# CHAPTER 18

# Chemical Kinetics

1. **(b)** Rate of disappearance of reactants = Rate of appearance of products

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt}=\frac{1}{4}\frac{d[NO_2]}{dt}=\frac{d[O_2]}{dt}$$

$$\frac{1}{2}k[N_2O_5]=\frac{1}{4}k'[N_2O_5]=k''[N_2O_5]$$

$$\frac{k}{2}=\frac{k'}{4}=k''$$

$$k'=2k,\quad k''=\frac{k}{2}$$

2. **(b)** Given: 75% reaction gets completed in 32 min

Thus, $k=\frac{2.303}{t}\log\frac{a}{(a-x)}$

$$=\frac{2.303}{32}\log\frac{100}{(100-75)}$$

$$=\frac{2.303}{32}\log 4=0.0433\ \text{min}^{-1}$$

Now we can use this value of $k$ to get the value of time required for 50% completion of reaction

$$t=\frac{2.303}{k}\log\frac{a}{(a-x)}=\frac{2.303}{0.0433}\log\frac{100}{50}$$

$$=\frac{2.303}{0.0433}\log 2=16\ \text{min}$$

3. **(b)** $k=\frac{2.303}{t}\log\frac{a}{(a-x)}$

$(a-x)$ is the concentration left after 100 sec.

$$2.7\times10^{-3}=\frac{2.303}{100}\log\frac{0.29}{(a-x)}$$

$$\Rightarrow\frac{0.27}{2.303}=\log\frac{0.29}{(a-x)}\Rightarrow 0.117=\log\frac{0.29}{(a-x)}$$

$$\Rightarrow\quad (a-x)=0.22\ \text{M}.$$

4. **(c)** $t_{90\%}=\frac{2.303}{k}\log\frac{100}{100-90}$ (I)

$$t_{50\%}=\frac{2.303}{k}\log\frac{100}{100-50}\qquad\text{(II)}$$

Dividing $\frac{t_{90\%}}{t_{50\%}}=\frac{\log 10}{\log 2}$

$\therefore t_{90\%}=3.3t_{50\%}$

5. **(d)** If rate = $k[A]^x[B]^y[C]^z$

$5.0\times10^{-3}=k[0.010]^x[0.005]^y[0.010]^z$ ...(i)
$5.0\times10^{-3}=k[0.010]^x[0.005]^y[0.015]^z$ ...(ii)
$1.0\times10^{-2}=k[0.010]^x[0.010]^y[0.010]^z$ ...(iii)
$1.25=k[0.005]^x[0.005]^y[0.010]^z$ ...(iv)

From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.
From 1st and 4th sets of data
Dividing eq. (iv) by eq. (i)

$$\frac{1.25\times10^{-3}}{5.0\times10^{-3}}=\left[\frac{0.005}{0.010}\right]^x$$

or $0.25=(0.5)^x$ or $(0.5)^2=(0.5)^x$
$\therefore x=2$

The order with respect to 'A' is 2 from the 1st and 3rd sets of data Dividing eq. (i) by eq. (iii)

$$\frac{5.0\times10^{-3}}{1.0\times10^{-2}}=\left[\frac{0.005}{0.010}\right]^y$$

or $(0.5)^1=(0.5)^y\Rightarrow y=1$

The order with respect to 'B' is 1
So the order with respective the reactants A, B and C is 2, 1 and 0.

**6.** **(d)** Units of *k* indicate that reaction *I* is of second order and reaction *II* is first order.

For *I* reaction, $t_{1/2} \propto 1/a$,

first $t_{1/2} = 1$ hr, second $t_{1/2} = 2$ hr

$$[A] = 1\text{M} \xrightarrow{1\text{hr}} 0.5\text{M} \xrightarrow{2\text{hr}} 0.25\text{M}$$

$$[B] = 1\text{M} \xrightarrow{1\text{hr}} 0.5\text{M} \xrightarrow{1\text{hr}}$$

$$0.25\text{M} \xrightarrow{1\text{hr}} 0.125\text{M}$$

$$\frac{[A]}{[B]} = \frac{0.25\text{M}}{0.125\text{M}} = 2$$

**7.** **(d)** $\text{A} \longrightarrow 3\text{B}; \quad P_T = P_0 + 2x$

After time t, $\quad P_0 - x \quad 3x$

$$x = \frac{P_T - P_0}{2} \quad k = \frac{1}{t}\ln\left(\frac{P_0}{P_0 - x}\right)$$

After long time, 0 $3P_0$

$$x = \frac{P_T - \frac{P_\infty}{3}}{2} \, k = \frac{1}{t}\ln\left(\frac{\frac{P_\infty}{3}}{\frac{P_\infty}{3} - \left(\frac{3P_T - P_\infty}{6}\right)}\right)$$

$$P_\infty = 3P_o \quad x = \frac{3P_T - P_\infty}{6} \, k = \frac{1}{t}\ln\left(\frac{P_\infty / 3}{\frac{P_\infty}{2} - \frac{P_T}{2}}\right)$$

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

**8.** **(a)**

| | A | $\longrightarrow$ | 2B | + C |
|---|---|---|---|---|
| t = 0 | $P_i$ | | 0 | 0 |
| t = t | $P_i - y$ | | 2y | y |

Total pressure $P_t = P_i - y + 2y + y = P_i + 2y$

$$\frac{P_t - P_i}{2} = y$$

$$k = \frac{2.303}{t}\log\frac{2P_i}{3P_i - P_t}$$

**9.** **(a)** $t_{1/2} = \dfrac{0.693}{k}$

$$= \frac{0.693}{2.772 \times 10^{-3}} = 250 \text{ sec}$$

Since volume is changing therefore half-life should be defined on the basis of moles, so moles of A remaining after 250 sec. Also final volume of the container

$$V_f = \frac{n_f}{n_i} \times V_i = \frac{0.05 + 0.15}{0.1} \times 2 = 4 \text{ litre}$$

$\therefore$ Final concentration of $\text{A} = \dfrac{0.05}{4} = 0.0125 \text{ M}$

**10.** **(d)** Let n is the moles of reagent 'R' when R is reacted with A at time t = 0

| | A | $\longrightarrow$ | B | + C |
|---|---|---|---|---|
| t = 0 | n | | 0 | 0 |
| at t | n – x | | 2x | 3x |
| at t → ∞ | 0 | | 2n | 3n |

$$\therefore \quad 5n = n_2 \Rightarrow n = \frac{n_2}{5}$$

$$n + 4x = n_1 \Rightarrow x = \frac{n_1 - n}{4}$$

$$k = \frac{2.303}{t}\log\left(\frac{n}{n - x}\right)$$

so $\quad k = \dfrac{1}{t}\ln\left(\dfrac{4n_2}{5(n_2 - n_1)}\right)$

**11.** **(b)**

| | 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 → ∞) | 0 | | $2P_0$ | $P_0$ |

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

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

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

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

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

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

**12.** **(c)** $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

2 mol of gaseous nitrogen pentoxide on complete decomposition gives 5 mol of gaseous products.

Therefore, initial pressure of $N_2O_5 = 584.5 \times \dfrac{2}{5}$

$= 233.8$ mm Hg.

Let *x* be the amount of $N_2O_5$ decomposed after 30 min.

∴ After 30 min.
Pressure due to $N_2O_5 = 233.8 - x$
Pressure due to $NO_2 = 2x$
and pressure due to $O_2 = \frac{x}{2}$
Total pressure after 30 min

$$= 284.5 \text{ mm Hg} = 233.8 - x + 2x + \frac{x}{2}$$

or $233.8 + \frac{3x}{2} = 284.5$
or $x = 33.8$ mm Hg
Hence pressure of $N_2O_5$ after 30 min.
$= 233.8 - 33.8 = 200$ mm Hg

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} = \frac{2.303}{30}\log\frac{233.8}{200}$$

$$k = \frac{2.303}{30} \times 0.0679 = 5.2 \times 10^{-3}\ \text{min}^{-1}$$

**13.** **(d)** The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.
As $\Delta H = E_a$ (forward reaction) $- E_a$ (backward reaction)
For exothermic reaction
$\Delta H = -\text{ve}$
∴ $-\Delta H = E_a(f) - E_a(b)$
or $E_a(f) = E_a(b) - \Delta H$
∴ $E_a(f) < E_a(b)$
for endothermic reaction
$\Delta H = +\text{ ve}$
∴ $\Delta H = E_a(f) - E_a(b)$ or $E_a(f) = \Delta H + E_a(b)$
∴ $E_a(f) > E_a(b)$.

**14.** **(b)** $T_2 = T$ (say), $T_1 = 25°C = 298K$,
$E_a = 104.4 \text{ kJ mol}^{-1} = 104.4 \times 10^3 \text{ J mol}^{-1}$
$k_1 = 3 \times 10^{-4}$, $k_2 = ?$,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3 \text{ J mol}^{-1}}{2.303\times(8.314 \text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{298} - \frac{1}{T}\right]$$

As $T \to \infty, \frac{1}{T} \to 0$

$$\therefore \log\frac{k_2}{3\times10^{-4}} = \frac{104.4\times10^3 \text{ J mol}^{-1}}{2.303\times8.314\times298}$$

$$\log\frac{k_2}{3\times10^{-4}} = 18.297, \frac{k_2}{3\times10^{-4}} = 1.98\times10^{18}$$

$$k_2 = (1.98\times10^{18})\times(3\times10^{-4}) = 6\times10^{14}\text{s}^{-1}$$

**15.** **(a)** $2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\log\frac{k_2}{k_1} = \frac{9.0\times10^3}{2.303\times2}\left[\frac{308-298}{308\times298}\right]$$

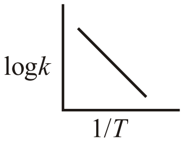
$$\frac{k_2}{k_1} = 1.63;\ k_2 = 1.63k_1;$$

$$\text{Increase in } k_1 = \frac{k_2 - k_1}{k_1}\times100$$

$$= \frac{1.63k_1 - k_1}{k_1}\times100 = 63.0\%$$

**16.** **(c)** $k = 1.2\times10^{14}e^{-25000/RT}\ \text{sec}^{-1}$ or

$$\log k = \log 1.2 \times 10^{14} - \frac{25000}{R}.\frac{1}{T}$$



Equation of straight line

$$\text{slope} = -\frac{2500}{R}$$

**17.** **(b)** $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{293} - \frac{1}{308}\right]$$

$$0.3 = \frac{E_a}{2.303\times8.314}\times\frac{15}{293\times308}$$

$$E_a = \frac{0.3\times2.303\times8.314\times293\times308}{15}.$$

$= 34558 \text{ J mol}^{-1} = 34.5 \text{ kJ mol}^{-1}$

**18.** **(c)** $k = Ae^{-E_a/RT}$

For methyl nitrite $k_1 = 10^{13} \times e^{[-152300/(8.314 \times T)]}$

For ethyl nitrite $k_2 = 10^{14} \times e^{[-157700/(8.314 \times T)]}$

if $k_1 = k_2$, then

$$10^{13} e^{[-152300/(8.314 \times T)]} = 10^{14} e^{[-155700/(8.314 \times T)]}$$

$$10 = e^{(+157700 - 152300)/(8.314 \times T)}$$

or $2.303 \log 10 = \dfrac{157700 - 152300}{8.314 \times T}$

$\therefore$ $T = 282\text{ K}$

**19.** **(a)** Given, $A \longrightarrow B$

and 20% solution of A decomposes 25% in 20 minute at 25°C

$\therefore$ Initial amount, $a = 20$

$\therefore$ Amount left, $(a - x) = 20 \times \dfrac{75}{100} = 15$

$\therefore$ $k_{25} = \dfrac{2.303}{20} \log_{10} \dfrac{20}{15}$ $\quad (\because t = 20 \text{ minute})$

$= 0.0144 \text{ minute}^{-1}$

Now, $2.303 \log_{10} \dfrac{k_{40}}{k_{25}} = \dfrac{E_a}{R} \dfrac{[T_2 - T_1]}{T_1 T_2}$

$\therefore$ $2.303 \log_{10} \dfrac{k_{40}}{k_{25}} = \dfrac{70 \times 10^3}{8.314} \left[\dfrac{313 - 298}{313 \times 298}\right]$

$$\frac{k_{40}}{k_{25}} = 3.872$$

$\therefore$ $k_{40} = 0.05575 \text{ min}^{-1}$ $\quad (\because k_{25} = 0.0144)$

Now suppose amount 'm' is left in 30% solution in 20 minute at 40°C.

$$k_{40} = \frac{2.303}{t} \log_{10} \frac{a}{(a - x)}$$

$$0.05575 = \frac{2.303}{20} \log_{10} \frac{30}{m}$$

$\therefore$ $m = 9.838$

$\therefore$ % decomposition

$$= \frac{(a - m)}{a} \times 100 = \frac{30 - 9.838}{30} \times 100 = 67.21\%$$

**20.** **(d)** An activity of 6.023 curie means $6.023 \times 3.7 \times 10^{10}$ dps.

Activity $= \lambda \times N$

$\therefore$ $6.023 \times 3.7 \times 10^{10} = 3.7 \times 10^4 \times N$

or $N = \dfrac{6.023 \times 3.7 \times 10^{10}}{3.7 \times 10^4}$

$\therefore$ Mass of $X^{100}$

$$= \left[\frac{6.023 \times 3.7 \times 10^{10}}{3.7 \times 10^4}\right] \times \frac{1}{6.023 \times 10^{23}} \times 100$$

$= 10^{-15}\text{ g}$

**21.** **(0.75)** $CH_3.O.CH_3 \rightarrow CH_4 + CO + H_2$

Total conc.

| | | | | | |
|---|---|---|---|---|---|
| Initial state | $a$ | 0 | 0 | 0 | $a$ |
| After 12 mts. | $a - x$ | $x$ | $x$ | $x$ | $a + 2x$ |

Calculation of initial concentration (a) of $CH_3OCH_3$

$PV = nRT$

or $\dfrac{n}{V} = \dfrac{P}{RT}$

$a = \dfrac{P}{RT} = \dfrac{0.4}{0.082 \times 773} = 6.31 \times 10^{-3}$ moles $L^{-1}$

Calculation of $k$

$k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{14.5} = 4.78 \times 10^{-2} \text{ min}^{-1}$

Substituting the values in the first order equation.

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$4.78 \times 10^{-2} = \frac{2.303}{12} \log \frac{a}{a - x}$$

$$\frac{a}{a - x} = 1.77446$$

$a - x = \dfrac{6.31 \times 10^{-3}}{1.77446}$ moles $L^{-1} = 3.556 \times 10^{-3}$ moles $L^{-1}$

$\therefore$ $x = (6.310 - 3.556) \times 10^{-3}$ moles/$l$

$= 2.754 \times 10^{-3}$ moles L

$\therefore$ After 12 min.

Total no. of moles $L^{-1}$

$= a + 2x = 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3}$

$= 11.818 \times 10^{-3}$

∴ $P=\frac{n}{V}RT=11.818\times 10^{-3}\times 0.082\times 773$

$=0.75$ atm

**22.** **(2.5)** $\underset{a_0-x-y}{A}\xrightarrow{k_1}\underset{2x}{2B}$; $\underset{a_0-x-y}{A}\xrightarrow{k_2}\underset{y}{C}$

$$\frac{d[A]}{dt}=(k_1+k_2)[A];\ \frac{[B]}{[C]}=\frac{2k_1}{k_2}=\frac{2x}{y}$$

$$=\frac{k_1}{k_2}=\frac{x}{y}$$

∵ $k_1=k_2=x=y$

$$(k_1+k_2)t=\ln\left[\frac{A_0}{A_t}\right]$$

$$2\times 6.93\times 10^{-3}\times 50=\ln\left[\frac{A_0}{A_t}\right]$$

$$=[A]_t=\frac{[A_0]}{2}=a_0-x-y=a_0/2\ (\because x=y)$$

∴ $x=a_0/4$. Total moles in container

$a_0-x-y+2x+y=a_0+x=1.25\,a_0$

% increase in moles ⇒ 25, So final pressure

$=2\times 1.25=2.5$ atm

**23.** **(18.39)** Let the initial concentration $(A)=100$
Final concentration at 298 K $=100-10=90$
Final concentration at 308 K $=100-25=75$
Substituting the values in the 1st order rate reaction

$$t=\frac{2.303}{k_{298}}\log\frac{100}{90}\qquad ...(i)$$

$$t=\frac{2.303}{k_{308}}\log\frac{100}{75}\qquad ...(ii)$$

From (i) and (ii) $\frac{k_{308}}{k_{208}}=2.73$

Substituting the value in the following relation

$$E_a=\frac{2.303\,R\times T_1\times T_2}{T_2-T_1}\log\frac{k_2}{k_1}$$

$$=\frac{2.303\times 8.314\times 298\times 308}{308-298}\log 2.73$$

$E_a=76.62\text{ kJ mol}^{-1}=18.39\text{ kcal mol}^{-1}$

**24.** **(378.74)** $\ln\frac{k_1'}{k_1}=\frac{E_1}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$ ...(i)

$$\ln\frac{k_2'}{k_2}=\frac{E_2}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]\qquad ...(ii)$$

Solving we get (ii)–(i),

$$\ln\frac{k_2'}{k_2}-\ln\frac{k_1'}{k_1}=\left(\frac{E_2-E_1}{R}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

(for equimolar formation of B and C, $k_2'=k_1'$)

$$\ln\left(\frac{k_1}{k_2}\right)=\left(\frac{8314}{8.314}\right)\frac{(T_2-300)}{300\times T_2}$$

$$\ln 2=(1000)\left(\frac{T_2-300}{300\times T_2}\right)$$

$T_2=378.74\text{K}$

**25.** **(1.8)** Rate constant at 300 K = k
∴ Rate constant at

$$310\text{ K}=k+\left[k\times\frac{7}{100}\right]=1.07\text{ k}$$

Thus, $2.303\log\frac{k_2}{k_1}=\frac{E_a(f)}{R}\frac{[T_2-T_1]}{T_2T_1}$

$$2.303\log\frac{1.07k}{k}=\frac{E_a(f)}{2}\left[\frac{310-300}{310\times 300}\right]$$

∴ $E_a(f)=1258.68$ cal

Now, equilibrium constant at 300 K = K′
Equilibrium constant at 310 K

$$=K'+\frac{3}{100}\times K'=1.03\,K'$$

Using $2.303\log\frac{K_2}{K_1}=\frac{\Delta H}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

$$2.303\log\frac{1.03K'}{K'}=\frac{\Delta H}{2}\left[\frac{310-300}{310\times 300}\right]$$

∴ $\Delta H=549.89$ cal

Since, $\Delta H=E_a(f)-E_a(b)$

∴ $549.89=1258.68-E_a(b)$

∴ $E_a(b)=708.79$ cal $\frac{E_a(f)}{E_a(b)}=1.8$

**26.** **(8.42)** $t = 4.5$ billion years and $T_{1/2}$ of $^{40}K = 1.26$ billion years.

Then, percentage of $^{40}K$ remaining $\left[\frac{a-x}{a}\right] \times 100$

$$t = \frac{2.303}{\lambda} \log \frac{a}{a-x}$$

$$\lambda = 0.693 / T_{1/2} = 0.693 / 1.26 = 0.55$$

$$\frac{a}{a-x} = 11.86 \quad \therefore \frac{a-x}{a} = \frac{1}{11.86} = 0.0843$$

$$\therefore \frac{a-x}{a} \times 100 = 0.0843 \times 100 = 8.42\%$$

**27.** **(8)** Since $[B] >>> [A]$, $[B]$ remains practically constant and the rate is dependent only on $[A]$. The reaction is pseudo first order w.r.t. $A$.

Rate $= k[A][B] = k[A] \times 5 = 5k[A] = k'[A]$

$$k' = \frac{2.303}{t} \log \frac{C_o}{C_t} = \frac{2.303}{100} \log \frac{C_o}{C_t}$$

$$\log \frac{C_o}{C_t} = \frac{100\,k'}{2.303} = \frac{100 \times 5k}{2.303}$$

$$= \frac{100 \times 5 \times 5.052 \times 10^{-3}}{2.303} = 1.0968$$

$$\frac{C_o}{C_t} = 12.5\ ,\ C_t = \frac{C_o}{12.5} = \frac{0.1}{12.5} = 0.008M$$

Hence, concentration of the reactant $A$ remaining after 100 s = 0.008 M = 8 mM

**28.** **(5)** Rate of reaction $= k[CO]^x[O_2]^y$

$4 \times 10^{-5} = k(0.02)^x(0.02)^y$ ...(i)

$1.6 \times 10^{-4} = k(0.04)^x(0.02)^y$ ...(ii)

$8 \times 10^{-5} = k(0.02)^x(0.04)^y$ ...(iii)

$$\frac{(i)}{(ii)}\ \frac{1}{4} = \left(\frac{1}{2}\right)^x$$

$x = 2$

$$\frac{(i)}{(iii)}\ \frac{1}{2} = \left(\frac{1}{2}\right)^y$$

$y = 1$

From eq. (1)

$4 \times 10^{-5} = k(0.02)^2(0.02)^1$

$$k = \frac{4 \times 10^{-5}}{4 \times 10^{-4} \times 2 \times 10^{-2}} = \frac{10}{2} = 5$$

**29.** **(8)** For I order reaction $r_1 = k[C]^1$

$$\therefore \frac{R_1}{R_2} = k_1 / k_2 = \text{temperature coefficient}$$

Let temperature coefficient be a $\frac{r_{35}}{r_{25}} = \frac{k_{35}}{k_{25}} = a$

$$\frac{r_{45}}{r_{35}} = \frac{k_{45}}{k_{35}} = a \quad \therefore \quad \frac{r_{45}}{r_{25}} = a \times a = a^2$$

Similarly, $\frac{r_{75}}{r_{25}} = a^5$

For I reaction $(r_{75})_I = 2^5 \times (r_{25})_I$

For II reaction $(r_{75})_{II} = 3^5 \times (r_{25})_{II}$

$$\therefore \frac{(r_{75})_{II}}{(r_{75})_I} = \frac{3^5}{2^5} = 7.594 \approx 8 \quad \left[\because (r_{25})_I = (r_{25})_{II}\right]$$

**30.** **(3)** Rate of reaction $= -\frac{1}{2}\frac{dP_{NO}}{dt} = -\frac{dP_{H_2}}{dt}$

For $P_{H_2}$ constant :

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 1.5 = k(359)^m (P_{H_2})^n$$

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 0.25 = k(152)^m (P_{H_2})^n$$

$$\therefore \frac{1.5}{0.25} = \left(\frac{359}{152}\right)^m \quad \therefore \quad m = 2$$

For $P_{NO}$ constant : $-\frac{dP_{H_2}}{dt} = 1.60 = (P_{NO})^m (289)^n$

$$-\frac{dP_{H_2}}{dt} = 0.79 = (P_{NO})^m (147)^n$$

$$\therefore \frac{1.60}{0.79} = \left(\frac{289}{147}\right)^n \quad \therefore \quad n = 1$$

$\therefore$ Rate $= k[P_{NO}]^2[P_{H_2}]^1$

$\therefore$ Order of reaction $= 2 + 1 = 3$