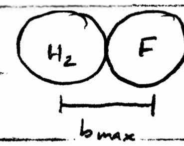
CHM5250 - Assignment # 5

H3.13 (1) $F + H_2 \longrightarrow H + HF$ $\qquad \varepsilon^* = 6.6$ kJ/mol

TS: $(HHF)^\ddagger$ $\qquad H_1-H_2\cdots F$ or $H_2-H_1\cdots F$

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

$A \sim \pi b_{max}^2 \left(\frac{8 k_B T}{\pi \mu}\right)^{1/2}$ $\qquad \pi b_{max}^2 = \sigma$




$\mu = \frac{(18.998)(2.016)}{18.998 + 2.016}$

$\mu = 1.8226$ amu $\times 1.661\times10^{-27}$ kg/amu $= 3.027\times10^{-27}$ kg

$\pi b_{max}^2(H_2) = 2.7\times10^{-19} m^2 = \pi(2 r_{H_2})^2$

$\pi b_{max}^2(F) = 1.8\times10^{-19} m^2 = \pi(2 r_F)^2$

$\pi b_{max}^2(tot) = \pi(r_{H_2} + r_F)^2$

$\left(\frac{1}{2}\right)(2.7\times10^{-19} m^2)^{1/2}\left(\frac{1}{\pi}\right)^{1/2} = r_{H_2}$

$\left(\frac{1}{2}\right)(1.8\times10^{-19} m^2)^{1/2}\left(\frac{1}{\pi}\right)^{1/2} = r_F$

$\pi b_{max}^2 = \pi\left[\left(\frac{1}{2}\right)(2.7\times10^{-19} m^2)^{1/2}\left(\frac{1}{\pi}\right)^{1/2} + \left(\frac{1}{2}\right)(1.8\times10^{-19} m^2)^{1/2}\left(\frac{1}{\pi}\right)^{1/2}\right]^2$

$\pi b_{max}^2 = \pi\left(\frac{1}{2\pi^{1/2}}\right)^2\left[(2.7\times10^{-19} m^2)^{1/2} + (1.8\times10^{-19} m^2)^{1/2}\right]^2$

$\pi b_{max}^2 = \frac{1}{4}(9.44\times10^{-10} m)^2 = 2.23\times10^{-19} m^2$

$A \sim (2.23\times10^{-19} m^2)\overbrace{\left(\frac{8(1.38\times10^{-23} J/K)(298 K)}{\pi \cdot 3.027\times10^{-27} kg}\right)^{1/2}}^{1859.99 m/s} = 4.15\times10^{-16} \frac{m^2 J^{1/2}}{kg^{1/2}} = m^3/s$

$\frac{m^2\, kg^{1/2}\, m}{s\, kg^{1/2}}$

$4.15\times10^{-16} m^3/s\left(\frac{1000 L}{1 m^3}\right)\left(\frac{6.022\times10^{23}}{mol}\right) = \boxed{2.49\times10^{11} \frac{L}{mol\cdot s}}$

agrees well with expt!

$k(T) = \pi b_{max}^2 \langle v_r \rangle \exp\left(-\frac{\varepsilon^*}{k_B T}\right) = \left(2.49\times10^{11}\frac{L}{mol\cdot s}\right)\exp\left(\frac{-(6.6\times10^3 J/mol)\left(\frac{1 mol}{6.022\times10^{23}}\right)}{(1.38\times10^{-23} J/K)(298 K)}\right)$

$\boxed{k(T) = 1.73\times10^{10} \frac{L}{mol\cdot s}}$

H 3.13

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b. $k = \frac{k_B T}{h} \frac{Q^{\ddagger}_{HHF}}{Q_{H_2} Q_F} e^{-E_0/k_B T}$ $\qquad \varepsilon^* = 6.6 \text{ kJ/mol}$

$Q^{\ddagger}_{HHF} = Q^{\ddagger}_{elect} Q^{\ddagger}_{vib} Q^{\ddagger}_{rot} Q^{\ddagger}_{trans}$ (linear)

$Q^{\ddagger}_{elect} = \boxed{4}$

$Q^{\ddagger}_{vib} = \prod_{i=1}^{3} \frac{1}{1-\exp(-h\nu_i/k_B T)}$ $\qquad \nu = 12.02 \times 10^{13}\ s^{-1},\ 1.19 \times 10^{13}\ s^{-1},\ 1.19 \times 10^{13}\ s^{-1}$

$\frac{h}{k_B T} = \frac{6.626 \times 10^{-34}\ J\,s}{(1.38 \times 10^{-23}\ J/K)(298\ K)} = 1.611 \times 10^{-13}\ s$

$\frac{1}{1-\exp(\underbrace{-(1.611 \times 10^{-13})(12.02 \times 10^{13}\ s^{-1})}_{19.37})} = \frac{1}{1-3.88 \times 10^{-9}} = 1$

$\frac{1}{1-\exp(-(1.611 \times 10^{-13}\ s)(1.19 \times 10^{13}\ s^{-1}))} = \frac{1}{1-0.1470} = 1.172$

$Q^{\ddagger}_{vib} = (1)(1.172)(1.172) = \boxed{1.374}$

$Q^{\ddagger}_{rot} = \frac{8\pi^2 I k_B T}{h^2} = \frac{8\pi^2 (7.43 \times 10^{-47}\ kg\,m^2)(1.38 \times 10^{-23}\ J/K)(298\ K)}{(6.626 \times 10^{-34}\ J\,s)^2}$

$Q^{\ddagger}_{rot} = \boxed{54.947}$

$m = (1.0079)2 + 18.99 = 21.0058$

$\frac{Q^{\ddagger}_{trans}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{2\pi (21.0058\ amu)(1.661 \times 10^{-27}\ kg/amu)(1.38 \times 10^{-23}\ J/K)(298\ K)}{(6.626 \times 10^{-34}\ J\,s)^2}\right)^{3/2}$

$\frac{\cancel{kg}\ \cancel{s^2}}{\cancel{kg}\ m^2\ \cancel{s^2}}$

$\frac{Q^{\ddagger}_{trans}}{V} = \boxed{9.305 \times 10^{31}\ m^{-3}}$

$Q^{\ddagger}_{HHF} = (4)(1.374)(54.947)(9.305 \times 10^{31}\ m^{-3}) = \boxed{2.81 \times 10^{34}\ m^{-3}}$

# 3.13

## $Q_{H_2}$

$Q_{elect} = \boxed{1}$

$$Q_{vib} = \frac{1}{1 - \exp(-(1.611\times10^{-13}s)(13.19\times10^{13}s^{-1}))} = \boxed{1.00}$$

$$Q_{rot} = \frac{8\pi^2 I k_B T}{h^2} = \frac{8\pi^2(0.46\times10^{-47}kg\,m^2)(298\,K)}{(1.611\times10^{-13}s)(6.626\times10^{-34}J\,s)} = \boxed{3.402}$$

$$\frac{Q_{trans}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{2\pi(1.0079)2(1.661\times10^{-27}kg/amu)(298)}{(1.611\times10^{-13}s)(6.626\times10^{-34}Js)}\right)^{3/2} = \boxed{2.766\times10^{30}m^{-3}}$$

$$Q_{H_2} = (1)(1.00)(3.402)(2.766\times10^{30}m^{-3}) = \boxed{9.41\times10^{30}m^{-3}}$$

## $Q_F$

$Q_{elect} = \boxed{4}$

$Q_{vib} = \boxed{1}$ $\quad Q_{rot} = \boxed{1}$

$$\frac{Q_{trans}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{2\pi(18.99\,amu)(1.661\times10^{-27}kg/amu)(298\,K)}{(6.626\times10^{-34}Js)^2}\right)^{3/2} = \boxed{7.998\times10^{+31}m^{-3}}$$

$$Q_F = (4)(1)(1)(7.998\times10^{31}m^{-3}) = \boxed{3.20\times10^{32}m^{-3}}$$

$$k = \frac{1}{1.611\times10^{-13}s}\overbrace{\left(\frac{2.81\times10^{34}m^{-3}}{(9.41\times10^{30}m^{-3})(3.20\times10^{32}m^{-3})}\right)}^{9.33\times10^{-30}}\exp\overbrace{\left(-\frac{(6.6\times10^{3}J/mol)(1\,mol/6.022\times10^{23})}{(1.38\times10^{-23}J/K)(298\,K)}\right)}^{2.665}$$

$$k = 5.793\times10^{-17}\exp(-2.665)$$

$A =$

$$5.793\times10^{-17}m^3 s^{-1}\left(\frac{6.022\times10^{23}}{1\,mol}\right)\left(\frac{1000\,L}{1\,m^3}\right)(2) = \boxed{6.98\times10^{10}\frac{L}{mol\,s}}$$

$H_2 - H_1 \cdots F$

$H_1 - H_2 \cdots F$

$$k = \left(6.98\times10^{10}\frac{L}{mol\cdot s}\right)(\exp(-2.665)) = \boxed{4.86\times10^{9}\frac{L}{mol\cdot s}}$$

5/10.8

(5) a. Do Arrhenius plot of $\ln k$ vs. $\frac{1}{T}$ or calc. slope manually since only two points.

$$\text{slope} = +213.53\ K$$
$$E_a = -(\text{slope})(8.3145\ \tfrac{J}{m\cdot l\cdot K})$$
$$E_a = -(213.53\ K)(8.3145\ \tfrac{J}{m\cdot l\cdot K}) = -1775.42\ J/mol$$
$$\boxed{E_a = -1.8\ kJ/mol}$$

Negative $E_a$ so reaction must go through a weakly bound complex intermediate

(12) b. $\Delta E^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, $A$ $\quad T = 298\,K$

(There were several possible equations for most of these calcs.)

$$E_a = RT + \Delta E^{\ddagger 0} \rightarrow \Delta E^{\ddagger} = E_a - RT = -1775.42\ J/mol - (8.3145\ \tfrac{J}{m\cdot l\cdot K})(298 K)$$
$$\boxed{\Delta E^{\ddagger}} = -4253.14\ J/mol = \boxed{-4.2\ kJ/mol}$$

actually, this is $n^{\ddagger} - n_{react} = 1 - 2 = -1$

so $E_a = \Delta H^{\ddagger} + (1 - \Delta n^{\ddagger})RT = \Delta H^{\ddagger} + 2RT$

so $\Delta H^{\ddagger} = E_a - 2RT$

$\boxed{\Delta H^{*} = -6731\ J/mol}$

$$\Delta H^{\ddagger} = \Delta E^{\ddagger} + P(\Delta V^{\ddagger}) \quad \Delta V^{\ddagger} = 0 \text{ since } \Delta n_{gas} = 0$$
$$\text{so, } \boxed{\Delta H^{\ddagger}} = \Delta E^{\ddagger} = -4253\ J/mol = \boxed{-4.2\ kJ/mol}$$

$$k = Ae^{-E_a/RT} \qquad \ln k = \ln A - \frac{E_a}{RT}$$

$$\ln A = \frac{E_a}{RT} + \ln k = \frac{-1775.42\ J/mol}{(8.3145\ \frac{J}{m\cdot l\cdot K})(298K)} + \ln\Big(\underbrace{6.1\times10^{-11}\ \tfrac{cm^3}{molec.\ s}\Big)\Big(\tfrac{1\ m^3}{100^3\ cm^3}\Big)\Big(\tfrac{6.02\times10^{23}\ molec}{1\ mol}\Big)}_{3.673\times10^{7}}$$

$$\ln A = -0.71655 + (17.4192) = 16.703$$
$$\boxed{A = 1.794\times10^{7}\ \tfrac{m^3}{mol\cdot s}} \quad (\text{or } 2.97\times10^{-11}\ \tfrac{cm^3}{molecule\cdot s})$$

units of k

L 23.61

or $\ln A$ = intercept from graph in $\frac{m^3}{mol\cdot s}$

$m^3$

$\ln A = 16.703$ (agrees w/ ↗)

$cm^3$ 24.23

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \qquad \ln k = \ln\left(\frac{k_B T}{h}\right) - \frac{\Delta G^{\ddagger}}{RT}$$

$$-RT\ln\left(\frac{kh}{k_B T}\right) = \Delta G^{\ddagger} = -(8.3145\ \tfrac{J}{mol\cdot K})(298K)\ln\overbrace{\left(\frac{(3.673\times10^{7}\ \frac{m^3}{m\cdot l\cdot s})(6.626\times10^{-34}\ J s)}{(1.38\times10^{-23}\ J/K)(298\ K)}\right)}^{5.918\times10^{-6}}$$

$$\Delta G^{\ddagger} = 29825.6\ J/mol = \boxed{29.8\ kJ/mol}$$

$\frac{510.8}{(\text{cont.})}$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

$$T\Delta S^{\ddagger} = \Delta H^{\ddagger} - \Delta G^{\ddagger}$$

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T} = \frac{(-67\underline{31}\ \text{J/mol} - 298\underline{25.6}\ \text{J/mol})}{298\ \text{K}}$$

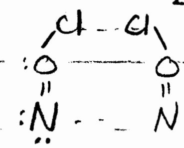
$$\Delta S^{\ddagger} = -122.7\ \text{J/mol}\cdot\text{K} \rightarrow \boxed{-0.12\ \text{kJ/mol}\cdot\text{K}}$$

Steinfeld Chp. 10 (continued)

S10.6 (continued)

c. $2\,NOCl \longrightarrow 2\,NO + Cl_2$

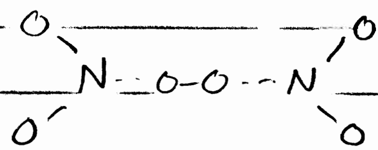
c: not graded

TS:  nonlinear

$Q^{\ddagger} \propto T^3 \qquad Q_{NOCl} \propto T^3$ (both nonlinear)

$$A \propto T \cdot \frac{T^3}{T^3 T^3} \longrightarrow \boxed{A \propto T^{-2}}$$

7 d. $2\,NO_2 + O_2 \longrightarrow 2\,NO_3$ ← note typo in book (doesn't affect calc.)

 TS → nonlinear

$Q^{\ddagger} \propto T^3 \qquad Q_{NO_2} \propto T^3 \qquad Q_{O_2} \propto T^{5/2}$

Assume two steps, w/ 1st step = RDS: $NO_2 + O_2 \rightarrow NO_2O_2^{\ddagger}$

$$A \propto T \cdot \frac{T^3}{T^3 T^{5/2}} \longrightarrow \boxed{A \propto T^{-3/2}}$$

e. $C_2H_4 + HCl \longrightarrow C_2H_5Cl$

TS → nonlinear

$Q^{\ddagger} \propto T^3 \qquad Q_{C_2H_4} \propto T^3 \qquad Q_{HCl} \propto T^{5/2}$

$$A \propto T \cdot \frac{T^3}{T^3 T^{3/2}} \longrightarrow \boxed{A \propto T^{-3/2}}$$