CHM5250 - Exam III

(1) $C_2H_4 + HCN$ $\quad \Delta H^\ddagger = 36.7\ kJ/mol$, $\Delta S^\ddagger = -145\ J/mol \cdot K$

a.

$$k = \frac{k_B T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \qquad T = -40°C = 233\ K$$

$$k = \frac{(1.38\times10^{-23}\ J/K)(233\ K)}{(6.626\times10^{-34}\ J\cdot s)} \exp\left(\frac{-145\ J/mol\cdot K}{8.3145\ J/mol\cdot K}\right) \exp\left(\frac{-36.7\times10^{3}\ J/mol}{(8.314\ \frac{J}{mol\cdot K})(233\ K)}\right)$$

$$k = 4.85\underline{3}\times10^{12}\ s^{-1} \exp(-17.44) \exp(-18.94)$$

$$k = 0.0007671\ s^{-1} \longrightarrow \boxed{7.67\times10^{-4}\ \frac{L}{mol\cdot s}}$$

since question says conc. in L/mol

b. $\Delta G^\ddagger$ from $k \rightarrow k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger o}/RT}$

from $\Delta H^\ddagger, \Delta S^\ddagger \longrightarrow \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

$$\frac{kh}{k_B T} = e^{-\Delta G^\ddagger/RT}$$

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta G^\ddagger}{RT}$$

$$-RT\left(\ln\frac{kh}{k_B T}\right) = \Delta G^\ddagger = (-8.3145\ \tfrac{J}{mol\cdot K})(233\ K)\ln\left(\frac{7.67\times10^{-4}\ s^{-1}}{4.85\underline{3}\times10^{12}\ s^{-1}}\right)$$

$$\Delta G^\ddagger = 70485\ J/mol = \boxed{70.5\ kJ/mol}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = (36.7\times10^{3}\ J/mol) - (233\ K)(-145\ \tfrac{J}{mol\cdot K})$$

$$\Delta G^\ddagger = 70485\ J/mol = \boxed{70.5\ kJ/mol}$$

Exam III (cont'd.)

2 a. $O + N_2 \longrightarrow NO + N$

$$k = \underbrace{\frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B}}_{\text{pre-exponential factor}} \exp\left(-\frac{E_0}{k_B T}\right)$$

Need to determine dependence of Q's on T. Each Q is

$$Q = Q_{elec} Q_{vib} Q_{rot} Q_{trans}$$

$Q_{elec} = \sum_i g_i e^{-E_i/k_B T}$ → no T dependence because E_i is usually zero, so exp term = 1

$Q_{vib} = \prod_{i=1}^{s} \frac{1}{1 - \exp(-hc\bar{\nu}/k_B T)}$ → no T dependence since $\exp\left(\frac{-hc\bar{\nu}}{k_B T}\right) \approx 0$

$Q_{rot} = \frac{8\pi^2 I k_B T}{h^2}$ if linear, so $Q_{rot,\,lin} \propto T$

$Q_{rot} = \pi^{1/2}\left(\frac{8\pi^2 I_a k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_b k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_c k_B T}{h^2}\right)^{1/2}$ if nonlinear, so $Q_{rot,\,non} \propto T^{3/2}$

$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$ so $Q_{trans} \propto T^{3/2}$

so $Q \propto \underbrace{1}_{\text{elect.}} \times \underbrace{1}_{\text{vib.}} \times \underbrace{T^{3/2}}_{\text{trans}} \times \underbrace{(\text{either } T \text{ or } T^{3/2})}_{\text{rot}}$

Then $A \propto \underbrace{T}_{\text{from } \frac{k_B T}{h}} \times$ contribution from Q's

for $O + N_2$: TS: linear so $Q^{\ddagger} \propto \overbrace{T^{5/2}}^{T \cdot T^{3/2}}$ N_2 ~~NO~~: linear so $Q_{NO} \propto T^{5/2}$

O: only translation so $Q_O \propto T^{3/2}$

(2) a. (continued)

$$\text{so } A \propto T\left(\frac{T^{5/2}}{T^{3/2}\,T^{5/2}}\right) \propto \boxed{T^{-1/2}}$$

b. $OH + H_2$ TS = nonlinear so $Q^{\ddagger} \propto T^{3}$ ($T^{3/2}T^{3/2}$)

OH: linear so $Q_{OH} \propto T^{5/2}$

H_2 linear so $Q_{H_2} \propto T^{5/2}$

$$\text{so } A \propto T\left(\frac{T^{3}}{T^{5/2}\,T^{5/2}}\right) \propto \boxed{T^{-1}}$$

(3) a. $S_2O_8^{2-} + 2I^- \longrightarrow I_2 + 2\,SO_4^{2-}$

The reaction rate will increase since the reacting ions are both negatively charged.

b. $H_2O_2 + 2H^+ + 2Br^- \longrightarrow 2H_2O + Br_2$

The reaction rate will decrease since the reacting ions have opposite charges.

(4) a. The laser (UV radiation) initiates the reaction by breaking Cl_2 into Cl atoms.

b. To measure the vibrational state distribution of the products, it is necessary to know what frequencies of radiation are emitted by the chemiluminescence process. To do this, a monochromator would have to be added in place of the IR filter. The IR filter will let all frequencies of IR light reach the detector at the same time, while the monochromator separates the frequencies so that the intensity of chemiluminescence at a particular frequency can be measured.

(5) a. The maximum rate constant is diffusion limited because the reactants can't react before they have diffused through the solution to meet each other.

For neutral reactants:

$k_D = 4\pi(D_A + D_B)R$ $\quad D_A = D_B = 3.0\times10^{-9}\ m^2 s^{-1}$ in CCl_4 $T = 25°C$

radius of $I = 2\times10^{-10}\ m$

$R = r_A + r_B = 4\times10^{-10}\ m$

$$k_D = 4\pi(6.0\times10^{-9}\ m^2 s^{-1})(4\times10^{-10}\ m) = 3.02\times10^{-17}\ m^3/s$$

$$k_D = 3.02\times10^{-17}\ m^3/s\left(\frac{1000\ L}{1\ m^3}\right)\left(\frac{6.022\times10^{23}}{1\ mol}\right) = 1.8\times10^{10}\ \frac{L}{mol\cdot s} \sim \boxed{2\times10^{10}\ \frac{L}{mol\cdot s}}$$

b. $\eta(CCl_4) = 9.7\times10^{-4}\ \frac{kg}{m\cdot s}$

$$k_D = \frac{2k_BT(r_A+r_B)^2}{3\eta r_A r_B} = \frac{2(1.38\times10^{-23}\ \frac{J}{K})(298\ K)(4\times10^{-10}\ m)^2}{3(9.7\times10^{-4}\ \frac{kg}{m\cdot s})(2\times10^{-10}\ m)(2\times10^{-10}\ m)}$$

$$k_D = \frac{1.316\times10^{-39}\ J\ m^2}{1.164\times10^{-22}\ kg\ m/s} = 1.13\times10^{-17}\ J\ m\ s/kg = 1.13\times10^{-17}\ m^3/s$$

$$\frac{kg\ m^2\ m\ s}{s^2\ kg} = m^3/s$$

$$k_D = 1.13\times10^{-17}\ m^3/s\left(\frac{1000\ L}{1\ m^3}\right)\left(\frac{6.022\times10^{23}}{1\ mol}\right)$$

$$k_D = 6.8\times10^{9}\ \frac{L}{mol\cdot s} \sim \boxed{7\times10^{9}\ \frac{L}{mol\cdot s}}$$