

Problem Set 7 Solution1. Problem 8.8

$$\sigma_{rec} = \pi \left( \frac{e}{4\pi\epsilon_0} \right)^2 \frac{1}{\epsilon \epsilon_{off} A}$$

$$\epsilon_{off} A = 1.463 \text{ V far } 0.$$

$$K = 4\pi \int_0^{\infty} v^3 dv f_m(v) \sigma_{rec}(v)$$

$$f_m = \left( \frac{m_R}{2\pi e \pi} \right)^{3/2} e^{-\frac{m_R v^2}{2e \pi}}$$

$$\text{Let } \epsilon = \frac{m_R}{2e} v^2 ; \quad d\epsilon = \frac{m_R}{e} v dv$$

$$K = 4\pi \cdot \left( \frac{m_R}{2\pi e \pi} \right)^{3/2} \frac{2e}{m_R} \frac{e}{m_R} \pi \left( \frac{e}{4\pi\epsilon_0} \right)^2 \frac{1}{\epsilon_{off} A} \int_0^{\infty} v d\epsilon \frac{1}{\epsilon} e^{-\epsilon/\pi}$$

$$m_R = \frac{16.32}{16+32} = 10.7 \text{ amu} = 1.78 \times 10^{-26} \text{ kg} \quad \underbrace{\quad}_{\pi}$$

$$e \pi = k T ; \quad k = \text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J/K}$$

$$\Rightarrow K = 1.32 \times 10^{-13} \left( \frac{300}{T} \right)^{1/2} \quad \text{m}^3/\text{s}$$

$$= 1.32 \times 10^{-7} \left( \frac{300}{T} \right)^{1/2} \quad \text{cm}^3/\text{s} //$$

Table 8.2 gives

$$K = 1.2 \times 10^{-7} \left( \frac{300}{T} \right)^{1/2}$$

2. Problem 8.9

$$K = 4\pi \int_0^{\infty} v_R^3 \sigma(v_R) \left( \frac{m_R}{2\pi kT} \right)^{3/2} e^{-\frac{m_R v_R^2}{2kT}} dv_R$$

$$\left( \frac{2\epsilon\epsilon_0}{m_A} \right)^{1/2}$$

where

$$\frac{1}{2} m_A v_A^2 = \frac{1}{2} m_R' v_R'^2 + e \epsilon_a$$

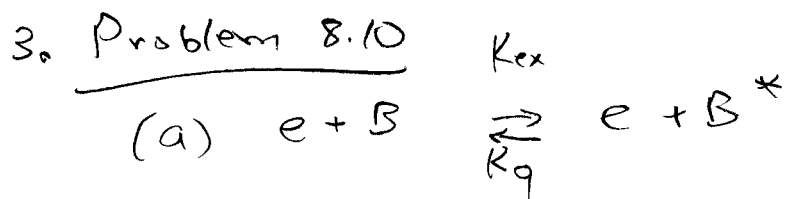
Hence  $m_A v_R dv_R = m_R' v_R' dv_R'$

$$K = 4\pi \frac{m_R'}{m_R} \left( \frac{m_R}{2\pi kT} \right)^{3/2} e^{-\frac{e\epsilon_a}{kT}} \int_0^{\infty} v_R' dv_R' v_R^2 \sigma(v_R) e^{-\frac{m_R' v_R'^2}{2kT}}$$

$$\frac{g_C g_D}{g_A g_B} \frac{m_R'^2}{m_R^2} v_R'^2 \sigma(v_R')$$

$$K = 4\pi \frac{m_R'}{m_R} \left( \frac{m_R}{2\pi kT} \right)^{3/2} \frac{m_R'^2}{m_R^2} \frac{g_C g_D}{g_A g_B} e^{-\epsilon_a/\pi} \int_0^{\infty} v_R'^3 \sigma(v_R') e^{-\frac{m_R' v_R'^2}{2kT}} dv_R'$$

$$K = \left( \frac{m_R'}{m_R} \right)^{3/2} \frac{g_C g_D}{g_A g_B} e^{-\epsilon_a/\pi} K'$$

3. Problem 8.10

$$\frac{K_{ex}}{K_q} = \frac{\bar{g}_*}{\bar{g}_B} e^{-\varepsilon/\pi_e}$$

$$K_q = \frac{\bar{g}_B}{\bar{g}_*} K_{ex} e^{+\varepsilon/\pi_e}$$

$$K_q = \frac{\bar{g}_B}{\bar{g}_*} K_0 e^{(\varepsilon - \varepsilon_0)/\pi_e}$$

(b) From Table 8.1  $\varepsilon = 1.97 \text{ V}$ 

$$B = 3P \quad * = 1D$$

$$g_B = (2L+1)(2S+1) = 3 \cdot 3 = 9$$

$$g_* = (2L+1)(2S+1) = 5 \cdot 1 = 5$$

From Table 8.2 reaction #23

$$K_{ex} = 4.54 \times 10^{-9} \exp(-2.36/\pi_e)$$

$$\Rightarrow K_q = \frac{9}{5} 4.54 \times 10^{-9} \exp \frac{1.97 - 2.36}{\pi_e} \text{ cm}^3/\text{s}$$

$$= 8.17 \times 10^{-9} e^{-0.39/\pi_e} \text{ cm}^3/\text{s}$$

checks with reaction #24 ✓

(c) Yes, since  $K_{ex}/K_q$  is set by thermodynamics so if  $K_{ex}$  is correct, then  $K_q$  is also