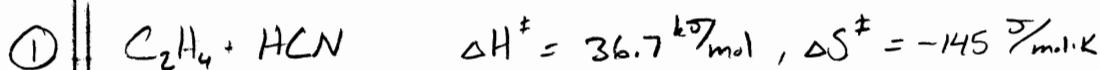


CHM5250 - Exam III

a.  $k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT} \quad T = -40^\circ C = 233 \text{ K}$

$$k = \frac{(1.38 \times 10^{-23} \text{ J/K})(233 \text{ K})}{(6.626 \times 10^{-34} \text{ J.s})} \exp\left(\frac{-145 \text{ J/mol}\cdot K}{8.3145 \text{ J/mol}\cdot K}\right) \exp\left(\frac{36.7 \times 10^3 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}(233 \text{ K})\right)$$

$$k = 4.853 \times 10^{12} \text{ s}^{-1} \exp(-17.44) \exp(-18.94)$$

$$k = 0.0007671 \text{ s}^{-1} \rightarrow \boxed{7.67 \times 10^{-4} \frac{\text{L}}{\text{mol}\cdot\text{s}}}$$

↑ since question says conc.  
in L/mol

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

$$\text{From } \Delta H^\ddagger, \Delta S^\ddagger \rightarrow \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

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

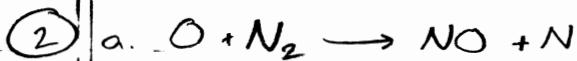
$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta G^\ddagger}{RT}$$

$$-RT \left( \ln \frac{kh}{k_B T} \right) = \Delta G^\ddagger = (-8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}})(233 \text{ K}) \ln\left(\frac{7.67 \times 10^{-4} \text{ s}^{-1}}{4.853 \times 10^{12} \text{ s}^{-1}}\right)$$

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

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = (36.7 \times 10^3 \frac{\text{J}}{\text{mol}}) - (233 \text{ K})(-145 \frac{\text{J}}{\text{mol}\cdot\text{K}})$$

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

Exam III (cont'd.)

$$k = \frac{k_B T}{h} \frac{Q^*}{Q_A Q_B} \exp\left(-\frac{E_0}{k_B T}\right)$$

pre-exponential  
factor

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

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

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

$$Q_{vib} = \prod_{i=1}^S \frac{1}{1 - \exp\left(-\frac{\hbar\omega_i}{k_B T}\right)} \rightarrow \text{n-T dependence since } \exp\left(\frac{-\hbar\omega_i}{k_B T}\right) \approx 0$$

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

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

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

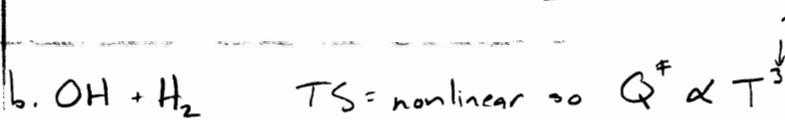
$$\text{so } Q \propto \underset{\substack{\uparrow \\ \text{elect.}}}{} \times \underset{\substack{\uparrow \\ \text{vib.}}}{} \times \underset{\substack{\uparrow \\ \text{trans}}}{} \times \underset{\substack{\uparrow \\ \text{rot}}}{} \times (\text{either } T \text{ or } T^{3/2})$$

Then  $A \propto T^x$  contribution from  $Q$ 's

$$\begin{array}{ccc} \uparrow & & \\ \text{sum } \frac{k_B T}{h} & & T \cdot T^{3/2} \\ \downarrow & & \downarrow \\ \text{for } O + N_2: TS = \text{linear so } Q^* \propto T^{5/2} & & NO: \text{linear so } Q_{NO} \propto T^{5/2} \\ O: \text{only translation so } Q_O \propto T^{3/2} & & \end{array}$$

(2) a. (continued)

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



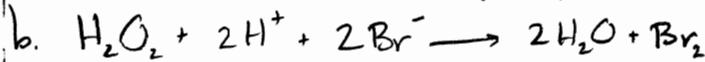
$$\text{OH: linear so } Q_{\text{OH}} \propto T^{5/2}$$

$$\text{H}_2 \text{ linear so } Q_{\text{H}_2} \propto T^{5/2}$$

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



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



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

(4) a. The laser <sup>(UV radiation)</sup> initiates the reaction by breaking  $\text{Cl}_2$  into  $\text{Cl}$  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 <sup>frequencies of</sup> 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:

$$k_D = 4\pi(D_A + D_B)R \quad D_A = D_B = 3.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ in } \text{CCl}_4 \quad T = 25^\circ\text{C}$$

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

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

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

$$k_D = 3.02 \times 10^{-17} \frac{\text{m}^3}{\text{s}} \left( \frac{1000 \text{ L}}{1 \text{ m}^3} \right) \left( \frac{6.022 \times 10^{23}}{1 \text{ mol}} \right) = 1.8 \times 10^{16} \frac{\text{L}}{\text{mol.s}} \approx 2 \times 10^{10} \frac{\text{L}}{\text{mol.s}}$$

$$b. \eta(\text{CCl}_4) = 9.7 \times 10^{-4} \frac{\text{kg}}{\text{m.s}}$$

$$k_D = \frac{2k_b T (r_A + r_B)^2}{3\eta r_A r_B} = \frac{2(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(298 \text{ K})(4 \times 10^{-10} \text{ m})^2}{3(9.7 \times 10^{-4} \frac{\text{kg}}{\text{m.s}})(2 \times 10^{-10} \text{ m})(2 \times 10^{-10} \text{ m})}$$

$$k_D = \frac{1.316 \times 10^{-39} \text{ J m}^2}{1.164 \times 10^{-22} \frac{\text{kg}}{\text{s}}} = 1.13 \times 10^{-17} \text{ J m s/kg} = 1.13 \times 10^{-17} \text{ m}^3/\text{s}$$

$$k_D = 1.13 \times 10^{-17} \frac{\text{m}^3}{\text{s}} \left( \frac{1000 \text{ L}}{1 \text{ m}^3} \right) \left( \frac{6.022 \times 10^{23}}{1 \text{ mol}} \right)$$

$$k_D = 6.8 \times 10^9 \frac{\text{L}}{\text{mol.s}} \approx 7 \times 10^9 \frac{\text{L}}{\text{mol.s}}$$

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