PHYSICAL / INORGANIC CHEMISTRY

DPP
DAILY PRACTICE PROBLEMS

DPP No. 53

Total Marks : 36

Max. Time : 40 min.

Topic : Chemical Kinetics

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.4	(3 marks 3 min.)	[12, 12]
Multiple choice objective ('–1' negative marking) Q.5 to Q.6	(4 marks 4 min.)	[8, 8]
Subjective Questions ('–1' negative marking) Q.7 to Q.10	(4 marks 5 min.)	[16, 20]

1. For a two step reaction

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R + B \qquad R + C \xrightarrow{K_3} \text{Products}$$

(where, R is a reactive intermediate, whose concentration is maintained at some low steady state throughout the reaction) the rate law expression will be

(A) $\frac{dx}{dt} = \frac{k_1[A]}{1+\frac{k_2[B]}{k_3[C]}}$ (B) $\frac{dx}{dt} = k_1[A]$ (C) $\frac{dx}{dt} = k_1[R][C]$ (D) $\frac{dx}{dt} = k_1[A][B][R]$

2. For $2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + 3C$, $2C \xrightarrow{k_2} 3D$, assuming all reactions to be single step (Elementary) reactions, which of the following is **correct**:

(A) $d[C]/dt = 3k_1[A]^2 - 3k_{-1}[B][C]^3 - 2k_2[C]^2$ (B) $d[B]/dt = k_1[A]^2$

(C) $d[A]/dt = 2k_{-1}[B][C]^3 - 2k_1[B][C]^3$ (D) None

3. For the following parallel chain reaction $A \begin{cases} \rightarrow B \\ \rightarrow C \end{cases}$ the overall half life of A is 12 hours. If rate of formation of C is 60% of a rate of decomposition of A then what will be half life of A while it is converting into B ?

(A) 40 hours (B) 60 hours (C) 50 hours (D) 30 hours

4. For the following parallel chain reaction $A \begin{cases} \xrightarrow{k_1 = 2\times10^{-4}\ s^{-1}} 2B \\ \xrightarrow{k_2 = 3\times10^{-4}\ s^{-1}} 3C \end{cases}$ if the sum of the concentration of B and C at any time is 2M then, what will be $[B]_t$ and $[C]_t$ respectively?

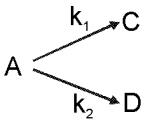
(A) $\frac{11}{12}M, \frac{13}{12}M$ (B) $\frac{3}{4}M, \frac{5}{4}M$ (C) $\frac{4}{5}M, \frac{6}{5}M$ (D) $\frac{8}{13}M, \frac{18}{13}M$

5. For the reaction $CH_4 + Br_2 \rightarrow CH_3Br + HBr$, the experimental data require the following rate equation:

$$\frac{d}{dt}[CH_3Br] = \frac{k_1[CH_4][Br_2]}{1+k_2[HBr]/[Br_2]}$$

Which of the following is/are true regarding this ?
(A) The reaction is a single step reaction
(B) The reaction is 2nd order in the initial stages {[HBr] ≈ 0}
(C) The reaction is 2nd order in the final stages {$[Br_2] \approx 0$}
(D) The molecularity of the reaction is two.

6. Consider the following case of COMPETING 1ST ORDER REACTIONS



After the start of the reaction at t = 0 with only A, the [C] is equal to the [D] at all times. The time in which all three concentrations will be equal is given by

7. For the reaction $Cl_2 + CO \rightarrow Cl_2CO$ the rate law is :

$$\frac{d[Cl_2CO]}{dt} = k[Cl_2]^{3/2}[CO]$$

The mechanism which is accepted is

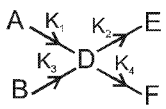
$Cl_2 + M \underset{}{\overset{K_1}{\rightleftharpoons}} 2Cl + M$ (fast)

$Cl + CO + M \overset{K_2}{\rightleftharpoons} ClCO + M$ (fast)

$ClCO + Cl_2 \xrightarrow{k_3} Cl_2CO + Cl$ (slow)

Find the expression relating k with the other constants given.

8. Write $\frac{dC_D}{dt}$ for the following parallel series 1st order reaction



9. For the reaction process A + B ⟶ products, the rate is first order w.r.t. A and second order w.r.t. B. If 1 mole each of A and B were introduced into a 1 L vessel and the initial rate was 1×10^{-2} (mol/L sec). Calculate the rate when half the reactants has been converted into products.

10. The catalysed decomposition of N_2O by gold at 900ºC and at an initial pressure of 200 mm, is 50% complete in 53 minutes and 73% complete in 100 minutes.
(A) What is the order of the reaction ?
(B) How much of it will decompose in 100 minutes at the same temperature but at initial pressure of 600 mm of Hg?

Answer Key

DPP No. # 53

1. $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} R + B \qquad R + C \xrightarrow{K_3} \text{product.}$

$A \xrightarrow{K_1} R + B\,; \qquad R + B \xrightarrow{K_2} A\,; \qquad R + C \xrightarrow{K_3} \text{Product.}$

$$\frac{d[A]}{dt} = -k_1[A] + K_2[R][B] \qquad \ldots\ldots (i)$$

$$\frac{d[R]}{dt} = K_1[A] - K_2[R][B] - K_3[R][C] \qquad \ldots\ldots (ii)$$

At steady state $\frac{d[R]}{dt} = 0$

$$[R] = \frac{K_1[A]}{K_2[B]+K_3[C]}$$

$$\frac{d[A]}{dt} = -K_1[A] + \frac{K_2[B]\,K_1[A]}{K_2[B]+K_3[C]} = \frac{-K_1[A]\{K_2[B]+K_3[C]\}+K_2[B]K_1[A]}{K_2[B]+K_3[C]}$$

$$\frac{d[A]}{at} = \frac{-K_1[A]K_3[C]}{K_2[B]+K_3[C]}$$

$$\Rightarrow \quad \frac{d[a-x]}{dt} = \frac{-K_1[A]K_3[C]}{K_2[B]+K_3[C]} \quad \Rightarrow \quad \frac{dx}{dt} = \frac{K_1[A]K_3[C]}{K_2[B]+K_3[C]} = \frac{K_1[A]}{1+\frac{K_2[B]}{K_3[C]}}$$

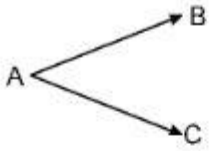
2. $2A \xrightarrow{k_1} B + 3C, \qquad \text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k_1[A]^2$

$B + 3C \xrightarrow{k_{-1}} 3D, \qquad \text{rate} = -\frac{1}{3}\frac{d[C]}{dt} = k_{-1}[B][C]^3$

$2C \xrightarrow{k_2} 3D, \qquad \text{rate} = -\frac{1}{2}\frac{d[C]}{dt} = k_2[C]^2$

$$\frac{d[C]}{dt} = 3k_1[A]^2 - 3k_{-1}[B][C]^3 - 2k_2[C]^2$$

3.



$$\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{0.4}{0.6} = \frac{2}{3}$$

$$\Rightarrow \quad k_2 = \frac{3}{2} k_1$$

$$\Rightarrow \quad k_{eff.} = k_1 + k_2$$

$$\frac{\ln 2}{(t_{1/2})_{overall}} = k_1 + \frac{3}{2} k_1 = \frac{5}{2} k_1$$

$$\Rightarrow \quad \frac{\ln 2}{12} = \frac{5}{2} \frac{\ln 2}{(t_{1/2})_{A \to B}}$$

$$\Rightarrow \quad (t_{1/2})_{A \to B} = 30 \text{ hrs.}$$

4. $[B] + [C] = 2\ M$

$$\frac{[B]}{[C]} = \frac{2k_1}{3k_2} = \frac{4}{9}$$

$$\Rightarrow \quad \frac{4}{9}[C] + [C] = 2M \quad \Rightarrow \quad \frac{13}{9}[C] = 2 \quad \Rightarrow \quad [C] = \frac{18}{13} M$$

$$\therefore \quad [B] = 2 - [C] = 2 - \frac{18}{13} = \frac{8}{13} M.$$

5. $$\frac{d}{dt}[CH_3Br] = \frac{k_1[CH_4][Br_2]}{1 + k_2[HBr]/[Br_2]}$$

At initial stages ($[HBr] \approx 0$)

$$\frac{d}{dt}[CH_3Br] = K_1 [CH_4] [Br_2] \longrightarrow \text{2nd order}$$

At final stages ($[Br_2] \approx 0$)

$$\frac{d}{dt}[CH_3Br] = \frac{K_1[CH_4][Br_2]^2}{[Br_2] + K_2[HBr]} = \frac{K_1[CH_4][Br_2]^2}{K_2[HBr]} \longrightarrow \text{2nd order}$$

6. $k_1 = k_2$ (Since [C] = [D] at all the times)

$$\Rightarrow \quad \frac{2}{3}\text{rd of A has reacted for } [A] = [C] = [D]$$

$$\therefore \qquad k_1 + k_2 = \frac{1}{t} \ln \frac{[A]_0}{\frac{1}{3}[A]_0}$$

$$\Rightarrow \qquad t = \frac{1}{k_1 + k_2} \ln 3 = \frac{1}{2k_1} \ln 3 = \frac{1}{2k_2} \ln 3$$

7. Using the r.d.s. approximation method

$$\frac{d[Cl_2CO]}{dt} = k_3 [ClCO]^1 [Cl_2]^1$$

but $\quad K_1 = \dfrac{[Cl]^2 [M]}{[Cl_2][M]}$ and $K_2 = \dfrac{[ClCO][M]}{[Cl][CO][M]}$

$$\Rightarrow \qquad [ClCO] = K_2 [Cl][CO] \qquad \text{and} \qquad [Cl] = \sqrt{K_1}\ \sqrt{[Cl_2]}$$

$$\therefore \qquad \frac{d[Cl_2CO]}{dt} = k_3 K_2 [Cl][CO][Cl_2]$$

$$= k_3 K_2 \sqrt{K_1}\ \sqrt{[Cl_2]}\ [CO][Cl_2]$$

$$= k_3 K_2 \sqrt{K_1}\ [Cl_2]^{3/2} [CO]$$

comparision with the rate law given shows that

$$k = k_3 K_2 \sqrt{K_1}$$

8. $\dfrac{dC_D}{dt} = K_1 C_A + K_3 C_B - K_2 C_D - K_4 C_D$.

9. $A + B \longrightarrow$ Products

rate $= K [A][B]^2$

$r_0 = K[1][1]^2 = 10^{-2} \quad \Rightarrow K = 10^{-2}\ M^{-2}\ S^{-1} \quad \Rightarrow \quad r = 10^{-2}\left[\frac{1}{2}\right]\left[\frac{1}{2}\right]^2 = \mathbf{1.25 \times 10^{-3}\ Ms^{-1}}$

10. 50% completion in 50 minutes.
73% competion in 100 minutes.
Checking for zero order :

$$t_{1/2} = \frac{C_0}{2K}.$$

$$53 \text{ min.} = \frac{200}{2K} \quad \Rightarrow \quad K = \frac{100}{53}\ \text{min}^{-1}.$$

$$C_t = C_0 - 2Kt.$$

$$C_t = 200 \quad \frac{200}{53} \times 100 = -\text{ve}.$$

So, it is not zero order.

For Ist order :

$$t_{1/2} = \frac{\ln 2}{K} \quad \Rightarrow \quad K = \frac{\ln 2}{53} = \frac{0.693}{53}.$$

$$Kt = \ln\left(\frac{a_0}{a}\right) \Rightarrow \frac{\ln 2}{53} \times 100 = \ln\left(\frac{a_0}{a}\right).$$

$$\frac{a_0}{a} = 3.6972. \quad \Rightarrow \quad a = \frac{200}{3.6972} = 54.1 \text{ mm of Hg}.$$

$$\text{Competion of reaction} = \frac{a_0 - a}{a_0} \times 100 = 73\%.$$

So, it is Ist order.

(b) In Ist order reaction, % completion is independent an initial concentration so, 73% completion takes place.