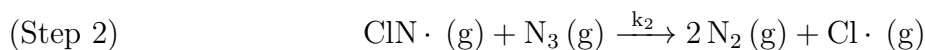
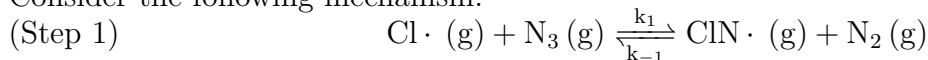


1. Consider the following mechanism.



(a) List all catalysts. $\text{Cl}\cdot$

(b) List all intermediates. $\text{ClN}\cdot$

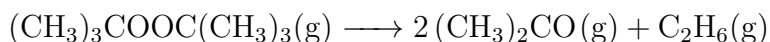
(c) Write out the rate law assuming step 1 is slow and step 2 is fast.

$$v(t) = k_1[\text{Cl}\cdot][\text{N}_3]$$

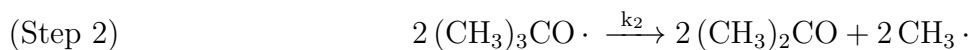
(d) Write out the rate law assuming step 1 is fast and step 2 is slow.

$$\begin{aligned} v(t) &= k_2[\text{ClN}\cdot][\text{N}_3] \\ k_1[\text{Cl}\cdot][\text{N}_3] &= k_{-1}[\text{ClN}\cdot][\text{N}_2] \\ [\text{ClN}\cdot] &= \frac{k_1}{k_{-1}} \frac{[\text{Cl}\cdot][\text{N}_3]}{[\text{N}_2]} \\ v(t) &= \frac{k_1 k_2}{k_{-1}} \frac{[\text{Cl}\cdot][\text{N}_3]^2}{[\text{N}_2]} \end{aligned}$$

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



Consider the following proposed mechanism:



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

$$\begin{aligned} v(t) &= k_2[(\text{CH}_3)_3\text{CO}\cdot]^2 \\ k_1[(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3] &= k_{-1}[(\text{CH}_3)_3\text{CO}\cdot]^2 \\ [(\text{CH}_3)_3\text{CO}\cdot]^2 &= \frac{k_1}{k_{-1}} [(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3] \\ v(t) &= \frac{k_1 k_2}{k_{-1}} [(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3] \end{aligned}$$

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

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

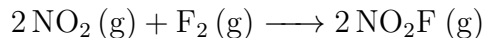
(c) Determine the sign of ΔS for step 2.

$\Delta S > 0$ $\Delta S = 0$ $\Delta S < 0$ 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:



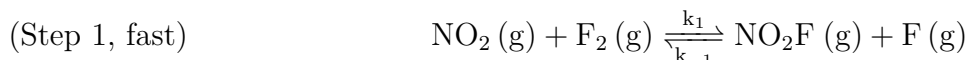
where the experimentally determined rate law is:

$$v(t) = k[\text{NO}_2][\text{F}_2]$$

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

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

(b) The following mechanism is proposed:



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

$$\begin{aligned} v(t) &= k_2[\text{NO}_2][\text{F}\cdot] \\ k_1[\text{NO}_2][\text{F}_2] &= k_{-1}[\text{NO}_2\text{F}][\text{F}\cdot] \\ [\text{F}\cdot] &= \frac{k_1}{k_{-1}} \frac{[\text{NO}_2][\text{F}_2]}{[\text{NO}_2\text{F}]} \\ v(t) &= \frac{k_1 k_2}{k_{-1}} \cdot \frac{[\text{NO}_2]^2[\text{F}_2]}{[\text{NO}_2\text{F}]} \end{aligned}$$

(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 $\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \xrightarrow{k_1} \text{NO}_2\text{F}(\text{g}) + \text{F}(\text{g})$ or slow equilibrium $\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} \text{NO}_2\text{F}(\text{g}) + \text{F}(\text{g})$ 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 F_2 bond:



Circle all true statements:

The half life depends on initial concentration

$E_a = 0 \frac{\text{kJ}}{\text{mol}}$

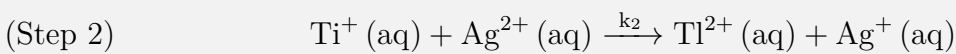
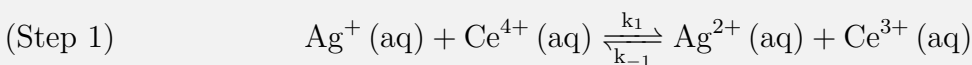
A plot of $\ln(P_{\text{F}_2})$ vs time is linear

The overall rate is independent of $[\text{NO}_2]$

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:



- (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.