

Arrhenius law

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

alternative

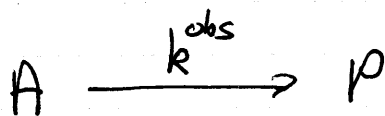
$$k = aT^m e^{-E'/RT}$$

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T}$$

OR

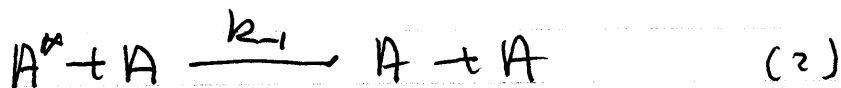
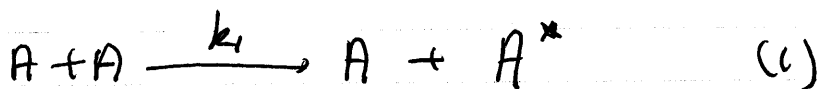
$$\ln k = \ln a + m \ln T - \frac{E_a}{R} \frac{1}{T}$$

MECHANISMS



overall rxn

Elem. rxn.



Intermediate species (not in the overall rxn)

$$\text{rate} = \frac{d[P]}{dt} = k_2 [A^*] = k^{\text{obs}} [A]^2 [P]^0$$

FOR THE INTERMEDIATES USE THE SSA

$$\frac{d[A^*]}{dt} = k_1 [A]^2 - k_{-1} [A][A^*] - k_2 [A^*] = 0$$

$$k_1 [A]^2 = (k_{-1} [A] + k_2) [A^*]$$

$$[A^*] = \frac{k_1 [A]^2}{k_2 + k_{-1} [A]}$$

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [A]^2}{k_2 + k_{-1} [A]} = \left(\frac{k_1 k_2 [A]}{k_2 + k_{-1} [A]} \right) [A]$$

$$\frac{d[A]}{dt} = k_{\text{obs}} [A]$$

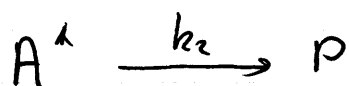
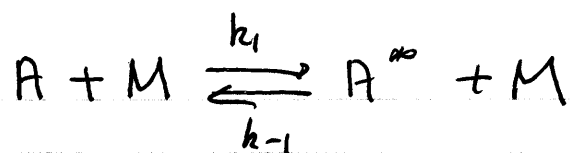
$$k_{\text{obs}} = \frac{k_1 k_2 [A]}{k_2 + k_{-1} [A]}$$

a) $k_{-1} [A] \gg k_2$

$$k_{\text{obs}} = \frac{k_1 k_2}{k_{-1}} = k_2 K^{\text{eq.}} \Rightarrow \text{rate} = k_2 K^{\text{eq.}} [A]$$

b) $k_{-1} [A] \ll k_2$

$$k_{\text{obs}} = k_1 [A] \Rightarrow \text{rate} = k_1 [A]^2$$



$$\text{Rate} = \frac{d[P]}{dt} = k_2 [A^*] = \frac{k_1 k_2 [M] [A]}{k_2 + k_{-1} [M]}$$

$$= k_{\text{obs}} [A]$$

$$k_{\text{obs}} = \frac{k_1 k_2 [M]}{k_2 + k_{-1} [M]}$$

a) $k_{-1} [M] \gg k_2$

b) $k_{-1} [M] \ll k_2$

c)

$$\frac{1}{k_{\text{obs}}} = \frac{k_{-1}}{k_1 k_2} + \left(\frac{1}{k_1}\right) \frac{1}{[M]}$$

$$\text{slope} = \frac{1}{k_1}$$

$$\text{Intercept} = \frac{k_{-1}}{k_2}$$