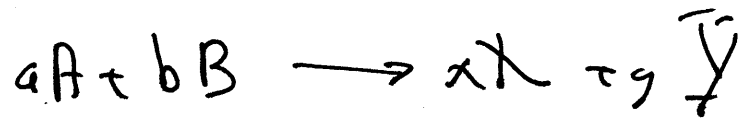


Note



$$\text{rate} = A^\alpha B^\beta X^\delta Y^\gamma$$

$$\textcircled{1} \quad \text{rate} = \frac{1}{\nu_P} \frac{dP}{dt} = \frac{1}{\nu_R} \frac{dR}{dt}$$

$$\nu_A = -a$$

$$\nu_B = -b$$

$$\nu_X = x$$

$$\nu_Y = y$$

$$\textcircled{2} \quad \text{rate} = \frac{1}{\nu_P} \frac{dP}{dt} = - \frac{1}{\nu_R} \frac{dR}{dt}$$

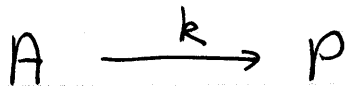
$$\nu_A = a$$

$$\nu_B = b$$

$$\nu_X = x$$

$$\nu_Y = y$$

FIRST ORDER



$$\text{rate} = k[A]$$

$$v_A = +1$$

$$v_P = +1$$

$$\text{rate} = \frac{1}{v_P} \frac{d[P]}{dt} = - \frac{1}{v_A} \frac{d[A]}{dt}$$

$$\frac{d[A]}{dt} = -k[A]$$

$$[A(t)] = A_0 e^{-kt}$$

$$\ln[A] = \ln A_0 - kt$$

$$[A(t_{1/2})] = \frac{A_0}{2} e^{-kt_{1/2}}$$

$$\frac{[A(t_{1/2})]}{A_0} = \frac{1}{2} = e^{-kt_{1/2}}$$

$$-\ln 2 = -kt_{1/2}$$

$$k = \frac{\ln 2}{t_{1/2}}$$

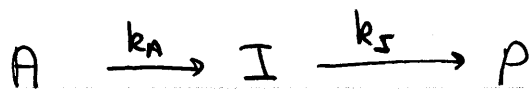
$$\frac{d[P]}{dt} = k[A(t)] = kA_0 e^{-kt}$$

$$[P(t)] = P_0 + k \int_0^t A_0 e^{-ks} ds$$

$$[P(t)] = P_0 + A_0 \int_0^t e^{-ks} k ds$$

$$P_0 - A_0 e^{-ks} \Big|_0^t$$

$$[P(t)] = P_0 + A_0 [1 - e^{-kt}]$$



$$\frac{d[A]}{dt} = -k_A [A]$$

$$\frac{d[I]}{dt} = k_A [A] - k_I [I]$$

$$\frac{d[P]}{dt} = k_I [I]$$

$$A_0 \neq 0 \quad I_0 = 0 \quad P_0 = 0$$

$$[A(t)] = A_0 e^{-k_A t}$$

$$\frac{d[I]}{dt} + k_I [I] = k_A [A] = k_A A_0 e^{-k_A t}$$

$$\frac{d}{dt} \left[e^{k_I t} [I] \right] = k_A A_0 e^{-k_A t} e^{k_I t}$$

$$e^{k_I t} [I(t)] = k_A A_0 \int_0^t e^{(k_I - k_A)s} ds$$

$$= \frac{k_A A_0}{k_I - k_A} \left[e^{(k_I - k_A)t} - 1 \right]$$

$$[I(t)] = \frac{k_A A_0}{k_I - k_A} \left[e^{-k_A t} - e^{-k_I t} \right]$$

$$A_0 = [A(t)] + [I] + [P]$$

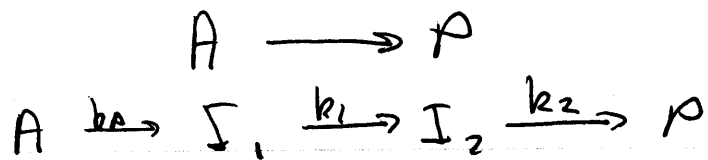
$$[P(t)] = A_0 - [A(t)] - [I(t)]$$

$$k_A \gg k_S$$

Rate determining step (II)

$$k_A \ll k_S$$

Rate determining step (I)



$$\frac{d[A]}{dt} = -k_A [A]$$

$$\frac{d[I_1]}{dt} = k_A [A] - k_1 [I_1]$$

$$\frac{d[I_2]}{dt} = k_1 [I_1] - k_2 [I_2]$$

$$\frac{d[P]}{dt} = k_2 [I_2]$$

Steady state approximation

$$\frac{dI_1}{dt} = \frac{dI_2}{dt} = 0$$

$$\textcircled{1} \quad [A(t)] = A_0 \mathcal{Q}^{-k_A t}$$

$$k_A [A(t)] = k_1 \bar{I}_1 \Rightarrow [\bar{I}_1(t)]_{ss} = \frac{k_A}{k_1} A_0 \mathcal{Q}^{-k_A t}$$

$$k_1 \bar{I}_1 = k_2 [\bar{I}_2] \Rightarrow [\bar{I}_2(t)]_{ss} = \frac{k_1}{k_2} \frac{k_A}{k_1} A_0 \mathcal{Q}^{-k_A t}$$

$$[\bar{I}_2(t)]_{ss} = \frac{k_A}{k_2} A_0 \mathcal{Q}^{-k_A t}$$

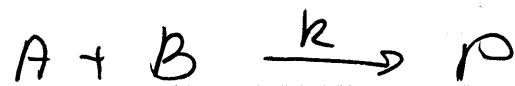
$$[P(t)] = \frac{k_A}{k_2} A_0 \mathcal{Q}^{-k_A t}$$

$$\frac{d}{dt} [I_1(t)]_{ss} = - \frac{k_A^2}{k_i} A_0 Q^{-k_A t} \neq 0$$

SS approximation valid when

$$\frac{k_A^2}{k_i} A_0 Q^{-k_A t} \ll 1$$

$$k_i \gg k_A$$



$$\text{rate} = k [A] [B]$$

$$\frac{d[A]}{dt} = -k [A] [B]$$

$$\frac{d[B]}{dt} = -k [A] [B]$$

$$\frac{d[P]}{dt} = k [A] [B]$$

$$X = \frac{[A] + [B]}{2} \quad \Rightarrow \quad [A] = X + Y$$

$$Y = \frac{[A] - [B]}{2} \quad \Rightarrow \quad [B] = X - Y$$

$$\frac{dX}{dt} = -k(X+Y)(X-Y) = -k(X^2 - Y^2)$$

$$\frac{dY}{dt} = 0 \quad \Rightarrow \quad Y(t) = \text{const} \\ = A_0 - B_0 \equiv Y_0$$

$$\frac{dX}{dt} = -kX^2 + kY_0^2$$