Homework # 4

S8.8

a. $k = 8\pi\mu^{-1/2}(2\pi k_B T)^{-3/2}\int_0^{\infty} E\,\sigma(E)\exp\left(\frac{-E}{k_B T}\right)dE$

if $E < E_0$, $\sigma(E) = 0$, so $\int = 0$ + $k = 0$

if $E \geq E_0$, $\sigma(E) = \pi d^2\left(1 - \frac{E_0}{E}\right)$

$$\text{so, } k = 8\pi\mu^{-1/2}(2\pi k_B T)^{-3/2}\underbrace{\int_{E_0}^{\infty} E\pi d^2\left(1 - \frac{E_0}{E}\right)\exp\left(\frac{-E}{k_B T}\right)dE}$$

$$\int = \pi d^2\int_{E_0}^{\infty}(E - E_0)\exp\left(\frac{-E}{k_B T}\right)dE$$

$$= \pi d^2\int_{E_0}^{\infty} \underbrace{E\exp\left(\frac{-E}{k_B T}\right)}_{\int x e^{ax}dx \,=\, e^{ax}\left(\frac{x}{a} - \frac{1}{a^2}\right)} - \underbrace{E_0\exp\left(\frac{-E}{k_B T}\right)}_{\int b e^{ax}dx \,=\, \frac{b}{a}e^{ax}}dE$$

$a = \frac{-1}{k_B T}$ $x = E$

$$= \pi d^2\left[e^{-E/k_B T}\left(-Ek_B T - k_B^2 T^2\right) + E_0 k_B T e^{-E/k_B T}\right]_{E_0}^{\infty}$$

$\int = 0$ for $E = \infty$ since $e^{-\infty} \to 0$

$$= -\pi d^2 e^{-E_0/k_B T}\left[-\cancel{E_0 k_B T} - k_B^2 T^2 + \cancel{E_0 k_B T}\right] = +\pi d^2 e^{-E_0/k_B T}(k_B T)^2$$

$$k = 8\pi\mu^{-1/2}(2\pi k_B T)^{-3/2}(+\pi d^2)(k_B T)^2\exp\left(\frac{-E_0}{k_B T}\right)$$

$$k = 8\pi^{1/2}\mu^{-1/2}(2)^{-3/2}(k_B)^{1/2}d^2(T)^{1/2}\exp\left(\frac{-E_0}{k_B T}\right)$$

$\mu = 10\text{ daltons}\left(\frac{1.661\times10^{-27}\text{ kg}}{1\text{ dalton}}\right) = 1.661\times10^{-26}\text{ kg}$

$E_0 = 100\text{ kJ/mol}\left(\frac{1\text{ mol}}{6.022\times10^{23}}\right)\left(\frac{1000\text{ J}}{1\text{ kJ}}\right) = 1.661\times10^{-19}\text{ J}$

$d = 0.1\text{ nm}\left(\frac{1\text{ m}}{1\times10^{9}\text{ nm}}\right) = 1\times10^{-10}\text{ m}$

$k_B = 1.381\times10^{-23}\text{ J/K}$

58.8 (continued)

$$8\pi^{1/2}\mu^{-1/2}2^{-3/2}k_B^{1/2}d^2$$
$$= 8\pi^{1/2}(1.661\times10^{-26}\,kg)^{-1/2}(2^{-3/2})(1.381\times10^{-23}\,J/K)^{1/2}(1\times10^{-10}\,m)^2$$
$$= 1.4455\times10^{-18}\,\frac{kg^{1/2}\,m\,m^2}{kg^{1/2}\,s\,K^{1/2}}$$

1000 K $$k = (1.4455\times10^{-18}\,\tfrac{m^3}{s\,K^{1/2}})(1000\,K)^{1/2}\exp\Bigg(\underbrace{\frac{-1.661\times10^{-19}\,J}{(1.381\times10^{-23}\,J/K)(1000\,K)}}_{-12.0275}\Bigg) = 2.732\times10^{-22}\,m^3/s$$
$$= 2.732\times10^{-16}\,cm^3/s$$

1500 K $$k = (1.4455\times10^{-18}\,\tfrac{m^3}{s\,K^{1/2}})(1500\,K)^{1/2}\exp\Bigg(\underbrace{\frac{-1.661\times10^{-19}\,J}{(1.381\times10^{-23}\,J/K)(1500\,K)}}_{-8.0183}\Bigg) = 1.844\times10^{-20}\,m^3/s$$
$$= 1.844\times10^{-14}\,cm^3/s$$

2000 K $$k = (1.4455\times10^{-18}\,\tfrac{m^3}{s\,K^{1/2}})(2000\,K)^{1/2}\exp\Bigg(\underbrace{\frac{-1.661\times10^{-19}\,J}{(1.381\times10^{-23}\,J)(2000\,K)}}_{-6.0138}\Bigg) = 1.580\times10^{-19}\,m^3/s$$
$$= 1.580\times10^{-13}\,cm^3/s$$

b. see attached plot of $\ln k$ vs. $1/T$ $\ln k = \ln A - \frac{E_a}{RT}$

These values do obey the Arrhenius law (that $\ln k$ vs. $1/T$ should give a straight line). Although the graph might be expected to deviate due to the difference between E_a and ε^* (which is more applicable to collision theory), the difference must be given by a constant factor ($E_a = \varepsilon^* x$) so that only the slope of the line varies or the difference is small enough ($\varepsilon^* + k = E_a \approx \varepsilon^*$) that it is not apparent on the scale of the graph.

S8.9

$$\chi(b) = \pi - 2b\int_{r_0}^{\infty} r^{-2}\left[1 - \frac{V(r)}{E} - \frac{b^2}{r^2}\right]^{-1/2} dr$$

E = kinetic energy , $r_0 = r_c = d$ for hard sphere

$V(r) = 0$ if $r \geq d$; $V(r) = \infty$ if $r < d$

$\hookrightarrow \chi(b) = 0$

$$\chi(b) = \pi - 2b\int_{d}^{\infty} r^{-2}\left[1 - 0 - \frac{b^2}{r^2}\right]^{-1/2} dr$$

$$\chi(b) = \pi - 2b\int_{d}^{\infty} \underbrace{r^{-2}\left[1 - \frac{b^2}{r^2}\right]^{-1/2}} dr$$

$$r^{-2}\left(1 - b^2 r^{-2}\right)^{-1/2}$$

Use substitution:

$$x = r^{-1} \rightarrow \boxed{dx = -r^{-2}\,dr} = -\frac{dr}{r^2}$$

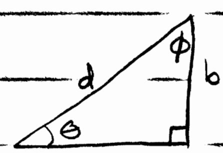
$$dr = -r^2\,dx$$

$$-\int_{d}^{\infty}\left[1 - b^2x^2\right]^{-1/2} dx = -\left[\frac{\sin^{-1}(bx)}{b}\right]_{r=d}^{r=\infty}$$

$$= -\left[\frac{\sin^{-1}(b/r)}{b}\right]_{d}^{\infty} = \frac{-1}{b}\left[\cancel{\sin^{-1}\left(\frac{b}{\infty}\right)}^{\,0} - \sin^{-1}\left(\frac{b}{d}\right)\right]$$

$$\chi(b) = \pi - 2b\left(\frac{+1}{b}\sin^{-1}\left(\frac{b}{d}\right)\right) = \pi - 2\sin^{-1}\left(\frac{b}{d}\right)$$

$$\boxed{\chi(b) = 2\cos^{-1}\left(\frac{b}{d}\right)}$$



$$\sin^{-1}\left(\frac{b}{d}\right) = \theta \qquad 180° \quad 90°$$

$$\cos^{-1}\left(\frac{b}{d}\right) = \phi = \pi - \frac{\pi}{2} - \theta$$

$$\theta = \pi/2 - \cos^{-1}(b/d)$$

$$\sin^{-1}\left(\frac{b}{d}\right) = \pi/2 - \cos^{-1}(b/d)$$

$$2\sin^{-1}\left(\frac{b}{d}\right) = \pi - 2\cos^{-1}(b/d)$$

$$2\cos^{-1}\left(\frac{b}{d}\right) = \pi - 2\sin^{-1}\left(\frac{b}{d}\right)$$

H3.10 a. $E_a = k_B T^2 \frac{\partial \ln k(T)}{\partial T}$ show: $\frac{1}{2}k_B T + \varepsilon^* = E_a$

eq. 3.7 : $\pi b_{max}^2 \langle v_r \rangle \exp\left(-\frac{\varepsilon^*}{k_B T}\right)$ $\langle v_r \rangle = \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}$

$$\ln k(T) = \ln(\pi b_{max}^2) + \frac{1}{2}\ln\left(\frac{8 k_B T}{\pi \mu}\right) + \left(-\frac{\varepsilon^*}{k_B T}\right)$$

$$\frac{\partial \ln k(T)}{\partial T} = 0 + \frac{1}{2}\left(\frac{8 \cancel{k_B}}{\cancel{\pi \mu}}\right)\left(\frac{8 \cancel{k_B} T}{\cancel{\pi \mu}}\right)^{-1} + \left(+\frac{\varepsilon^*}{k_B T^2}\right)$$

$$\frac{\partial \ln k(T)}{\partial T} = \frac{1}{2T} + \frac{\varepsilon^*}{k_B T^2}$$

$$E_a = k_B T^2\left(\frac{1}{2T} + \frac{\varepsilon^*}{k_B T^2}\right) = \boxed{\frac{k_B T}{2} + \varepsilon^*}$$

b. $CH_3 + H_2 \longrightarrow CH_4 + H$ $E_a/R = 6250\,K$ $T = \frac{2500\,K + 300\,K}{2} = 1400\,K$

$$\varepsilon^* = E_a - \frac{1}{2}k_B T$$

$$\varepsilon^* = (6250\,K)\left(8.314 \frac{J}{mol \cdot K}\right)\left(\frac{1\,mol}{6.022 \times 10^{23}}\right) - \frac{1}{2}(1.381 \times 10^{-23}\,J/K)(1400\,K)$$

$$\varepsilon^* = (6250\,K)(1.381 \times 10^{-23}\,J/K) - (6.905 \times 10^{-24}\,J/K)(1400\,K)$$

$$\varepsilon^* = 7.665 \times 10^{-20}\,J$$

$CH_3 + O_2 \longrightarrow CH_3O + O$ $E_a/R = 14{,}520\,K$ $T = \frac{3000 + 298}{2} = 1649\,K$

$$\varepsilon^* = (14520\,K)(1.381 \times 10^{-23}\,J/K) - (6.905 \times 10^{-24}\,J/K)(1649\,K)$$

$$\varepsilon^* = 1.891 \times 10^{-19}\,J$$

$F + H_2 \longrightarrow HF + H$ $E_a/R = 500\,K$ $T = 250\,K$

$$\varepsilon^* = (500\,K)(1.381 \times 10^{-23}\,J/K) - (6.905 \times 10^{-24}\,J/K)(250\,K)$$

$$\varepsilon^* = 5.179 \times 10^{-21}\,J$$

(1) $\%\,error = \left(\frac{\varepsilon^* - E_a}{E_a}\right) \times 100\% = \frac{\overbrace{[(7.665 \times 10^{-20}\,J)(6.022 \times 10^{23}\,mol^{-1})/8.314\,J/mol \cdot K]}^{5551.6} - 6250\,K}{6250\,K} = 11\%$

(2) $\%\,error = \frac{[(1.891 \times 10^{-19}\,J)/(1.381 \times 10^{-23}\,J/K)] - 14520\,K}{14520\,K} = 5.7\%$

(3) $\%\,error = \frac{[(5.179 \times 10^{-21}\,J)/(1.381 \times 10^{-23}\,J/K)] - 500\,K}{500\,K} = 25\%$