Special Cases of First Order Reactions

① Parallel or Side Reactions

$$A \longrightarrow B \quad \text{(Simple)}$$

$$A \begin{cases} \xrightarrow{K_1} B \\ \xrightarrow{K_2} C \end{cases} \quad \text{(Parallel)}$$

$$\text{rate} = -\frac{dA}{dt} = K_1[A] + K_2[A] = (K_1+K_2)[A]$$

$$\text{rate} = -\frac{dA}{dt} = (K_1+K_2)[A] = K_{eff}[A]$$

effective order = 1

$$\boxed{K_{eff} = K_1 + K_2}$$

$$(t_{1/2})_{eff} = \frac{0.693}{K_{eff}} = \frac{0.693}{K_1+K_2} = \frac{0.693}{\frac{0.693}{(t_{1/2})_1} + \frac{0.693}{(t_{1/2})_2}}$$

$$\boxed{\frac{1}{(t_{1/2})_{eff}} = \frac{1}{(t_{1/2})_1} + \frac{1}{(t_{1/2})_2}}$$ Effective Half Life

Effective Activation Energy :-

$$K_{eff} = K_1 + K_2$$

$$A_{eff} \cdot e^{-(E_a)_{eff}/RT} = A_1 \cdot e^{-(E_a)_1/RT} + A_2 \cdot e^{-(E_a)_2/RT}$$

differentiate w.r.t Temperature 'T'

$$A_{eff} \cdot e^{-(E_a)_{eff}/RT} \left(\frac{-(E_a)_{eff}}{RT}\right) = A_1 \cdot e^{-(E_a)_1/RT} \left(\frac{-(E_a)_1}{RT}\right) + A_2 \cdot e^{-(E_a)_2/RT} \left(\frac{-(E_a)_2}{RT}\right)$$

$$-K_{eff}(E_a)_{eff} = -K_1 (E_a)_1 - K_2 (E_a)_2$$

$$(E_a)_{eff} = \frac{K_1 Ea_1 + K_2 Ea_2}{K_{eff}}$$

$$\boxed{Ea_{eff} = \frac{K_1 Ea_1 + K_2 Ea_2}{K_1 + K_2}}$$

Finding Concentration of [A] & [B] & [C]

$$[A] = A_0 e^{-K_{eff} t} = A_0 \cdot e^{-(K_1 + K_2)t}$$

First order kinetics

$$\frac{d[B]}{dt} = K_1[A] \Rightarrow \frac{d[B]}{dt} = K_1 A_0 . e^{-(K_1+K_2)t}$$

$$\int_0^B \frac{d[B]}{dt} = \int_0^t K_1 A_0 . e^{-(K_1+K_2)t}$$

$$[B]_0^B = K_1 A_0 \left[\frac{e^{-(K_1+K_2)t}}{-(K_1+K_2)}\right]_0^t$$

$$[B] = \frac{K_1 A_0}{-(K_1+K_2)} \left(e^{-(K_1+K_2)t} - 1\right)$$

$$[B] = \frac{K_1 A_0}{K_1+K_2} \left(1 - e^{-(K_1+K_2)t}\right)$$

Similarly

$$[C] = \frac{K_2 A_0}{K_1+K_2} \left(1 - e^{-(K_1+K_2)t}\right)$$

$$\boxed{\frac{[B]}{[C]} = \frac{K_1}{K_2}}$$

% of B in product $= \frac{[B]}{[B]+[C]} \times 100 = \frac{K_1}{K_1+K_2} \times 100$

% of C in product $= \frac{[C]}{[B]+[C]} \times 100 = \frac{K_2}{K_1+K_2} \times 100$