Houston Chapter 3 (3.1- 3.3)

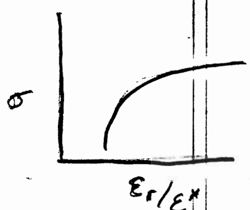
H3.1 5 atoms (nonlinear)

$3N-6$ coord. $= 3(5)-6 = \boxed{9 \text{ coordinates}}$

H3.2 simple collision theory -

$$\sigma(\mathcal{E}_r) = \pi b_{max}^2\left(1 - \frac{\mathcal{E}^*}{\mathcal{E}_r}\right) \quad \mathcal{E}^*\mathcal{E}_r^{-1}$$

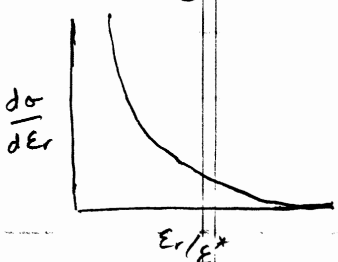
"most dependent" on $\mathcal{E}_r$; $\frac{d\sigma(\mathcal{E}_r)}{d\mathcal{E}_r} = \max$



$$\frac{d\sigma(\mathcal{E}_r)}{d\mathcal{E}_r} = \pi b_{max}^2\left(0 - (-\mathcal{E}^*\mathcal{E}_r^{-2})\right) = \pi b_{max}^2\left(\frac{\mathcal{E}^*}{\mathcal{E}_r^2}\right)$$

$$\frac{d\sigma(\mathcal{E}_r)}{d\mathcal{E}_r} = 0 \text{ at max. } \sigma$$

want change in slope to be maximized



$$\frac{d}{d\sigma}\left(\frac{d\sigma}{d\mathcal{E}_r}\right) = 0 = \pi b_{max}^2\,\mathcal{E}^*(-2)(\mathcal{E}_r^{-3})$$

$$\boxed{\mathcal{E}_r = 0}$$

But $\mathcal{E}_r \geq \mathcal{E}^*$ for simple collision theory, so max. change at $\boxed{\mathcal{E}_r = \mathcal{E}^*}$ This is obvious by looking at Figure 3.7.

H3.3 $\boxed{\text{(d)}}$ The thermal rate constant ($k(T)$) is the average of the energy dependent rate constant ($k(\mathcal{E}_r)$) over the thermal energy distribution ($G(\mathcal{E}_r)$). This gives a single rate constant that accounts for the range of kinetic energies present in the sample at a given temperature.

Houston Chp 3, con't.

H3.4 $\boxed{b}$ The steric factor p depends on the requirements for the reactants to be in a particular orientation. This is the main contribution to $k(T)$ that is not accounted for in simple collision theory.

H3.7 Note error - eqn. at top of p.112 (1[st] line of page) should be:

From question

$$1-\cos\gamma_{max} = \left[\mathcal{E}_r\left(1-\frac{b^2}{b^2_{max}}\right)-\mathcal{E}^*\right]/\mathcal{E}'$$

γ_{max} = max angle for rxn.

$$P(\mathcal{E}_r, b) = \frac{\int_0^{\gamma_{max}} 4\pi b^2_{max}\sin\gamma\, d\gamma}{4\pi b^2_{max}} = 1-\cos\gamma_{max}$$

$$P(\mathcal{E}_r, b) = \left[\mathcal{E}_r\left(1-\frac{b^2}{b^2_{max}}\right)-\mathcal{E}^*\right]/\mathcal{E}'$$

$$\sigma(\mathcal{E}_r) = \int P(\mathcal{E}_r, b)\, 2\pi b\, db = \frac{1}{\mathcal{E}'}\int_0^{b_{max}}\left[\mathcal{E}_r\left(1-\frac{b^2}{b^2_{max}}\right)-\mathcal{E}^*\right]2\pi b\, db$$

$$= \frac{2\pi}{\mathcal{E}'}\int_0^{b_{max}} \mathcal{E}_r b - \frac{\mathcal{E}_r}{b^2_{max}}b^3 - \mathcal{E}_r\mathcal{E}^* b\; db$$

$$= \frac{2\pi}{\mathcal{E}'}\left[\frac{1}{2}\mathcal{E}_r b^2 - \left(\frac{1}{4}\right)\frac{\mathcal{E}_r}{b^2_{max}}b^4 - \frac{1}{2}\mathcal{E}_r\mathcal{E}^* b^2\right]_0^{b_{max}}$$

$$= \frac{2\pi}{\mathcal{E}'}\left[\frac{1}{2}\mathcal{E}_r b^2_{max} - \frac{\mathcal{E}_r b^{\cancel{4}\,2}_{max}}{4\cancel{b^2_{max}}} - \frac{1}{2}\mathcal{E}_r\mathcal{E}^* b^2_{max}\right]$$

$$\sigma(\mathcal{E}_r) = \frac{2\pi}{\mathcal{E}'}b^2_{max}\left[\frac{1}{2}\mathcal{E}_r - \frac{1}{4}\mathcal{E}_r - \frac{1}{2}\mathcal{E}_r\mathcal{E}^*\right] = \frac{\pi}{2\mathcal{E}'}b^2_{max}\mathcal{E}_r(1-2\mathcal{E}^*)$$

Now average this cross section over the thermal distribution $(G(\mathcal{E}_r))$.

(next page)

Houston Chp. 3 (con't)

H3.7 (continued)

$$k(\varepsilon_r) = v_r \sigma(\varepsilon_r)$$

$$G(\varepsilon_r)\,d\varepsilon_r = 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} (\varepsilon_r)^{1/2} \exp\left(-\frac{\varepsilon_r}{k_B T}\right) d\varepsilon_r$$

$$k(T) = \int_{\varepsilon^*}^{\infty} 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} (\varepsilon_r)^{1/2} \exp\left(\frac{-\varepsilon_r}{k_B T}\right) v_r\, \sigma(\varepsilon_r)\, d\varepsilon_r$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2}\left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}\int_{\varepsilon^*}^{\infty} \varepsilon_r^{1/2} \exp\left(\frac{-\varepsilon_r}{k_B T}\right)\left(\frac{\pi}{2\varepsilon'} b_{max}^2\, \varepsilon_r (1 - 2\varepsilon^*)\right) d\varepsilon_r$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2}\left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}\left(\frac{\pi}{2\varepsilon'} b_{max}^2 (1 - 2\varepsilon^*)\right)\int_{\varepsilon^*}^{\infty} \varepsilon_r^{3/2} \exp\left(\frac{-\varepsilon_r}{k_B T}\right) d\varepsilon_r$$

Yes, but $d\varepsilon_r = 2\varepsilon_r^{1/2} dx$ $= 2x\,dx$ so integral is then $\int 2x^4 e^{-ax^2} dx$

$$\int x^3 e^{-ax^2} dx = \frac{-(ax^2+1)e^{-ax^2}}{2a^2}$$

$$x = \varepsilon_r^{1/2} \qquad a = \frac{1}{k_B T}$$

This won't work out because my integral is incorrect – will keep working on this ☺ RdP

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2}\left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}\left(\frac{\pi}{2\varepsilon'} b_{max}^2 (1 - 2\varepsilon^*)\right)\left[\frac{-\left(\frac{\varepsilon_r}{k_B T} + 1\right)e^{-\varepsilon_r/k_B T}}{2/k_B^2 T^2}\right]_{\varepsilon^*}^{\infty}$$

$$= \left[\frac{-(\infty\, e^{-\infty})}{2/k_B^2 T^2} - \frac{-\left(\varepsilon^*/k_B T + 1\right)e^{-\varepsilon^*/k_B T}}{2/k_B^2 T^2}\right]$$

$$= +e^{-\varepsilon^*/k_B T}\left(\frac{(\varepsilon^* + k_B T)\, k_B^{\cancel{2}} T^{\cancel{2}}}{(\cancel{k_B T})(2)}\right)$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{3/2} v_r \left(\frac{\pi}{2\varepsilon'} b_{max}^2 (1 - 2\varepsilon^*)\right)\left(e^{-\varepsilon^*/k_B T}\right)\left(\frac{1}{2}\right)(\varepsilon^* + k_B T)(k_B T)$$

$$= \frac{k_B T}{\varepsilon'}\left[(\pi b_{max}^2) v_r \left(\frac{1}{\pi k_B T}\right)^{3/2}\left(\frac{\pi}{2} - \pi\varepsilon^*\right)\left(e^{-\varepsilon^*/k_B T}\right)(\varepsilon^* + k_B T)\right]$$

$$= \frac{k_B T}{\varepsilon'}\left[\pi b_{max}^2 v_r e^{-\varepsilon^*/k_B T}\left(\frac{1}{\pi k_B T}\right)^{3/2}\left(\frac{\pi\varepsilon^*}{2} + \frac{\pi k_B T}{2} - \pi\varepsilon^{*2} - \pi\varepsilon^* k_B T\right)\right]$$

$$= \frac{k_B T}{\varepsilon'}\left[\pi b_{max}^2 v_r e^{-\varepsilon^*/k_B T}\left(\frac{1}{\pi k_B T}\right)^{3/2}(\pi\varepsilon^*)\left(\frac{1}{2} + \frac{k_B T}{2\varepsilon^*} - \varepsilon^* - k_B T\right)\right]$$