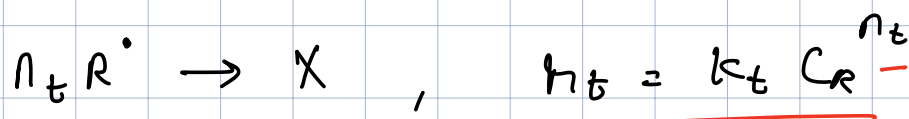
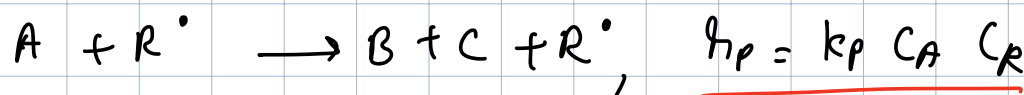
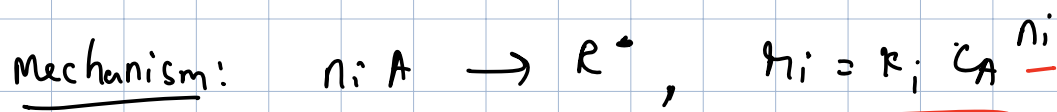
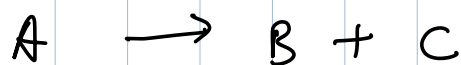


Chp to

chain reaction:



Overall reaction rate:

$$r = r_p = k_p C_A C_R$$

Applying PSSA to C_R .

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

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

∴ overall reaction rate :

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

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

which is of the form :

$$r = k_{eff} C_A^{n_{eff}}$$

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

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

$$\therefore k = k_0 \exp(-E_a/RT) \rightarrow \text{Arrhenius eq.}$$

For k_{eff} :

$$k_{eff} = k_{p0} \cdot \exp\left(-\frac{E_p}{RT}\right) \cdot \left[\frac{k_{i0} \exp(-E_i/RT)}{n_t \cdot k_{t0} \exp(-E_t/RT)} \right]^{1/n_t}$$

$$k_{eff} = k_{p0} \cdot \left(\frac{k_{i0}}{n_t \cdot k_{t0}} \right)^{1/n_t} \cdot \exp\left\{ -\frac{1}{RT} \left[\frac{E_i}{n_t} - \frac{E_t}{n_t} + E_p \right] \right\}$$

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

effective
activation
energy

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

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

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

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