Steinfeld Chp. 10 (continued)

S10.5

$A + BC \longrightarrow AB + C$

(i) trans. d.o.f.: 3 for A, 3 for BC

rot. d.o.f.: 0 for A, 1 for BC

vib. d.o.f.: 0 for A, 1 for BC

(ii) trans. d.o.f.: 3 for A···B···C

rot. d.o.f.: 2 for A···B···C

vib. d.o.f.: (3)(3) − 5 = 4 for A···B···C

a. $Q_{elect} = \sum_i \underset{\substack{\uparrow \\ \text{unitless number} \\ \text{(degeneracy)}}}{g_i}\, \underbrace{e^{-E_i/k_BT}}_{\text{unitless}} = \boxed{\text{unitless}}$

$$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{kg \cdot \cancel{J}/\cancel{K} \cdot \cancel{K}}{J^{\cancel{2}} s^2}\right)^{3/2} = \left(\frac{kg}{J\,s^2}\right)^{3/2}$$

$$Q_{trans} = \left(\frac{\cancel{kg}\,\cancel{s^2}}{\underbrace{\cancel{kg}\, m^2\, \cancel{s^2}}_{J}}\right)^{3/2} = (m^{-2})^{3/2} = \boxed{m^{-3}} \quad (\text{for } Q_{trans}/V)$$

$$Q_{rot} = \frac{8\pi^2 I k_B T}{h^2} = \frac{(kg\,m^2) \cdot \cancel{J}/\cancel{K} \cdot \cancel{K}}{J^{\cancel{2}}\, s^2} = \frac{kg\,m^2}{J\,s^2}$$

$$Q_{rot} = \left(\frac{\cancel{kg}\,\cancel{m^2}\,\cancel{s^2}}{\underbrace{\cancel{kg}\,\cancel{m^2}\,\cancel{s^2}}_{J}}\right) = \boxed{\text{unitless}}$$

$$Q_{vib} = \prod \frac{1}{1 - \exp(\underbrace{-hc\tilde{\nu}/k_BT}_{\text{unitless}})} = \boxed{\text{unitless}} \qquad Q_{total} = (1)(m^{-3})(1)(1) = m^{-3}$$

b. $$k = \frac{k_B T}{h}\frac{Q^{\ddagger}}{Q_A Q_B}\, \underbrace{e^{-E_0/k_BT}}_{\text{unitless}} = \frac{(\cancel{J}/\cancel{K})(\cancel{K})}{\cancel{J} \cdot s} \cdot \frac{\cancel{m^{-3}}}{\cancel{m^{-3}}\, m^{-3}} = \frac{1}{s\, m^{-3}} = \frac{m^3}{s}$$

for 2nd order: $\text{rate} = k[A][B] = \left(\frac{\cancel{m^3}}{s}\right)(\cancel{m^{-3}})(m^{-3})$

$\text{rate} = s^{-1} m^{-3} \rightarrow \text{correct}: \dfrac{\text{concentration}}{\text{time}}$

c. $H + Br_2 \rightarrow HBr + Br$ In general: need T

For TS: need geometry, ν_{vib} (2 or 3 freq. dep. on structure), $I^{\ddagger}$, degen. of ground elect. state

For $H + Br_2$: ν_{vib} for Br_2, I for Br_2, degen. of H ground state (= 2)

Steinfeld Chp. 10 (continued)

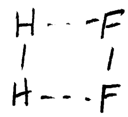
S10.6

a. $H_2 + F_2 \longrightarrow 2HF$ pre-exp. factor $= \frac{k_B T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} = A$

$Q_{rot} \propto T$ (linear), $Q_{trans} \propto T^{3/2}$ $Q_{elec} \propto T^0$, $Q_{vib} \propto T^0$

$Q_{rot} \propto T^{3/2}$ (nonlinear)

TS → (must guess/predict linear or not)



nonlinear

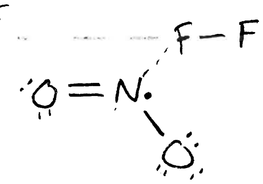
$Q^{\ddagger} \propto T^{3/2} \cdot T^{3/2} \propto T^3$

$Q_{H_2} \propto T \cdot T^{3/2} \propto T^{5/2}$ $Q_{F_2} \propto T \cdot T^{3/2} \propto T^{5/2}$

so $A \propto T \cdot \frac{T^3}{T^{5/2} T^{5/2}} \propto \frac{T^4}{T^5} \longrightarrow \boxed{A \propto T^{-1}}$

b. $NO_2 + F_2 \longrightarrow NO_2F + F$

TS ⟶ nonlinear



$Q^{\ddagger} \propto T^3$

Q_{NO_2} (nonlinear) $\propto T^3$

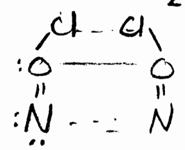
$Q_{F_2} \propto T^{5/2}$

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

Steinfeld Chp. 10 (continued)

S10.6 (continued)

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

TS:  nonlinear

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

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