Chp 10

Chain reaction:

$$A \longrightarrow B + C$$

Mechanism: $n_i A \longrightarrow R^\bullet$, $\quad r_i = k_i C_A^{n_i}$

$$A + R^\bullet \longrightarrow B + C + R^\bullet, \quad r_p = k_p C_A C_R$$

$$n_t R^\bullet \longrightarrow X, \quad r_t = k_t C_R^{n_t}$$

Overall reaction rate:

$$r = r_p = k_p C_A C_R$$

Applying PSSA to C_R.

$$\frac{dC_R}{dt} = r_i - n_t r_t = k_i C_A^{n_i} - n_t k_t C_R^{n_t} = 0$$

$$\therefore \boxed{C_R = \left[\frac{k_i}{n_t k_t} C_A^{n_i}\right]^{1/n_t}}$$

$\therefore$ overall reaction rate :

$$r = k_p \cdot C_A \cdot \left(\frac{k_i}{n_t k_t} \right)^{1/n_t} \cdot C_A^{1 + n_i/n_t}$$

$$\therefore \boxed{ r = \underbrace{\left(\frac{k_i}{n_t k_t} \right)^{1/n_t} k_p}_{k_{eff}} C_A^{\overbrace{1 + n_i/n_t}^{n_{eff}}} }$$

which is of the form :

$$\underline{r = k_{eff} \; C_A^{n_{eff}}}$$

where, $\underline{n_{eff} = 1 + \frac{n_i}{n_t}}$

& $\underline{k_{eff} = k_p \left(\frac{k_i}{n_t k_t} \right)}^{1/n_t}$

$\because$ $\underline{k = k_0 \exp(-Ea/RT)}$ → Arrhenius eq.

For k_{eff} :

$$k_{eff} = k_{po} \cdot \exp\left(-\frac{E_p}{RT}\right) \cdot \left[\frac{k_{io}\exp(-E_i/RT)}{n_t \cdot k_{to}\exp(-E_t/RT)}\right]^{1/n_t}$$

$$k_{eff} = k_{po} \cdot \left(\frac{k_{io}}{n_t \cdot k_{to}}\right)^{1/n_t} \cdot \exp\left\{-\frac{1}{RT}\underbrace{\left[\frac{E_i}{n_t} - \frac{E_t}{n_t} + E_p\right]}_{\text{effective activation energy}}\right\}$$

$$k_{eff} = k_o' \exp\left(-\frac{E_{eff}}{RT}\right)$$

$\therefore$ overall reaction : $r = k_{eff}\, C_A^{\,n_{eff}}$

where, $n_{eff} = 1 + \frac{n_i}{n_t}$

$$k_{eff} = k_p \left(\frac{k_i}{n_t\, k_t}\right)^{1/n_t}$$

$$E_{eff} = \frac{E_i}{n_t} - \frac{E_t}{n_t} + E_p$$