Arrhenius law

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

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

alternative

$$k = a T^m e^{-E'/RT}$$

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

or

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

MECHANISMS

$$A \xrightarrow{k^{obs}} P \qquad \text{overall RXN}$$

Elem. RXN.

$$A + A \xrightarrow{k_1} A + A^* \qquad (1)$$

$$A^* + A \xrightarrow{k_{-1}} A + A \qquad (2)$$

$$A^* \xrightarrow{k_2} P \qquad (3)$$

Intermediate species (not in the overall rxn)

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

FOR THE INTERMEDIATES USE THE SSA

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

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

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

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

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

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

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

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

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

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

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + M$$

$$A^* \xrightarrow{k_2} P$$

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

$$= k_{uni}[A]$$

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

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

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

c)

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

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

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