

1.(4) $\sigma(\varepsilon)=0$ when $\varepsilon < \varepsilon_a$: threshold kinetic energy.

$$\varepsilon = \frac{1}{2} \mu v_{\text{rel}}^2$$

$$v_{\text{rel}, A-B} = v_{\text{rel}} \cdot \cos\theta = v_{\text{rel}} \left(\frac{d^2 - a^2}{d^2} \right)^{\frac{1}{2}}$$

$$\Sigma_{A-B} = \varepsilon \left(\frac{d^2 - a^2}{d^2} \right) \frac{1}{2}$$

a_{\max} : max. impact parameter (no reaction when $a > a_{\max}$)

$$a_{\max}^2 = (1 - \varepsilon_a/\varepsilon) d^2 \rightarrow \pi a_{\max}^2 = (1 - \frac{\varepsilon_a}{\varepsilon}) \pi d^2$$

$$\therefore \sigma(\varepsilon) = (1 - \frac{\varepsilon_a}{\varepsilon}) \sigma$$

$$(2) k_2 = N_A \int_0^\infty \sigma(\varepsilon) v_{\text{rel}} f(\varepsilon) d\varepsilon$$

$$\begin{aligned} f(v) dv &= 1 \cdot dv \quad \text{for } 1 \leq v \leq 2 \\ &= 0 \quad \text{for } v < 1, v > 2 \end{aligned}$$

$$\varepsilon = \frac{1}{2} \mu v^2, \quad v = \left(\frac{2\varepsilon}{\mu} \right)^{\frac{1}{2}}, \quad dv = \frac{d\varepsilon}{(2\mu\varepsilon)^{\frac{1}{2}}}$$

$$k_2 = N_A \int_{\frac{1}{2}\mu}^{\mu} (1 - \frac{\varepsilon_a}{\varepsilon}) \left(\frac{2\varepsilon}{\mu} \right)^{\frac{1}{2}} \frac{d\varepsilon}{(2\mu\varepsilon)^{\frac{1}{2}}}$$

$$= \frac{N_A}{\mu} \int_{\frac{1}{2}\mu}^{\mu} (1 - \frac{\varepsilon_a}{\varepsilon}) d\varepsilon$$

$$= \frac{N_A}{\mu} (\varepsilon - \varepsilon_a \ln \varepsilon) \Big|_{\frac{1}{2}\mu}^{\mu}$$

$$= \frac{N_A}{\mu} \left(\frac{3}{2}\mu - \varepsilon_a \ln 4 \right) = N_A \left(\frac{3}{2} - \frac{\varepsilon_a}{\mu} \ln 4 \right)$$



$$k_2 = e^2 B e^{\Delta f s / k} e^{-E_a / RT} \quad \text{where } \beta = \frac{kT}{h} \frac{RT}{P_0}$$

$$A = e^2 B e^{\Delta f s / k}$$

$$\ln A = 2 + \ln B + \Delta f s / R$$

$$\therefore \Delta f s = R (\ln A / R - 2)$$

$$= R \left(\ln \frac{A}{\frac{kT}{h} \frac{RT}{P_0}} - 2 \right)$$

$$= (8.314) \left(\ln \frac{4.07 \times 10^5 \frac{\text{dm}^3}{\text{mol.s}} \times \frac{1 \text{m}^3}{10^3 \text{dm}^3}}{(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(300 \text{K})^2} \frac{8.314 \frac{\text{J}}{\text{K.mol}}}{6.626 \times 10^{-34} \frac{\text{J.s}}{\text{s}}} \right) - 2$$

$$= 8.314 (\ln 2.631 \times 10^{-9} - 2)$$

$$= -180.8 \text{ J/K.mol}$$

$$\Delta f H = E_a - 2RT = 65.43 \frac{\text{kJ}}{\text{mol}} - 2 \times 8.314 \frac{\text{J}}{\text{K.mol}} \times (300 \text{K}) \times \frac{1 \text{kJ}}{10^3 \text{J}}$$

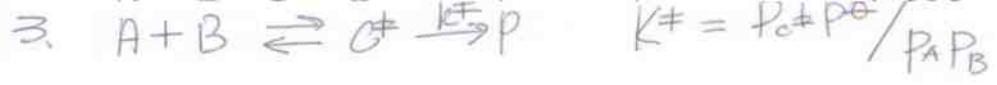
$$= 60.44 \text{ kJ/mol}$$

$$\Delta f H = \Delta f U + \Delta f (PV)$$

$$\Delta f U = \Delta f H - \Delta f (PV) = \Delta f H - \Delta v RT$$

$$= (60.44 \frac{\text{kJ}}{\text{mol}}) - (-1) (8.314 \frac{\text{J}}{\text{K.mol}})(300 \text{K})$$

$$= 62.9 \frac{\text{kJ}}{\text{mol}} \times \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right)$$



$$[C^{\pm}] = \frac{RT}{p_0} k^{\pm} [A][B]$$

$$v = k^{\pm} [C^{\pm}] = k_2 [A][B], \quad k^{\pm} = Kv$$

$$\therefore k_2 = \frac{RT}{p_0} k^{\pm} K^{\pm}$$

$$\text{Since } K = \frac{1}{v} \left(\frac{g_{\text{m.s.}}^{\pm}}{N_A} \right)^{v_i} \exp^{-\Delta E_0 / RT}, \quad K^{\pm} = \frac{N_A g_{\text{c}}^{\pm}}{g_A g_B} e^{-\Delta E_0 / RT}$$

for small v ,

$$g = \frac{1}{1 - e^{-hv/kT}} = \frac{1}{1 - (1 - \frac{hv}{kT} + \dots)} = \frac{kT}{hv}$$

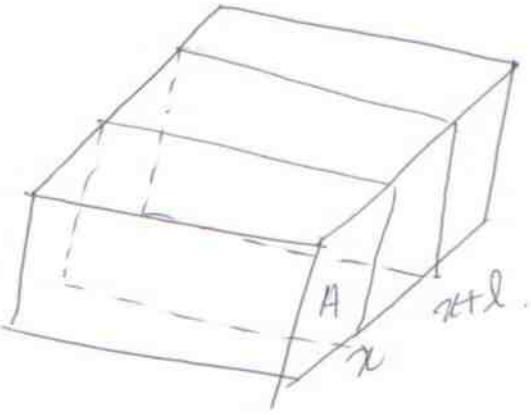
$$\therefore g^{\pm} = \frac{kT}{hv} \bar{g}_{\text{c}}^{\pm}$$

\hookrightarrow partition function for all the other mode of complex.

$$\therefore K^{\pm} = \frac{kT}{hv} \bar{K}^{\pm} \quad \text{where } \bar{K}^{\pm} = \frac{N_A \bar{g}_{\text{c}}^{\pm}}{\bar{g}_A \bar{g}_B} e^{-\Delta E_0 / RT}$$

$$\therefore k_2 = k^{\pm} \frac{RT}{p_0} \cdot \frac{kT}{hv} \bar{K}^{\pm}$$

$$= K \frac{kT}{hv} \bar{K}_0^{\pm}, \quad \text{where } \bar{K}_0^{\pm} = \frac{RT}{p_0} \cdot \bar{K}^{\pm}$$



$$\begin{aligned}
 & J(x) \cdot A \Big|_{x=x} + \nu [J] A \Big|_{x=x} - (J(x) \cdot A \Big|_{x=x+l} + \nu [J] A \Big|_{x=x+l}) \\
 & \quad - k[J] \cdot A \cdot l \\
 = & Al \frac{\partial [J]}{\partial t}.
 \end{aligned}$$

$$\begin{aligned}
 & \frac{1}{l} A \cdot l, \lim_{l \rightarrow 0} \quad \lim_{l \rightarrow 0} \left(\frac{J(x) \Big|_{x=x} - J(x) \Big|_{x=x+l}}{l} + \nu \frac{[J] \Big|_{x+l} - [J] \Big|_x}{l} \right) \\
 & \quad - k[J] = \frac{\partial [J]}{\partial t}
 \end{aligned}$$

$$\text{where } J(x) = -D \frac{\partial [J]}{\partial x}$$

$$\frac{\partial}{\partial x} (D \frac{\partial [J]}{\partial x}) - \nu \frac{\partial [J]}{\partial x} - k[J] = \frac{\partial [J]}{\partial t}$$

if $D = \text{const.}$

$$\frac{\partial [J]}{\partial t} = D \frac{\partial^2 [J]}{\partial x^2} \rightarrow \frac{\partial [J]}{\partial x} - k[J]$$



$$k_2 = K \frac{kT}{h} e^{-\Delta^{\ddagger} G / RT}$$

$$= \frac{kT}{h} e^{\Delta^{\ddagger} S / R} e^{-\Delta^{\ddagger} H / RT}$$

$$= e \cdot \frac{kT}{h} e^{\Delta^{\ddagger} S / k} e^{-E_a / kT}$$

↑

$$E_a = RT^2 \left(\frac{\partial \ln k}{\partial T} \right) \rightarrow \frac{\partial \ln k_2}{\partial T} = \frac{1}{T} + \frac{\Delta^{\ddagger} H}{kT}$$

$$\rightarrow E_a = \Delta^{\ddagger} H + RT$$

$$\therefore \Delta H^{\ddagger} = E_a - RT = 368 - 8.314 \times 870 \times 10^3 \\ = 361 \text{ (kJ/mol)}$$

$$e^{\Delta^{\ddagger} S / k} = 5 \times 10^{16} \frac{h}{e \cdot kT} = \frac{(5 \times 10^{16}) (6.63 \times 10^{-4})}{(1.38 \times 10^{-23}) 870 \text{ e}}$$

$$= 1.04 \times 10^3$$

$$\therefore \Delta^{\ddagger} S = 57.8 \text{ J/K-mol}$$