PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 50

Total Marks : 47

Max. Time : 52 min.

Topic : Chemical Kinetics

Type of Questions		**M.M., Min.**
Single choice Objective ('–1' negative marking) Q.1 to Q.9	**(3 marks 3 min.)**	**[27, 27]**
Subjective Questions ('–1' negative marking) Q.10 to Q.14	**(4 marks 5 min.)**	**[20, 25]**

1. For a 1st order reaction (gaseous) (cont. V, T)

$a\,A \longrightarrow (b-1)\,B + 1\,C$ (with b > a), the pressure of the system rose by $50\left(\frac{b}{a}-1\right)$ % in a time of 10 min. The half life of the reaction is therefore.

(A) 10 min (B) 20 min (C) 30 min (D) 40 min

2. Two first order reaction have half-lives in the ratio 8 : 1. Calculate the ratio of time intervals $t_1 : t_2$. The time t_1 and t_2 are the time period for $\left(\frac{1}{4}\right)^{th}$ completion of 1st reaction and $\left(\frac{3}{4}\right)^{th}$ 2nd completion rxn repectively.

(A) 1 : 0.301 (B) 0.125 : 0.602 (C) 1 : 0.62 (D) none of these

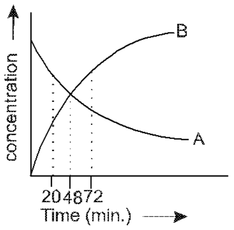
3. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is.

(A) 0.5 mol^{-1} dm^3 (B) 1.0 mol dm^{-3} (C) 1.5 mol dm^{-3} (D) 2.0 mol^{-1} dm^3

4. For a first order reaction, the ratio of time for the completion of 99.9% and half of the reaction is

(A) 8 (B) 10 (C) 9 (D) 12

5. For a first order reaction, $nA \longrightarrow B$ whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes . Find out the value of n.

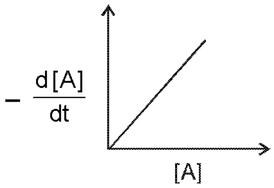


(A) 1
(B) 2
(C) 3
(D) 4

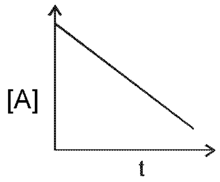
6. Number of natural life times (T_{av}) required for a first-order reaction to achieve 99.9% level of completion is:

(A) 2.3 (B) 6.9 (C) 9.2 (D) 0.105

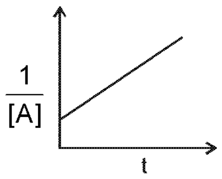
7. Consider the plots for the types of reaction $nA \rightarrow B + C$



(i)



(ii)



(iii)

These plots respectively correspond to the reaction orders :

(A) 0, 2, 1 (B) 0, 1, 2 (C) 1, 1, 2, (D) 1, 0, 2

8. Reaction A + B $\rightarrow$ C + D follows rate law, $r = k[A]^{1/2}[B]^{1/2}$ starting with 1 M of A and B each. What is the time taken for concentration of A become 0.1 M ?
Given $k = 2.303 \times 10^{-2}\ sec^{-1}$.

(A) 10 sec (B) 100 sec (C) 1000 sec (D) 434 sec

9. At high temperature (504°C) dimethyl ether decomposes as per the reaction

$$(CH_3)_2O\ (g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

time (sec.) :	0	400	1200	∞
p_{total} (mm) :	312	412	560	935

Determine the half life of the reaction during this run. ($\ln\left(\frac{623}{523}\right) = 0.175$, $\ln\left(\frac{623}{375}\right) = 0.5076$)

(A) 1311 sec (B) 1411 sec (C) 1511 sec (D) 1611 sec

10. A reaction between A and B is represented stoichiometrically by A + B $\rightarrow$ C. Observations on the rate of this reaction are obtained in three separate experiments as follows :

	initial concentrations			**final concentration**
	$[A]_0$, M	$[B]_0$, M	duration of experiment Δt, hr	$[A]_f$, M
(1)	0.1000	1.0	0.5	0.0975
(2)	0.1000	2.0	0.5	0.0900
(3)	0.0500	1.0	2.0	0.0450

What is the order of the reaction with respect to each reactant and what is the value of the rate constant?

11. The gas phase decomposition of NOBr is second-order in [NOBr], with $k = 0.810\ M^{-1}\ s^{-1}$ at 10°C. We start with 4.00×10^{-3} M NOBr. in a flask at 10°C. How many seconds does it take to use up 1.50×10^{-3} M NOBr?

$2NOBr(g) \longrightarrow 2NO(g) + Br_2(g)$; Rate = $k[NOBr]^2$

12. Let there be as first-order reaction of the type, A $\longrightarrow$ B + C. Let us assume that all the three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	T	∞
Partial pressure of A	P_0	P_t	–

13. Let there be a first order reaction, A $\longrightarrow$ B + C. Let us assume all three are gases. We are required to calculate the value of rate constant based on the following data

Time	0	t	∞
Total pressure	P_0	P_t	–

Calculate the expression of rate constant.

14. $A(g) \longrightarrow B(g) + C(g)$

Time	0	t	∞
Total pressure of B + C	0	P_t	P_∞

Calculate the expression of rate constant.

Answer Key

DPP No. # 50

1.	(A)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(C)
6.	(B)	**7.**	(D)	**8.**	(B)	**9.**	(D)		

10. Rate = $k\,[A]^1\,[B]^2$, $k = 5 \times 10^{-2}\ M^{-2}\ hr^{-1}$ **11.** $t = 92.6$ s.

12. $k = \frac{1}{t}\ln\left(\frac{P_0}{P_t}\right)$ **13.** $k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0 - P_t}\right)$ **14.** $k = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty - P_t}\right)$

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

DPP No. # 50

1.

	aA	$\longrightarrow$	$(b-1)B$	+	C
$t=0$	a'				$a' \propto P_0$
$t=10\text{min}$	$a' - x$		$\frac{(b-1)}{a'}x$		$\frac{x}{a}$

$$\frac{x}{a}\left[(a'-x)+\frac{(b-1)x}{a}+\frac{x}{a}\right] \propto P_0 + P_0\,\frac{50\left(\frac{b}{a}-1\right)}{100}$$

$$\left[a'-x+\frac{b}{a}x\right] \propto P_0\left[1+\frac{1}{2}\left(\frac{b}{a}-1\right)\right]$$

$$\left[a'+x\left(\frac{b}{a}-1\right)\right] \propto P_0 + \frac{P_0}{2}\left(\frac{b}{a}-1\right)$$

$\Rightarrow x \propto \frac{P_0}{2}$. $\Rightarrow$ $x \propto \frac{a'}{2}$

$\Rightarrow$ half life = 10 minute.

2. (C) $t_1 = \frac{(t_{1/2})_1}{0.693} \ln\left(\frac{1}{1-(1/4)}\right)$

$t_2 = \frac{(t_{1/2})_2}{0.693} \ln\left(\frac{1}{1-3/4}\right)$

$\frac{t_1}{t_2} = \frac{8}{1} \times \frac{\ln(4/3)}{\ln(4)}$ = **1 : 0.62.**

3. For Ist order reaction

$k_1 = \frac{\ell n2}{t_{1/2}} = \frac{0.693}{40}$ second^{-1}

For zero order reaction

$k_0 = \frac{C_0}{2\,t_{1/2}} = \frac{1.386}{2 \times 20}$

$\Rightarrow \frac{k_1}{k_0} = \frac{0.693}{1.386} = 0.5$

4. $t = \frac{2.303}{k} \log\left(\frac{100}{0.1}\right) = \frac{2.303}{k} \times 3$

$t = \frac{2.303 \times 3}{\frac{0.693}{t_{1/2}}} = \frac{2.303 \times 3 \times t_{1/2}}{0.693}$ $\left(t_{1/2} = \frac{0.693}{k}\right)$

$\Rightarrow \frac{t_{99.9\%}}{t_{1/2}} = \frac{2.303 \times 3}{0.693} = 10$

5. $nA \longrightarrow B$

a

$a-x$ $\frac{x}{n}$ $t_{½} = 24$ min

at $t = 48$ $a-x = \frac{x}{n}$

$$a = \frac{(1+n)x}{n} \ ; \ \frac{na}{1+n} = x$$

$$\frac{\ell n2}{24} = \frac{1}{48} \quad \ell n \frac{a}{a - \dfrac{na}{(1+n)}}$$

$$4 = \frac{a(1+n)}{a} \qquad \Rightarrow \qquad n = 3.$$

6. We know, $k = \dfrac{2.303}{t} \log \dfrac{a}{(a-x)}$

99.9% completion

$a = 100$

$a - x = (100 - 99.90) = .10$

Then $t = \dfrac{2.303}{k} \log \left(\dfrac{100}{.10}\right)$

$$t = 2.303 \times 3 \times \left[\frac{1}{k}\right] \quad ; \quad t = 6.9 \times t_{av}$$

7. $nA \longrightarrow B + C$

$\dfrac{-d[A]}{dt} \ \alpha \ [A]$ (Ist order)

$[A]_t \ \alpha \ t$ (zero order)

$\dfrac{1}{[A]_t} \ \alpha \ t$ (2nd order)

8.

$$\begin{array}{lccccccc} & A & + & B & \rightarrow & C & + & D \\ t=0 & 1 & & 1 & & 0 & & 0 \\ t=t & 1-x & & 1-x & & x & & x \end{array}$$

$$r = k[A]^{1/2}\,[B]^{1/2}$$

$$\Rightarrow \quad \frac{dx}{dt} = k\,(1-x)^{1/2}\,(1-x)^{1/2}.$$

$$\text{or} \quad \frac{dx}{dt} = k\,(1-x).$$

$$\Rightarrow \quad t = \frac{1}{k} \ln\left(\frac{1}{1-x}\right) ; \qquad t = \frac{2.303}{2.303 \times 10^{-2}} \log\left(\frac{1}{0.1}\right) = 100 \text{ sec.}$$

9. $(CH_3)_2\,O\,(g) \longrightarrow CH_4(g) + H_2\,(g) + CO(g)$

t=0	a	0	0	0	$a \ \alpha \ P_o = 312$ mm
t=400 sec	a–x	x	x	x	$a+2x \ \alpha \ p_{400} = 412$mn
t=1200 sec	a – y	y	y	y	$a+2y \ \alpha \ p_{1200} = 560$ mm
t= ∞	0	a	a	a	$3a \ \alpha \ P_{\infty} = 935$ mm

$$Kt = \ln\left(\frac{C_o}{C_t}\right) = \ln\left(\frac{a}{a-x}\right) \qquad \Rightarrow \qquad Kt = \ln\left(\frac{p_\infty - p_o}{p_\infty - p_t}\right)$$

$$(t = 400\text{sec}) \qquad K_1 = \frac{1}{400}\ \ln\left(\frac{935-312}{935-412}\right) = \frac{1}{400}\ \ln\left(\frac{623}{523}\right)\ \text{sec}^{-1} = 0.175 \times \frac{1}{400}$$

$$(t = 1200\text{sec}) \qquad K_2 = \frac{1}{1200}\ \ln\left(\frac{935-312}{935-560}\right) = \frac{1}{1200}\ \ln\left(\frac{623}{375}\right)\ \text{sec}^{-1} = 0.5076 \times \frac{1}{1200}$$

$$t_{1/2} = \frac{\ln 2}{\frac{k_1+k_2}{2}} = \frac{2\ln 2}{(k_1+k_2)} = \frac{1584+1638}{2} = 1611\ \text{sec.}$$

10.

Initial conc.		duration of experiment (hr)	final conc. $[A]_f$	Rate
$[A]_0$,M	$[B]_0$, M			
0.1000	1.0	0.5	0.0975	5×10^{-3} M hr^{-1}
0.1000	2.0	0.5	0.0900	20×10^{-3} M hr^{-1}
0.0500	1.0	2.0	0.0450	2.5×10^{-3} M hr^{-1}

$$A + B \longrightarrow C$$

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

$\text{Rate} = K[A]^a[B]^b$

$R_1 = K\,[0.1]^a\,[1]^b \quad = \quad 5 \times 10^{-3}\ \text{M hr}^{-1}$

$R_2 = K\,[0.1]^a\,[2]^b \quad = \quad 20 \times 10^{-3}\ \text{M hr}^{-1}$

$$\frac{R_1}{R_2} = \left[\frac{1}{2}\right]^b = \frac{1}{4} \qquad \Rightarrow \qquad b = 2$$

$R_3 = K\,[0.05]^a\,[1]^2 = 2.5 \times 10^{-3}\ \text{M hr}^{-1}$

$R_1 = K\,[0.1]^a\,[1]^2 = 5 \times 10^{-3}\ \text{M hr}^{-1}$

$$\frac{R_3}{R_1} = \left[\frac{1}{2}\right]^a = \frac{1}{2} \qquad \Rightarrow \qquad a = 1$$

$R_1 = K\,[0.1]\,[1]^2 = 5 \times 10^{-3}\ \text{M hr}^{-1}$

$$K = \frac{5 \times 10^{-3}}{0.1} = 5 \times 10^{-2}\ \text{M}^{-2}\ \text{hr}^{-1}$$

11. $[NOBr]_t = 4.00 \times 10^{-3} - 1.50 \times 10^{-3} = 2.50 \times 10^{-3}$

$$k = \frac{1}{2t}\left[\frac{1}{[NOBr]_t} - \frac{1}{[NOBr]_0}\right]$$ (due to cofficients of the reactant = 2)

$$0.810 = \frac{1}{2t}\left[\frac{1}{2.50\times10^{-3}} - \frac{1}{4.00\times10^{-3}}\right]$$

$$t = \frac{1}{2\times0.810}\left[\frac{(4.00-2.50)\times10^{-3}}{2.50\times10^{-3}\times4.00\times10^{-3}}\right]$$

t = **92.6 s.**

12.

	$A \longrightarrow B$		+	C	
t=0	a	0		0	$a \propto P_0$
t=t	a-x	x		x	$(a-x) \propto P_t$

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

13.

	$A \longrightarrow B$		+	C			
t=0	a	0		0	$a \propto P_0$		
t=t	a-x	x		x	$(a+x) \propto P_t$	$\Rightarrow$	$x \propto (P_t - P_0)$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_0}{P_0-(P_t-P_0)}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_0}{2P_0-P_t}\right)$$

14.

	$A \longrightarrow B$		+	C			
t=0	a	0		0			
t=t	a-x	x		x	$2x \propto P_t$	$\Rightarrow$	$x \propto \frac{P_t}{2}$
t=∞	0	a		a	$2a \propto P_\infty$	$\Rightarrow$	$a \propto \frac{P_\infty}{2}$

$$Kt = \ln\left(\frac{a}{a-x}\right) \Rightarrow k = \frac{1}{t}\ln\left(\frac{P_\infty}{P_\infty - P_t}\right)$$