1. Consider the following mechanism.

(Step 1) $$Cl\cdot\ (g) + N_3\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ClN\cdot\ (g) + N_2\ (g)$$

(Step 2) $$ClN\cdot\ (g) + N_3\ (g) \xrightarrow{k_2} 2\,N_2\ (g) + Cl\cdot\ (g)$$

(a) List all catalysts. $Cl\cdot$

(b) List all intermediates. $ClN\cdot$

(c) Write out the rate law assuming step 1 is slow and step 2 is fast.

$$v(t) = k_1[Cl\cdot][N_3]$$

(d) Write out the rate law assuming step 1 is fast and step 2 is slow.

$$\begin{aligned} v(t) &= k_2[ClN\cdot][N_3] \\ k_1[Cl\cdot][N_3] &= k_{-1}[ClN\cdot][N_2] \\ [ClN\cdot] &= \frac{k_1}{k_{-1}}\frac{[Cl\cdot][N_3]}{[N_2]} \\ v(t) &= \frac{k_1k_2}{k_{-1}}\frac{[Cl\cdot][N_3]^2}{[N_2]} \end{aligned}$$

2. The decomposition of Di-t-butylperoxide is given by the reaction:

$$(CH_3)_3COOC(CH_3)_3(g) \longrightarrow 2\,(CH_3)_2CO\,(g) + C_2H_6(g)$$

Consider the following proposed mechanism:

(Step 1) $$(CH_3)_3COOC(CH_3)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,(CH_3)_3CO\cdot$$

(Step 2) $$2\,(CH_3)_3CO\cdot \xrightarrow{k_2} 2\,(CH_3)_2CO + 2\,CH_3\cdot$$

(Step 3) $$2\,CH_3\cdot \xrightarrow{k_3} C_2H_6$$

(a) Assuming the second step is rate determining, write out the rate law for this mechanism.

$$\begin{aligned} v(t) &= k_2[(CH_3)_3CO\cdot]^2 \\ k_1[(CH_3)_3COOC(CH_3)_3] &= k_{-1}[(CH_3)_3CO\cdot]^2 \\ [(CH_3)_3CO\cdot]^2 &= \frac{k_1}{k_{-1}}[(CH_3)_3COOC(CH_3)_3] \\ v(t) &= \frac{k_1k_2}{k_{-1}}[(CH_3)_3COOC(CH_3)_3] \end{aligned}$$

(b) Determine the sign of ΔH for step 1.

■ $\Delta H > 0$ ☐ $\Delta H = 0$ ☐ $\Delta H < 0$ ☐ Cannot be determined

(c) Determine the sign of ΔS for step 2.

■ $\Delta S > 0$ ☐ $\Delta S = 0$ ☐ $\Delta S < 0$ ☐ Cannot be determined

(d) Step 3 would be spontaneous under what temperature conditions?

☐ All temps ☐ High temps ■ Low temps ☐ No temps

3. Consider the reaction:

$$2\,\mathrm{NO_2}\,(g) + \mathrm{F_2}\,(g) \longrightarrow 2\,\mathrm{NO_2F}\,(g)$$

where the experimentally determined rate law is:

$$v(t) = k[\mathrm{NO_2}][\mathrm{F_2}]$$

(a) Name two ways that the rate constant k could be increased.

$k = Ae^{-E_a/RT}$, increase T, add catalyst

(b) The following mechanism is proposed:

(Step 1, fast) $\mathrm{NO_2}\,(g) + \mathrm{F_2}\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2F}\,(g) + \mathrm{F}\,(g)$

(Step 2, slow) $\mathrm{NO_2}\,(g) + \mathrm{F}\,(g) \xrightarrow{k_2} \mathrm{NO_2F}\,(g)$

Derive the rate law predicted by the mechanism and verify if it matches the experiment.

$$\begin{aligned} v(t) &= k_2[\mathrm{NO_2}][\mathrm{F}\cdot] \\ k_1[\mathrm{NO_2}][\mathrm{F_2}] &= k_{-1}[\mathrm{NO_2F}][\mathrm{F}\cdot] \\ [\mathrm{F}\cdot] &= \frac{k_1}{k_{-1}}\frac{[\mathrm{NO_2}][\mathrm{F_2}]}{[\mathrm{NO_2F}]} \\ v(t) &= \frac{k_1k_2}{k_{-1}}\cdot\frac{[\mathrm{NO_2}]^2[\mathrm{F_2}]}{[\mathrm{NO_2F}]} \end{aligned}$$

(c) By only modifying the reaction arrows and the magnitude of k (not the mechanism itself), how could the mechanism be adjusted to match the experiment rate law? List all possibilities.

We need step 1 to be RDS. So slow first step single–sided reaction $\mathrm{NO_2}\,(g) + \mathrm{F_2}\,(g) \xrightarrow{k_1} \mathrm{NO_2F}\,(g) + \mathrm{F}\,(g)$ or slow equilibrium $\mathrm{NO_2}\,(g) + \mathrm{F_2}\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{NO_2F}\,(g) + \mathrm{F}\,(g)$ both work since the slow equilibrium becomes single–sided as step 2 must be fast.

(d) An alternative mechanism shows a slow first step involving the breaking of the $\mathrm{F_2}$ bond:

(Step 1, slow) $\mathrm{F_2}\,(g) \longrightarrow 2\,\mathrm{F}\,(g)$

Circle all true statements:

☐ The half life depends on initial concentration

☐ $E_a = 0\,\frac{\mathrm{kJ}}{\mathrm{mol}}$

■ A plot of $\ln(P_{\mathrm{F_2}})$ vs time is linear

■ The overall rate is independent of $[\mathrm{NO_2}]$

4. Which statement(s) are true when the temperature of a reaction mixture is increased?

   ☐ Temperature increases cause the equilibrium constant and final product concentration to increase.

   ☐ Temperature increases reduce the activation energy.

   ■ Temperature increases speed up reactions by increasing the number of collisions.

   ■ Temperature increases raise both forward and reverse reaction rates.

Homework Problem 36

1. Consider the mechanism:

(Step 1) $\mathrm{Ag^{+}\,(aq) + Ce^{4+}\,(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ag^{2+}\,(aq) + Ce^{3+}\,(aq)}$

(Step 2) $\mathrm{Ti^{+}\,(aq) + Ag^{2+}\,(aq) \xrightarrow{k_2} Tl^{2+}\,(aq) + Ag^{+}\,(aq)}$

(Step 3) $\mathrm{Ti^{2+}\,(aq) + Ce^{4+}\,(aq) \xrightarrow{k_3} Tl^{3+}\,(aq) + Ce^{3+}\,(aq)}$

   (a) Write the overall reaction.

   (b) List all catalysts.

   (c) List all intermediates.

   (d) Write the rate law and overall reaction order if step 1 is slow.

   (e) Write the rate law and overall reaction order if step 2 is slow.