PHYSICAL / INORGANIC CHEMISTRY

**DPP**

DAILY PRACTICE PROBLEMS

# DPP No. 51

**Total Marks : 47**

**Max. Time : 54 min.**

**Topic : Chemical Kinetics**

| **Type of Questions** | | **M.M., Min.** |
|---|---|---|
| **Single choice Objective ('–1' negative marking) Q.1 to Q.5** | **(3 marks 3 min.)** | **[15, 15]** |
| **Multiple choice objective ('–1' negative marking) Q.6** | **(4 marks 4 min.)** | **[4, 4]** |
| **Subjective Questions ('–1' negative marking) Q.7 to Q.13** | **(4 marks 5 min.)** | **[28, 35]** |

**1.** The decomposition of $N_2O_5$ in chloroform was followed by measuring the volume of $O_2$ gas evolved : $2N_2O_5(CCl_4) \rightarrow 2N_2O_4(CCl_4) + O_2(g)$. The maximum volume of $O_2$ gas obtained was 100 $cm^3$. In 500 minutes, 90 $cm^3$ of $O_2$ were evolved. The first order rate constant (in $min^{-1}$) for the disappearance of $N_2O_5$ is :

(A) $\frac{2.303}{500}$ (B) $\frac{2.303}{500}\log\frac{100}{90}$ (C) $\frac{2.303}{500}\log\frac{90}{100}$ (D) $\frac{100}{10 \times 500}$

**2.** The reaction $A(g) + 2B(g) \rightarrow C(g)$ is an elementary reaction. In an experiment involving this reaction, the initial partial pressures of A and B are $P_A = 0.40$ atm and $P_B = 1.0$ atm respectively. When pressure of C becomes 0.3 atm in the reaction the rate of the reaction relative to the initial rate is :

(A) $\frac{1}{12}$ (B) $\frac{1}{50}$ (C) $\frac{1}{25}$ (D) none of these

**3.** A reaction is catalysed by $H^+$ ion;and in the rate law the dependence of rate is of first order with respect to the concentration of $H^+$ ions, in presence of HA rate constant is $2 \times 10^{-3}$ $min^{-1}$ and in presence of HB rate constant is $1 \times 10^{-3}$ $min^{-1}$. HA and HB (both strong acids) have relative strength as :

(A) 0.5 (B) 0.002 (C) 0.001 (D) 2

**4.** The gaseous decomposition reaction, $A(g) \longrightarrow 2B(g) + C(g)$ is observed to first order over the excess of liquid water at 25ºC. It is found that after 10 minutes the total pressure of system is 188 torr and after very long time it is 388 torr. The rate constant of the reaction (in $hr^{-1}$) is : [Given : vapour pressure of $H_2O$ at 25º is 28 torr (ln 2 = 0.7, ln 3 = 1.1, ln 10 = 2.3)]

(A) 0.02 (B) 1.2 (C) 0.2 (D) none of these.

**5.** The hydrolysis of cane sugar was studied using an optical polarimeter and the following readings were taken:

| | | | |
|---|---|---|---|
| time (min.) : | 0 | 84 min | $\infty$ |
| observed rotation (degrees) : | 50 | 20 | –10 |

When was the mixture optically inactive? (log 2 = 0.3, log 3 = 0.48)

(A) 118 min (B) 218 min (C) 318 min (D) 418 min

**6.** For a certain reaction $A \longrightarrow$ products, the $t_{1/2}$ as a function of $[A]_0$ is given as below :

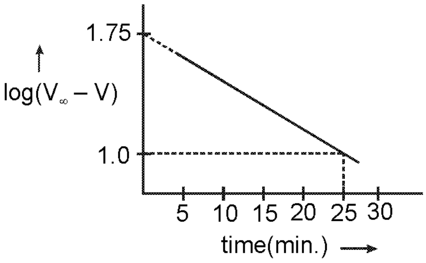
| | | |
|---|---|---|
| $[A]_0$ (M) : | 0.1 | 0.025 |
| $t_{1/2}$ (min.) : | 100 | 50 |

Which of the following is/are true ?

(A) The order is $\frac{1}{2}$ (B) $t_{1/2}$ would be $100\sqrt{10}$ min for $[A]_0 = 1$ M

(C) The order is 1 (D) $t_{1/2}$ would be 100 min for $[A]_0 = 1$ M

**7.** The plot of log ($V_\infty - V$) versus t (where V is the volume of nitrogen collected under constant temperature and pressure conditions) for the decomposition of $C_6H_5N_2Cl$ is given at 50°C with an amount of $C_6H_5N_2Cl$ equivalent to 58.3 cc $N_2$.



Calculate the rate constant for the reaction in $hr^{-1}$ expressing your answer in a single significant digit.

**8.** Now, let us assume a first-order reaction, $A \longrightarrow B + C$, such that A, B and C, such that A, B and C are in solution. At time zero, a small amount of the solution is taken, cooled (to stop the reaction from proceeding) and titrated with a suitable reagent. Let us assume that the reagent reacts only with A and not with B and C. The same process is repeated at time t.

| Time | 0 | t |
|---|---|---|
| Volume of reagent | $V_0$ | $V_t$ |

Calculate the expression of rate constant.

**9.** $A(soln.) \longrightarrow B(soln.) + C(soln.)$

Reagent reacts with all species A, B and C.

| Time | 0 | t | $\infty$ |
|---|---|---|---|
| Volume of reagent | $V_0$ | $V_t$ | $V_\infty$ |

The n factor of A, B and C with the reagent and that of the reagent with A, B and C are not known. Calculate the expression of rate constant.

**10.** $A(soln.) \xrightarrow{D(soln.)} B(soln.) + C(soln.)$

D is catalyst present in the solution whose n-factor is not known. Catalyst have a constant concentration throughout the reaction.

| Time | 0 | t | $\infty$ |
|---|---|---|---|
| Volume of reagent | $V_0$ | $V_t$ | $V_\infty$ |

Calculate the expression of rate constant.

**11.** Now, let us assume that A, B and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.

$A(soln.) \longrightarrow B(soln.) + C(soln.)$

| Time | 0 | t | $\infty$ |
|---|---|---|---|
| Total rotation in degrees | $r_0$ | $r_t$ | $r_\infty$ |

Calculate the expression of rate constant.

**12.** For the reaction, $2NO + H_2 \longrightarrow N_2O + H_2O$ the value of -dp/dt was found to be 1.50 Torr $s^{-1}$ for a pressure of 359 Torr of NO and 0.25 Torr $s^{-1}$ for a pressure of 152 Torr, the pressure of $H_2$ being constant. On the other hand, when the pressure of NO was kept constant, –dp/dt was 1.60 Torr $s^{-1}$ for a hydrogen pressure of 289 Torr and 0.79

Torr $s^{-1}$ for a pressure of 147 Torr. Determine the order of the reaction.

**13.** Decomposition of $N_2O_5$ follows first-order kinetics, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$. If pressure of the system at time, t and $\infty$ are $P_t$ and $P_\infty$ respectively, find the expression of rate contant (k).

# Answer Key

### DPP No. # 51

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | (A) | **2.** | (C) | **3.** | (D) | **4.** | (B) | **5.** | (B) |
| **6.** | (A, B) | **7.** | 4 | **8.** | $k = \frac{1}{t}\ln\left(\frac{V_0}{V_t}\right)$ | **9.** | $k = \frac{1}{t}\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ | | |
| **10.** | $k = \frac{1}{t}\ln\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$ | **11.** | $k = \frac{1}{t}\ln\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$ | **12.** | 3 | **13.** | $k = \frac{1}{t}\ln\left(\frac{3P_\infty}{5(P_\infty - P_t)}\right)$ | | |

# Hints & Solutions

## PHYSICAL / INORGANIC CHEMISTRY

### DPP No. # 51

**1.** $kt = \ln\left(\frac{C_O}{C_t}\right)$

| | $2\,N_2O_5$ | $\longrightarrow$ | $2N_2O_4$ | + | $O_2$ |
|---|---|---|---|---|---|
| t=0 | 200 cm$^3$ | | 0 | | 0 |
| t=t | 20 cm$^3$ | | 180cm$^3$ | | 90 cm$^3$ |
| $t=\infty$ | 0 | | 200cm$^3$ | | 100 cm$^3$ |

Initial volume of $N_2O_5$ = 200 cm$^3$.
because Max. volume of $O_2$ = 100 cm$^3$.

$$\therefore \quad K \times 500 = \ln\left(\frac{200}{20}\right) \Rightarrow k = \frac{\ln 10}{500} = \frac{2.303}{500}.$$

**2.**

| | A(g) | + | 2B(g) | $\rightarrow$ | C(g) |
|---|---|---|---|---|---|
| t = 0 | 0.4 atm | | 1 atm | | 0 atm |
| t = t | (0.4 –0.3)atm | | (1 – 0.6)atm | | 0.3 atm |

Since reaction is elementary.
So, Rate of reaction w.r.t. A & B will be of order equal to stoichiometric coefficient
Rate = K [A] [B]$^2$
Rate$_{\text{(Initial)}}$ = K [0.4] [1]$^2$
Rate$_{\text{(aftar t = t)}}$ = K [0.1][0.4]$^2$

$$\frac{R_{(t=t)}}{R_{(t=o)}} = \frac{K[0.1]\,[0.4]^2}{K[0.4]\,[1]} = \frac{1}{25}$$

**3.** We know

Rate = k [conc.]

Given Rxn catalysed by HA and HB

Rate constant $k_A = k_1\,[H^+]_A$

$k_B = k_1\,[H^+]_B$

Then relative strength of acids A and B is

$$\frac{k_A}{k_B} = \frac{[H^+]_A}{[H^+]_B} \qquad \frac{2}{1} = \frac{[H^+]_A}{[H^+]_B} = \text{strength of } \frac{[\text{Acid A}]}{[\text{Acid B}]}$$

**4.**

| | $A(g)$ | $\longrightarrow$ | $2B(g)$ + | $C(g)$ |
|---|---|---|---|---|
| Let initial pressure | $P_0$ | | 0 | 0 |
| After 10 min. | $(P_0 - x)$ | | $2x$ | $x$ |
| After long time $(t \to \infty)$ | 0 | | $2P_0$ | $P_0$ |

as per given $(P_0 - x) + 2x + x +$ vaour pressure of $H_2O = 188$

$P_0 + 2x = 160$ and $3P_0 + 28 = 388$

so, $P_0 = 120$ and $x = 20$ torr

$$k = \frac{1}{t}\ln\left(\frac{P_0}{P_0 - x}\right)$$

$$k = \frac{1}{t}\ln\left(\frac{P_0}{P_0 - x}\right)$$

$$\Rightarrow \qquad \frac{1}{10}\ln\left(\frac{120}{100}\right) = \frac{1}{10} \times (\ln 4 + \ln 3 - \ln 10)$$

$$= 0.02\ \text{min}^{-1} = 1.2\ \text{hr}^{-1}$$

**5.** $$Kt = \ln\left(\frac{r_\infty - r_0}{r_\infty - r_t}\right)$$

$$K = \frac{1}{84}\ln\left(\frac{-10-50}{-10-20}\right) = \frac{1}{84}\ln(2)$$

Solution is optically inactive i.e. optical rotation is zero.

$$\left(\frac{1}{84}\ln 2\right) t = \ln\left(\frac{-10-50}{-10-0}\right) \qquad \Rightarrow \qquad t = 84\,\frac{\ln 6}{\ln 2} = \mathbf{218}$$

**6.** A → Products.

$t_{1/2} = [\text{conc.}]^{1-n}$   n → order of reaction.

$$\frac{100}{50} = \left(\frac{0.1}{0.025}\right)^{1-n}$$

$$2 = 2 - 2n$$

$\Rightarrow$ $2n = 1.$

$\Rightarrow$ $n = \frac{1}{2}.$

order of reaction is $\frac{1}{2}$.

$$\frac{100}{t_{1/2}} = \left(\frac{0.1}{1}\right)^{1/2}$$

$\Rightarrow$ $t_{1/2} = 100\sqrt{10}$ min for $[A_0] = 1M$.

**7.** Slope $= \frac{(1-1.75)}{25-0} = -0.03$

$k = -2.303\ (\text{slope})\ \text{min}^{-1}$

$= -2.303\ (-0.03)\ \text{min}^{-1} = 0.06909\ \text{min}^{-1} = 4.14\ \text{hr}^{-1} \approx 4\ \text{hr}^{-1}$

**8.**

| | $A \longrightarrow$ | $B$ | + | $C$ | |
|---|---|---|---|---|---|
| t=0 | a | 0 | | 0 | $a \propto V_0$ |
| t=t | a-x | x | | x | $(a-x) \propto V_t$ |

$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{V_0}{V_t}\right)$

**9.**

| | A(soln.) $\longrightarrow$ | B(soln.) | + C(soln.) |
|---|---|---|---|
| t=0 | a | 0 | 0 |
| t=t | a-x | x | x |
| t=∞ | 0 | a | a |

Let n-factor of A, B & C are $n_1$, $n_2$ & $n_3$ & that of reagent is n & molarity of reagent is M

At  t= 0,

meq. of A = meq. of reagent

$n_1 \times a = M \times n \times V_0$  ....... (i)

At  t= t,

meq. of reagent = meq. of A + meq of B + meq of C

$MV_t n = (a-x)n_1 + xn_2 + xn_3$  ....... (ii)

At $t = \infty$,

meq. of reagent = meq of B + meq of C

$MV_{\infty} n = an_2 + an_3$ ....... (iii)

From (iii) & (i)

$$(n_2 + n_3) = \frac{MV_{\infty} n}{a} \quad \& \quad n_1 = \frac{MV_0 n}{a}$$

$$\Rightarrow \quad MV_t n = (a - x)\frac{MV_0 n}{a} + x\frac{MV_{\infty} n}{a} \quad \Rightarrow \quad \frac{a}{a - x} = \left(\frac{V_{\infty} - V_0}{V_{\infty} - V_t}\right)$$

$$Kt = \ln\frac{a}{a - x} \quad \Rightarrow \quad K = \frac{1}{t}\ln\left(\frac{V_{\infty} - V_0}{V_{\infty} - V_t}\right)$$

**10.** Same as of question 9.

**11.** $A(\text{soln.}) \longrightarrow B(\text{soln.}) + C(\text{soln.})$

| | A(soln.) | B(soln.) | C(soln.) |
|---|---|---|---|
| t=0 | a | 0 | 0 |
| t=t | a-x | x | x |
| $t=\infty$ | 0 | a | a |

Let $\alpha$, $\beta$ & $\gamma$ are specific rotation of A, B & C respectively.

At t=0, $r_0 = a\alpha$ ........... (i)

At t=t, $r_t = (a-x)\alpha + x\beta + x\gamma$ ........... (ii)

At $t=\infty$, $r_{\infty} = a\beta + a\gamma$ ........... (iii)

From (i) & (iii)

$$\alpha = \frac{r_0}{a} \quad \& \quad (\beta + \gamma) = \frac{r_{\infty}}{a}$$

Putting in (ii)

$$r_t = (a - x)\frac{r_0}{a} + \frac{r_{\infty}}{a}x \Rightarrow \frac{a}{a - x} = \frac{r_{\infty} - r_0}{r_{\infty} - r_t} \Rightarrow Kt = \ln\frac{a}{a - x} \Rightarrow k = \frac{1}{t}\ln\left(\frac{r_{\infty} - r_0}{r_{\infty} - r_t}\right)$$

**12.** rate $= K[NO]^a[H_2]^b$

$$\frac{r_1}{r_2} = \frac{1.5}{0.25} = \left(\frac{359}{152}\right)^a \Rightarrow \frac{6}{1} = (2.36)^a \Rightarrow a = 2$$

$$\frac{r_3}{r_4} = \frac{1.6}{0.79} = \left(\frac{289}{147}\right)^b \quad \Rightarrow \quad 2 = (1.966)^b \quad \Rightarrow \quad b = 1$$

order of the reaction = 1 + 2 = **3**

**13.**

|  | $2N_2O_5(g) \longrightarrow$ | $4NO_2(g)$ | $+ O_2(g)$ |  |
|---|---|---|---|---|
| $t = 0$ | $a$ | $0$ | $0$ |  |
| $t = t$ | $a - x$ | $2x$ | $\frac{x}{2}$ | $\left(a + \frac{3x}{2}\right) \propto P_t$ |
| $t = \infty$ | $0$ | $2a$ | $\frac{a}{2}$ | $\frac{5a}{2} \propto P_\infty$ |

$$kt = \ln\left(\frac{a}{a-x}\right)$$

$$a \propto \frac{2}{5}P_\infty \qquad \& \qquad x \propto \frac{2}{3}\left(P_t - \frac{2}{3}P_\infty\right)$$

$$k = \frac{1}{t}\ln\left(\frac{\frac{2}{5}P_\infty}{\frac{2}{5}P_\infty - \frac{2}{3}\left(P_t - \frac{2}{5}P_\infty\right)}\right) = \frac{1}{t}\ln\left(\frac{3P_\infty}{5(P_\infty - P_t)}\right)$$