of Physical Science, Department Name: Chemistry

Programme Name: B.Sc. Hons. (with Research), 3rd Semester

Course Code with Title: CYC-203 (713113)

Physical Chemistry III: Phase Equilibrium and chemical Kinetics

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Time Allowed 2.00 Hours *Date: 16.12.23* *Maximum Marks: 30*

SECTION: A (Very Short Answer Type Questions)

1. For $3A \Rightarrow 2B$, rate of reaction + $d[B]/dt$ is equal to [1]
   a) $-3/2\ d[A]/dt$ b) $-2/3\ d[A]/dt$
   c) $-1/3\ d[A]/dt$ d) $+2d[A]/dt$

2. The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be: [1]
   a) 230.3 minutes b) 23.03 minutes
   c) 46.06 minutes d) 406.6 minutes

3. If the initial concentration of the reactant is doubled, time for half reaction is also doubled; the order of reaction is: [1]
   a) zero b) first
   c) second d) third

4. An increase in the concentration of the reactants of a reaction leads to change in [1]
   a) heat of reaction
   b) threshold energy
   c) collision frequency
   d) activation energy

5. In a steady state approximation the assumption is [1]
   a) the flow of reactants occur at constant speed
   b) the temperature do not alter the rate of reaction
   c) the concentration of the intermediates is constant
   d) the concentration of the intermediates are zero

6. State the phase rule. [1]

SECTION: B (Short Answer Type Questions)

7. Explain general acid catalysis. [3]

8. a) Explain collision theory of bimolecular reactions. [2+1]

b) Under what conditions the distribution law is valid?

9 The following mechanism has been proposed for the pyrolysis of methane: [3]

$$CH_4 \xrightarrow{k_1} {}^*CH_3 + H^*$$

$$CH_4 + {}^*CH_3 \xrightarrow{k_2} C_2H_6 + H^*$$

$$CH_4 + {}^*H \xrightarrow{k_3} {}^*CH_3 + H_2$$

$$^*CH_3 + {}^*H + M \xrightarrow{k_4} CH_4 + M$$

Assuming the steady state approximation for H* and $^*CH_3$, derive the rate law for the formation of C_2H_6.

10 Derive the rate law expression for the chemical reaction, $2O_3 \rightarrow 3O_2$ which proceeds as follows: [3]

a) $O_3 \rightarrow O_2 + O$. (Fast)

b) $O + O_3 \rightarrow 2O_2$ (slow)

SECTION : C (Long Answer Type Questions)

11 Derive the rate law for enzyme catalysed reaction. [4]

12 The rate of the following reaction in aqueous solution is monitored by measuring the number of moles of Hg_2Cl_2 that precipitate per litre per min. The data obtained are listed in the table. [4]

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2 + Hg_2Cl_2(s)$$

$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	rate, mol/L/min
0.105	0.15	1.8×10^{-5}
0.052	0.15	9×10^{-6}
0.052	0.30	7.2×10^{-5}

a) Determine the order of reaction with respect to $HgCl_2$, with respect to $C_2O_4^{2-}$ and overall order.

b) Calculate the rate constant for the above reaction.

13 Discuss the kinetics of parallel reactions. [4]