Steinfeld 10.12 (In class, 11/9/07)

$CH + N_2 \longrightarrow (CHN_2)^{\ddagger} \longrightarrow HCN + N$ $T = 298\,K$

linear → 2 rotational dof
3 translational dof
$3(4)-5 = 7$ vibrational dof → one of these is the reaction coordinate

each has 3 translational
1 vibrational $(3(2)-5)$
2 rotational
} degrees of freedom

(experimental $k = 7.1\times10^{-14}$ $cm^3\,molecule^{-1}\,s^{-1}$)

$$k = \frac{k_B T}{h}\frac{Q^{\ddagger}}{Q_{CH}Q_{N_2}}\, e^{-E_0/k_B T} \qquad E_0 = 221\ kJ/mol$$

$$Q = Q_{elect.}\,Q_{rot}\,Q_{vib}\,Q_{trans}$$

(eq. 10-58) $$Q_{elect.} = \sum_i g_i e^{-E_i/k_B T}$$ E_i = electronic energy above the ground state $= 0$ (for $R + X^{\ddagger}$)

$g_{CH} = 2$ $g_{N_2} = 1$ $g_{HCN_2} = 2$

(eq. 10-72) $$Q_{rot} = \frac{8\pi^2 I k_B T}{h^2} \text{ (for linear)}$$ $I_{CH} = 1.935\times10^{-40}\,g\,cm^2$ $I_{N_2} = 13.998\times10^{-40}\,g\,cm^2$

$I_{HCN_2} = 73.2\times10^{-40}\,g\,cm^2$

(eq. 10-69) $$Q_{vib} = \prod_{i=1}^{s}\frac{1}{1-\exp(-hc\bar{\nu}_i/k_B T)}$$ $\bar{\nu}_{CH} = 2733\,cm^{-1}$ $\bar{\nu}_{N_2} = 2330\,cm^{-1}$

$\bar{\nu}_{HCN_2} = 3130, 2102, 1252, 1170, 564, 401\ cm^{-1}$

(eq. 10- $$\frac{Q_{trans}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$ $M_{CH} = 13.019\,g/mol$ $M_{N_2} = 28.013\,g/mol$ $M_{HCN_2} = 41.032\,g/mol$

$Q^{\ddagger}_{HCN_2}$: $Q^{\ddagger}_{elect.} = g_i e^{-E_i/k_BT} = (2)e^{-0} = \boxed{2}$

$\frac{kg\,m^2\,J\,K}{K\,J^2\,s^2} = \frac{kg\,m^2\,s^2}{kg\,m^2\,s^2} = \text{unitless}$

$$Q^{\ddagger}_{rot} = \frac{8\pi^2(73.2\times10^{-40}\,g\,cm^2)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\left(\frac{1\,m}{100\,cm}\right)^2\left(\frac{1\,kg}{1000\,g}\right)$$

$Q^{\ddagger}_{rot} = \boxed{541.4}$

Q_{vib} : $\frac{hc}{k_BT} = \frac{(6.626\times10^{-34}\,J\cdot s)(2.998\times10^{8}\,m/s)}{(1.38\times10^{-23}\,J/K)(298\,K)} = 4.830\times10^{-5}\,m$

$$Q^{\ddagger}_{vib} = \left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(3130\,cm^{-1})(100\,cm/m)]}\right)\left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(2102\,cm^{-1})(100\,cm/m)]}\right)$$
$$\times\left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(1252\,cm^{-1})(100\,cm/m)]}\right)\left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(1170\,cm^{-1})(100\,cm/m)]}\right)$$
$$\times\left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(564\,cm^{-1})(100\,cm/m)]}\right)\left(\frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(401\,cm^{-1})(100\,cm/m)]}\right)$$

$$Q^{\ddagger}_{vib} = \left(\frac{1}{1-\exp(-15.119)}\right)\left(\frac{1}{1-\exp(-10.154)}\right)\left(\frac{1}{1-\exp(-6.0477)}\right)\left(\frac{1}{1-\exp(-5.6516)}\right)$$
$$\times\left(\frac{1}{1-\exp(-2.7244)}\right)\left(\frac{1}{1-\exp(-1.9370)}\right)$$

$Q^{\ddagger}_{vib} = (1.0006)(1.0000)(1.0024)(1.0035)(1.0702)(1.1684) = \boxed{1.2578}$

$\frac{g\,kg\,mol\,J\,K}{mol\,g\,K\,J^2\,s^2} = \left(\frac{kg\,s^2}{kg\,m^2\,s^2}\right)^{3/2} = m^{-3}$

$$Q^{\ddagger}_{trans} = \left(\frac{2\pi(41.032\,g/mol)(1.661\times10^{-27}\,kg\,mol/g)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\right)^{3/2} = \boxed{2.5404\times10^{32}\,m^{-3}}$$

$Q^{\ddagger}_{HCN_2} = (2)(541.4)(1.2578)(2.5404\times10^{32}\,m^{-3}) = \boxed{3.4599\times10^{35}\,m^{-3}} \times 2 = \boxed{6.9198\times10^{35}}$

H-C…N₁-N₂
or H-C…N₂-N₁

Q_{CH} : $Q^{CH}_{elect} = (2)e^{-0} = \boxed{2}$

$$Q^{CH}_{rot} = \frac{8\pi^2(1.935\times10^{-40}\,g\,cm^2)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\left(\frac{1\,m}{100\,cm}\right)^2\left(\frac{1\,kg}{1000\,g}\right) = \boxed{14.311}$$

$$Q^{CH}_{vib} = \frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(2733\,cm^{-1})(100\,cm/m)]} = \boxed{1.0000}$$

$$Q^{CH}_{trans} = \left(\frac{2\pi(13.019\,amu)(1.661\times10^{-27}\,kg/amu)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\right)^{3/2} = \boxed{4.5402\times10^{31}\,m^{-3}}$$

$Q_{CH} = (2)(14.311)(1.0000)(4.5402\times10^{31}\,m^{-3}) = \boxed{1.2995\times10^{33}\,m^{-3}}$

Q_{N_2} : $Q^{N_2}_{elect} = (1)e^{-0} = \boxed{1}$

$$Q^{N_2}_{rot} = \frac{8\pi^2(13.998\times10^{-40}\,g\,cm^2)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\left(\frac{1\,m}{100\,cm}\right)^2\left(\frac{1\,kg}{1000\,g}\right) = \boxed{103.5}$$

$$Q^{N_2}_{vib} = \frac{1}{1-\exp[(-4.830\times10^{-5}\,m)(2330\,cm^{-1})(100\,cm/m)]} = \boxed{1.0000}$$

$$Q^{N_2}_{trans} = \left(\frac{2\pi(28.013\,amu)(1.661\times10^{-27}\,kg/amu)(1.38\times10^{-23}\,J/K)(298\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\right)^{3/2} = \boxed{1.4330\times10^{32}\,m^{-3}}$$

$Q_{N_2} = (1)(103.5)(1.0000)(1.4330\times10^{32}\,m^{-3}) = \boxed{1.4832\times10^{34}\,m^{-3}}$

$$k = \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_{CH} Q_{N_2}} e^{-\varepsilon_0 / k_B T} \qquad \frac{k_B T}{h} = \frac{(1.38\times10^{-23}\ J/K)(298\ K)}{6.626\times10^{-34}\ J\cdot s} = 6.206\times10^{12}\ s^{-1}$$

$$k = (6.206\times10^{12}\ s^{-1}) \frac{(6.9198\times10^{35}\ m^{-3})}{(1.2995\times10^{33}\ m^{-3})(1.4832\times10^{34}\ m^{-3})} \exp\left(\frac{-221\ kJ/mol \left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1\ mol}{6.022\times10^{23}}\right)}{(1.38\times10^{-23}\ J/K)(298\ K)}\right)$$

$$k = (6.206\times10^{12}\ s^{-1})(3.6013\times10^{-32}\ m^3)\exp(-89.239) = 3.9198\times10^{-58}\ m^3/s$$

Pre-exponential factor $= \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B}$ (from comparison w/ Arrhenius eqn: $k = A e^{-E_a/RT}$)

for $Q^{\ddagger}$: $Q^{\ddagger}_{elect} \propto T^0$; $Q^{\ddagger}_{rot} \propto T$; $Q^{\ddagger}_{vib} \propto T^0$; $Q^{\ddagger}_{trans} \propto T^{3/2}$

$$Q^{\ddagger} \propto (T)(T^{3/2}) \propto T^{5/2}$$

for Q_{CH} and Q_{N_2}: $Q_{elect} \propto T^0$; $Q_{rot} \propto T$; $Q_{vib} \propto T^0$; $Q_{trans} \propto T^{3/2}$

$$Q \propto (T)(T^{3/2}) \propto T^{5/2}$$

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