1. Is this a valid elementary step? Explain your reasoning.

$$IO_3^-\,(aq) + 3\,HSO_3^-\,(aq) \longrightarrow I^-\,(aq) + 3\,HSO_4^-\,(aq)$$

No, 4 colliding molecules unlikely and not a simple collision

2. (**Chemical Engineering Science**, 55, 21, 2000, 5141.)

A proposed two-step mechanism for the Claus reaction is shown below.

(Step 1) $$H_2S\,(g) + \frac{3}{2}\,O_2(g) \xrightarrow{k_1} SO_2(g) + H_2O(g)$$

(Step 2) $$2\,H_2S\,(g) + SO_2(g) \xrightarrow{k_2} \frac{3}{2}\,S_2(g) + 2\,H_2O\,(g)$$

(a) Write the overall reaction.

$$3\,H_2S\,(g) + \tfrac{3}{2}\,O_2(g) \longrightarrow \tfrac{3}{2}\,S_2(g) + 3\,H_2O\,(g)$$

(b) List all intermediates.

$SO_2(g)$

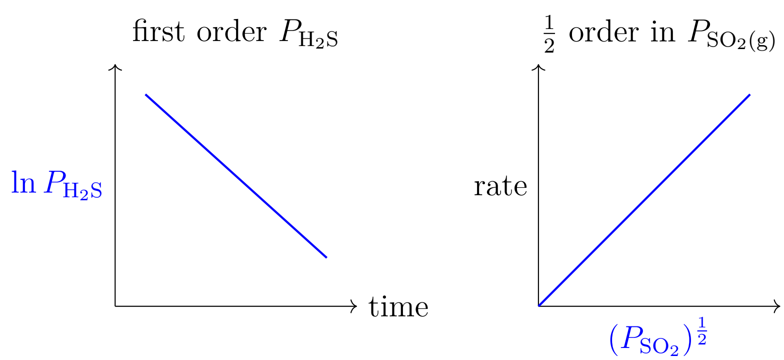
(c) List all catalysts.

None

(d) The study found the rate law for the second step to be first order in $H_2S\,(g)$ and one-half order in $SO_2(g)$. Is step 2 an elementary step or not? Explain.

No, $v(t) = k[H_2S]^2[SO_2]^1$, so the rate constant is not derived from coefficients.

(e) Sketch the straight line plots and provide labels for any missing axes to confirm orders.



(f) In the study of step 2, $\ln k_2$ vs. $1/T$ was plotted producing a line with slope $= -25{,}114\,K$. What is the activation energy for step 2?

$$m = -\frac{E_a}{R} \implies E_a = -mR$$
$$E_a = -\left(-25114\,K\right)\left(8.314\,\frac{J}{mol\cdot K}\right)$$
$$= \boxed{209\,\frac{kJ}{mol}}$$

3. In General Chemistry, we study the decomposition of hydrogen peroxide catalyzed by iodine. Propose a two-step mechanism, including labeling slow/fast steps, for:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

where the experimentally determined rate law is:

$$v(t) = k[H_2O_2][I^-]$$

(Step 1) $H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ slow

(Step 2) $IO^- + H_2O_2 \xrightarrow{k_2} H_2O + O_2 + I^-$ fast

(Overall) $2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$

4. Propose a two-step mechanism, including labeling slow/fast steps, for:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

where the experimentally determined rate law is:

$$v(t) = k\frac{[NO]^2[O_2]}{[NO_2]}$$

Simple collision between NO and O_2 yields $NO_2 + O$ or NO_3.

(Step 1) $NO + O_2 \xrightarrow{k_1} NO_2 + O$

(Step 2) $NO + O \xrightarrow{k_2} NO_2$

(Overall) $2\,NO + O_2 \longrightarrow 2\,NO_2$

For the first one, if step 1 is slow, then rate law is $v(t) = k_1[NO][O_2]$ which is wrong. If step 2 is slow, then step 1 needs to become equilibrium to get rid of intermediate [O].

(Step 1) $NO + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + O$

(Step 2) $NO + O \xrightarrow{k_2} NO_2$

(Overall) $2\,NO + O_2 \longrightarrow 2\,NO_2$

$$\begin{aligned} k_1[NO][O_2] &= k_{-1}[NO_2][O] \\ [O] &= \frac{k_1}{k_{-1}} \cdot \frac{[NO][O_2]}{[NO_2]} \\ v(t) &= k_2[NO][O] \\ &= k_2[NO] \cdot \frac{k_1}{k_{-1}} \cdot \frac{[NO][O_2]}{[NO_2]} = k\frac{[NO]^2[O_2]}{[NO_2]} \end{aligned}$$

Doing NO_3 as the intermediate produces the wrong rate law so we eliminate that.

Homework Problem 35

1. Consider the following mechanism.

(Step 1) $NO\ (g) + O_2\ (g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_3\ (g)$

(Step 2) $NO_3\ (g) + CO\ (g) \xrightarrow{k_2} NO_2\ (g) + CO_2\ (g)$

(Step 3) $NO_2\ (g) + CO\ (g) \xrightarrow{k_3} NO\ (g) + CO_2\ (g)$

(a) Write the overall reaction.

(b) List all catalysts.

(c) List all intermediates.

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

(e) Write out the rate law assuming that step 2 is slow and the others are fast.

(f) Experimentally it is determined the overall order is 3. Between step 1 and step 2, which one could be the rate determining step?