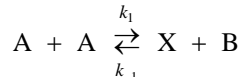
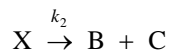


ChemE 2200 - Physical Chemistry II for Engineers
Solutions to Exercises for Calculation Session 14

1. The rate equation suggests an elementary step that is bi-molecular in A and is opposed by B.



The intermediate X (the unknown) then decomposes into the remaining products, B and C.



Derive a rate equation based on these two elementary steps. Use the second reaction to write a rate equation for [C].

$$\frac{d[C]}{dt} = k_2[X] \quad (1)$$

We need an expression for the concentration of intermediate X. Apply the steady-state approximation to X and solve for [X].

$$\begin{aligned} \frac{d[X]}{dt} = 0 &= k_1[A]^2 - k_{-1}[X][B] - k_2[X] \\ [X] &= \frac{k_1[A]^2}{k_{-1}[B] + k_2} \end{aligned} \quad (2)$$

Substituting eqn (2) into eqn (1) yields

$$\frac{d[C]}{dt} = k_2[X] = k_2 \frac{k_1[A]^2}{k_{-1}[B] + k_2}$$

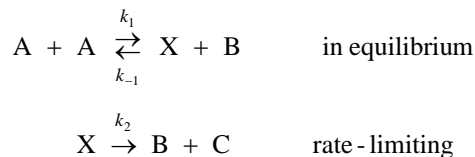
This expression would be correct if k_2 were negligible. That is, we need to instead assume that the second step is rate limiting and the first step is in equilibrium. Applying pre-equilibrium yields the following relation.

$$\begin{aligned} k_1[A]^2 &= k_{-1}[X][B] \\ [X] &= \frac{k_1[A]^2}{k_{-1}[B]} \end{aligned} \quad (3)$$

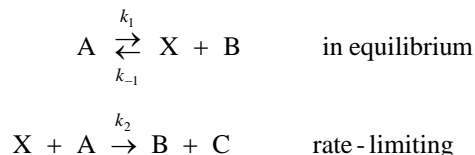
Substitute eqn (3) into eqn (1).

$$\frac{d[C]}{dt} = k_2[X] = \frac{k_1 k_2}{k_{-1}} \frac{[A]^2}{[B]}$$

This is the correct form for the rate equation. In summary, the mechanism of elementary steps is -



The observed rate equation is also obtained with the following mechanism.



As before, use the second reaction to write a rate equation for [C].

$$\frac{d[C]}{dt} = k_2[X][A] \quad (1a)$$

Apply pre-equilibrium and solve for [X].

$$k_1[A] = k_{-1}[X][B]$$

$$[X] = \frac{k_1[A]}{k_{-1}[B]} \quad (2a)$$

Substitute eqn (2a) into eqn (1a).

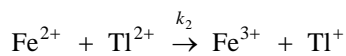
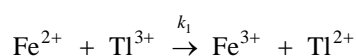
$$\frac{d[C]}{dt} = k_2[X][A] = \frac{k_1 k_2}{k_{-1}} \frac{[A]}{[B]} [A] = \frac{k_1 k_2}{k_{-1}} \frac{[A]^2}{[B]}$$

Again this is the correct form for the rate equation.

2. The facts require the following conclusions:

- Tl^{3+} may react only with Fe^{2+} . Tl^{3+} cannot react with the only other Fe cation, Fe^{3+} , because Fe^{3+} can transform only to Fe^{2+} which would require Tl^{3+} to transform to Tl^{4+} , and Tl^{4+} is not allowed.
- Tl^{2+} may react with both Fe^{2+} and Fe^{3+} .
- Tl^+ may react only with Fe^{3+} , for reasons similar to the first conclusion.

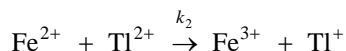
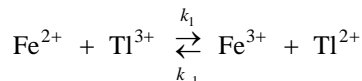
Try the simplest mechanism.



This mechanism yields the following rate equation.

$$\frac{d[Tl^{3+}]}{dt} = -k_1[Fe^{2+}][Tl^{3+}]$$

The rate equation needs more. The rate equation given in the exercise statement suggests that Fe^{3+} opposes the overall mechanism. This suggests that one or two of the elementary steps are reversible. Try the first step.



This mechanism yields

$$\frac{d[Tl^{3+}]}{dt} = -k_1[Fe^{2+}][Tl^{3+}] + k_{-1}[Fe^{3+}][Tl^{2+}] \quad (1)$$

We need an expression for $[Tl^{2+}]$. Apply the steady-state approximation to Tl^{2+} .

$$\frac{d[Tl^{2+}]}{dt} = 0 = k_1[Fe^{2+}][Tl^{3+}] - k_{-1}[Fe^{3+}][Tl^{2+}] - k_2[Fe^{2+}][Tl^{2+}]$$

$$k_1[Fe^{2+}][Tl^{3+}] - k_{-1}[Fe^{3+}][Tl^{2+}] = k_2[Fe^{2+}][Tl^{2+}] \quad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[Tl^{3+}]}{dt} = -k_2[Fe^{2+}][Tl^{2+}] \quad (3)$$

Solve eqn (2) for $[\text{Ti}^{2+}]$.

$$[\text{Ti}^{2+}] = \frac{k_1[\text{Fe}^{2+}][\text{Ti}^{3+}]}{k_2[\text{Fe}^{2+}] + k_{-1}[\text{Fe}^{3+}]} \quad (4)$$

Substitute eqn (4) into eqn (3),

$$\begin{aligned} \frac{d[\text{Ti}^{3+}]}{dt} &= -k_2[\text{Fe}^{2+}] \frac{k_1[\text{Fe}^{2+}][\text{Ti}^{3+}]}{k_2[\text{Fe}^{2+}] + k_{-1}[\text{Fe}^{3+}]} \\ &= \frac{-k_1[\text{Fe}^{2+}]^2[\text{Ti}^{3+}]}{[\text{Fe}^{2+}] + (k_{-1}/k_2)[\text{Fe}^{3+}]} \end{aligned}$$

This agrees with the observed rate equation such that $\alpha = k_1$ and $\beta = k_{-1}/k_2$.

3.(A) Reaction 1 is initiation; reactants form a propagating radical. Reaction 2 is propagation; a propagating radical and a reactant create a product and a different propagating radical. Reaction 3 is also initiation; a molecule forms propagating radicals. Albeit the initiator is a product molecule, reaction 3 is still initiation. Reaction 4 is propagation; a propagating radical and a reactant create a product and a different propagating radical. Reaction 5 is termination; two propagating radicals combine to form an inert molecule.

(B) Use reaction 4 to write a rate equation for N_2 .

$$\frac{d[\text{N}_2]}{dt} = k_4[\text{N}\cdot][\text{NO}] \quad (1)$$

We need an expression for $[\text{N}\cdot]$. Assume the rate of propagation step 2 equals the rate of propagation step 4.

$$\begin{aligned} k_2[\cdot\text{O}\cdot][\text{NO}] &= k_4[\text{N}\cdot][\text{NO}] \\ [\text{N}\cdot] &= \frac{k_2[\cdot\text{O}\cdot]}{k_4} \quad (2) \end{aligned}$$

We need an expression for $[\cdot\text{O}\cdot]$. Apply the chain reaction principle that “the rate of initiation equals the rate of termination.” There are two initiation steps, but note that the two initiation steps are not in series. Rather, the two initiation steps are in parallel. Thus the total rate of initiation equals the rate of initiation step 1 plus the rate of initiation step 2.

$$\begin{aligned} k_1[\text{NO}]^2 + 2k_3[\text{M}][\text{O}_2] &= 2k_5[\text{M}][\cdot\text{O}\cdot]^2 \\ [\cdot\text{O}\cdot] &= \left(\frac{k_1[\text{NO}]^2 + 2k_3[\text{M}][\text{O}_2]}{2k_5[\text{M}]} \right)^{1/2} \quad (3) \end{aligned}$$

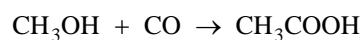
Substitute eqn (3) into eqn (2).

$$[\text{N}\cdot] = \frac{k_2[\cdot\text{O}\cdot]}{k_4} = \frac{k_2}{k_4} \left(\frac{k_1[\text{NO}]^2 + 2k_3[\text{M}][\text{O}_2]}{2k_5[\text{M}]} \right)^{1/2} \quad (4)$$

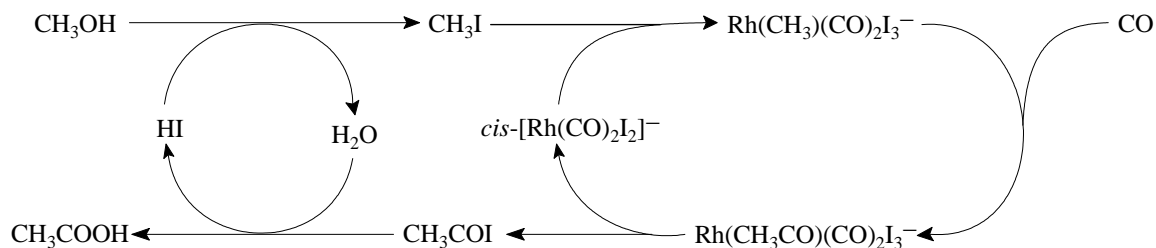
Finally, substitute eqn (4) into eqn (1).

$$\frac{d[\text{N}_2]}{dt} = k_2 \left(\frac{k_1[\text{NO}]^2 + 2k_3[\text{M}][\text{O}_2]}{2k_5[\text{M}]} \right)^{1/2} [\text{NO}]$$

4.(A) Adding the five elementary reactions and canceling substances that appear on both sides of the chemical equation yields the overall reaction:



(B)



5. Catalyst I: The supplier's claims are possible. After A has completely reacted, $[G]/[B] > 1$.
 Catalyst II: The supplier's claims are possible. After A has completely reacted, $[G]/[B] = 1$. Although the catalyzed path for $A \rightarrow B$ has a higher E_a , the uncatalyzed path remains open.
 Catalyst III: The supplier's claims are impossible. A catalyst cannot change the thermodynamic levels of a stable substance.
 Catalyst IV: The supplier's claims are possible. After A has completely reacted, $[G]/[B] = 1$. Because B and G have the same thermodynamic levels, an equilibrium between B and G will have equal amounts of B and G.
 Catalyst I is the better catalyst. It is the only catalyst for which $[G]/[B] > 1$.
6. Assume the rate equation is in the form of a power law,

$$\frac{d[A]}{dt} = k[A]^a[B]^b.$$

This assumption seems reasonable because the lines at constant $[B]$ are straight and the slopes of the lines do not change when $[B]$ varies from 1 mol/L to 100 mol/L.

Apply the method of initial rates to determine the reaction order with respect to $[A]$. Measure the slope of the line for $[B] = 1$ mol/L. Extend the line to the edges of the plot. The line intersects $[A] = 1$ mol/L at rate = 0.17 mol/L/min and the line intersects $[A] = 1000$ mol/L at rate = 5400 mol/L/min.

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{\log_{10} 5400 - \log_{10} 0.17}{\log_{10} 1000 - \log_{10} 1} = \frac{3.7 - (-0.8)}{3 - 0} = 1.5 = \frac{3}{2}$$

The reaction is $3/2$ order with respect to $[A]$.

To determine the slope with respect to $[B]$, measure the change in rate at constant $[A]$ when $[B]$ is increased from 1 mol/L to 10 mol/L to 100 mol/L. Set $[A] = 10$ mol/L:

$[B]$	rate
1	5.4
10	54
100	540

By inspection, we see that when $[B]$ increases by a factor of 10, the rate increases by a factor of 10. The reaction is first order with respect to $[B]$.

To determine k , solve the rate equation for k , then plug in values of $[A]$, $[B]$, and the rate obtained from the plot.

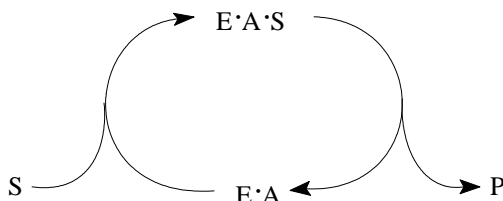
$$k = \frac{\frac{d[A]}{dt}}{[A]^{3/2}[B]} [=] \frac{\frac{\text{mol}}{\text{L} \cdot \text{min}}}{\left[\frac{\text{mol}}{\text{L}}\right]^{3/2} \frac{\text{mol}}{\text{L}}} [=] \text{mol}^{-3/2} \cdot \text{L}^{3/2} \cdot \text{min}^{-1}$$

[A]	[B]	rate	k
10	1	5.4	0.17
3	10	9	0.17
50	100	6000	0.17

Thus $k = 0.17 \text{ mol}^{-3/2}\text{L}^{3/2}\text{min}^{-1}$. Note that trying different points from different lines tests whether the reaction orders are correct. If the reaction orders were incorrect, each point would yield a different value for k .

- 7.(A) The sum of the propagation reactions should be the overall reaction; no creation of propagating species and no consumption of propagating species. The sum of reactions 3 and 4 is the overall reaction, $S \rightarrow P$. Thus the propagating reactions are reactions 3 and 4 and the propagating species are $E \cdot A$ and $E \cdot A \cdot S$. A propagating species is created in the first reaction; this is initiation. A propagating species is consumed in the second reaction; this is termination.

(B)



- (C) The fourth reaction provides an equation for the rate of formation of P.

$$\frac{d[P]}{dt} = k_4[E \cdot A \cdot S] \quad (1)$$

We must express $[E \cdot A \cdot S]$ in terms of $[E]_0$, $[A]$, and $[S]$. Assume the rate of propagation reaction 3 equals the rate of propagation reaction 4.

$$k_4[E \cdot A \cdot S] = k_3[E \cdot A][S]$$

$$[E \cdot A \cdot S] = \frac{k_3}{k_4}[E \cdot A][S] \quad (2)$$

We must express $[E \cdot A]$ in terms of $[E]_0$, $[A]$, and $[S]$. Assume the rate of initiation equals the rate of termination.

$$k_2[E \cdot A] = k_1[E][A]$$

$$[E \cdot A] = \frac{k_1}{k_2}[E][A] \quad (3)$$

Substitute eqn (3) into equation (2).

$$[E \cdot A \cdot S] = \frac{k_3}{k_4}[E \cdot A][S] = \frac{k_1 k_3}{k_2 k_4}[E][A][S] \quad (4)$$

And substitute eqn (4) into eqn (1).

$$\frac{d[P]}{dt} = k_4[E \cdot A \cdot S] = \frac{k_1 k_3}{k_2}[E][A][S] \quad (5)$$

We must express $[E]$ in terms of $[E]_0$, $[A]$, and $[S]$. Write an expression for the $[E]_0$ in terms of free enzyme and the various enzyme complexes.

$$[E]_0 = [E] + [E \cdot A] + [E \cdot A \cdot S] \quad (6)$$

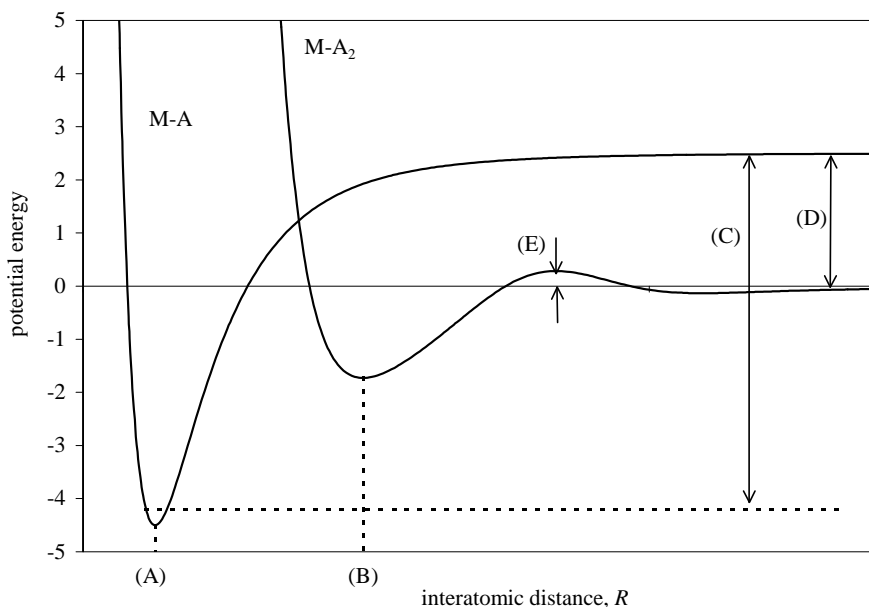
Substitute eqns (3) and (4) into eqn (6) and solve for $[E]$.

$$\begin{aligned}
 [E]_0 &= [E] + \frac{k_1}{k_2}[E][A] + \frac{k_1 k_3}{k_2 k_4}[E][A][S] \\
 &= \left(1 + \frac{k_1}{k_2}[A] \left(1 + \frac{k_3}{k_4}[S] \right) \right) [E] \\
 [E] &= \frac{[E]_0}{1 + \frac{k_1}{k_2}[A] \left(1 + \frac{k_3}{k_4}[S] \right)} \quad (7)
 \end{aligned}$$

Finally, substitute eqn (7) into the rate equation, eqn (5).

$$\begin{aligned}
 \frac{d[P]}{dt} &= \frac{k_1 k_3}{k_2} \frac{[E]_0}{1 + \frac{k_1}{k_2}[A] \left(1 + \frac{k_3}{k_4}[S] \right)} [A][S] \\
 \frac{d[P]}{dt} &= \frac{k_3 [A][S][E]_0}{\frac{k_2}{k_1} + [A] \left(1 + \frac{k_3}{k_4}[S] \right)}
 \end{aligned}$$

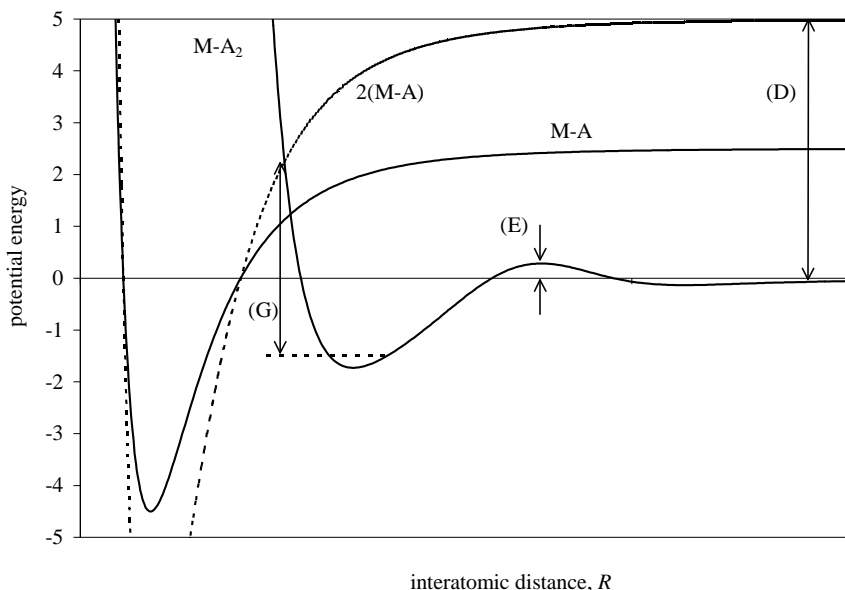
8.(A) The equilibrium bond distance for an adsorbed A atom is at the minimum of the potential energy curve for M-A, indicated on the graph below.



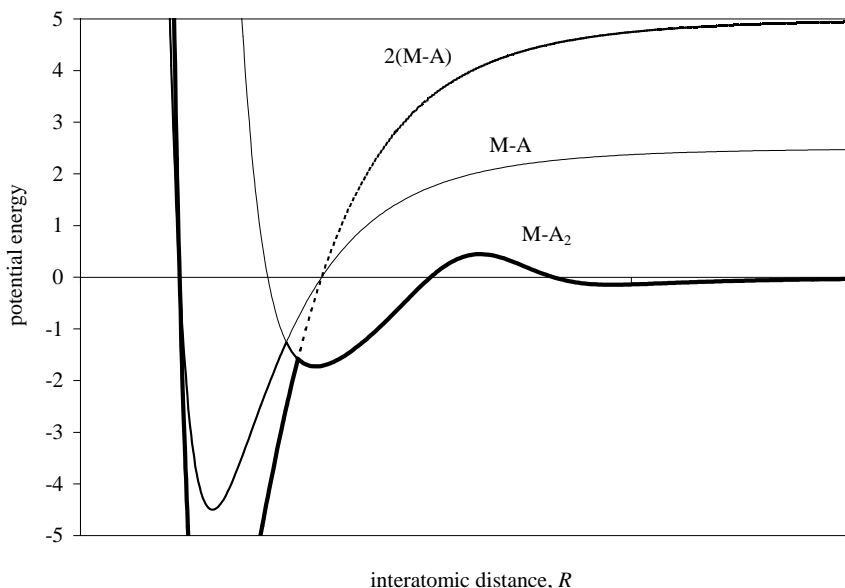
- (B) The equilibrium bond distance for an adsorbed A_2 molecule is at the minimum of the potential energy curve for M- A_2 , indicated on the graph above.
- (C) The adsorption energy of an A atom is the vertical distance between the lowest vibrational level of M-A and the energy of an A atom far from the surface. The approximate distance is indicated on the graph above.
- (D) The vertical distance indicated on the graph above is one-half the bond energy of an A_2 molecule, the energy of $\frac{1}{2}A_2 \rightarrow A$. The energy of $A_2 \rightarrow 2A$ is double this distance.
- (E) The activation energy for the adsorption of A_2 is the energy barrier that precedes the M- A_2 bound state, indicated on the graph above.
- (F) This somewhat of a trick question. The activation energy for the adsorption of an A atom is zero. There is no energy barrier that precedes the M-A bound state. The M-A potential monotonically decreases to the minimum at

R_{eq} . Because the A atom is a free radical and the truncated metal surface is a collection of unbonded metal atoms, it is reasonable there is no activation energy.

- (G) The activation energy for the conversion of adsorbed A_2 to adsorbed A, $M-A_2 + M \rightarrow M-A + M-A$, requires an addition to the curve, as suggested by the hint. This is the curved dotted line on the graph below. The activation energy is approximately the barrier between the lowest vibrational state of $M-A_2$ and the potential energy curve for $2(M-A)$.



- (H) The activation barrier for the reaction $M-A_2 + M \rightarrow M-A + M-A$ (labeled G on the graph) is larger than the activation barrier for the adsorption of A_2 (labeled E on the map.) The adsorbed diatomic will persist in the $M-A_2$ state for a significant time.
- (I) The potentials for a A_2 diatomic that adsorbs dissociatively are shown below. The barrier from the $M-A_2$ state to two $M-A$ states is smaller than the activation barrier for adsorption of A_2 . Imagine an A_2 molecule approaching the surface - follow the $M-A_2$ potential from large R to small R . The system will follow the path shown by the bold line; the system will switch to the two $M-A$ potentials at the intersection.



Team Competition Champions

Team “A”– 42/44!

Carter Knight, Kylie Kaneshige,
and Sophia Wu



Team Competition Solution:

<p>Overall Reaction: $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$</p> <p>Rate Equation: $\frac{d[\text{N}_2\text{O}]}{dt} = \frac{k_1 k_2 [\text{NO}]^2 [\text{H}_2]}{k_{-1} + k_2 [\text{NO}]}$</p> <p>Mechanism: $\text{NO} + \text{H}_2 \xrightleftharpoons[k_{-1}]{k_1} \text{NOH}_2$</p> <p>$\text{NOH}_2 + \text{NO} \xrightarrow{k_2} \text{N}_2\text{O} + \text{H}_2\text{O}$</p> <p>steady-state approximation on NOH_2</p>	<p>Overall Reaction: $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$</p> <p>Rate Equation: $\frac{d[\text{O}_2]}{dt} = k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [\text{NO}][\text{O}_2]^{1/2}$</p> <p>Mechanism: $\text{O}_2 + \text{M} \xrightleftharpoons[k_{-1}]{k_1} 2\text{O} + \text{M}$</p> <p>$\text{NO} + \text{O} \xrightarrow{k_2} \text{O}_2 + \text{N}$</p> <p>$\text{NO} + \text{N} \xrightarrow{k_3} \text{N}_2 + \text{O}$</p> <p>steady-state approximation on $\cdot\text{O}\cdot$</p> <p>steady-state approximation on N</p>
<p>Overall Reaction: $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$</p> <p>Rate Equation: $\frac{d[\text{SO}_3]}{dt} = 2k_1 [\text{NO}][\text{O}_2]$</p> <p>Mechanism: $\text{NO} + \text{O}_2 \xrightarrow{k_1} \text{NO}_2 + \cdot\text{O}\cdot$</p> <p>$\text{NO} + \cdot\text{O}\cdot \xrightarrow{k_2} \text{NO}_2$</p> <p>$\text{NO}_2 + \text{SO}_2 \xrightarrow{k_3} \text{NO} + \text{SO}_3$</p> <p>steady-state approximation on $\cdot\text{O}\cdot$</p> <p>steady-state approximation on NO_2</p>	<p>Overall Reaction: $\text{Cl}_2 + \text{CO} \rightarrow \text{Cl}_2\text{CO}$</p> <p>Rate Equation: $\frac{d[\text{Cl}_2\text{CO}]}{dt} = k[\text{Cl}_2]^{3/2}[\text{CO}]$</p> <p>Mechanism: $\text{Cl}_2 + \text{M} \xrightleftharpoons[k_{-1}]{k_1} \text{Cl}\cdot + \text{Cl}\cdot + \text{M}$</p> <p>$\text{Cl}\cdot + \text{CO} \xrightleftharpoons[k_{-2}]{k_2} \text{ClCO}$</p> <p>$\text{Cl}_2 + \text{ClCO} \xrightarrow{k_3} \text{Cl}_2\text{CO} + \text{Cl}\cdot$</p> <p>pre-equilibrium approximation on rxn 1</p> <p>pre-equilibrium approximation on rxn 2</p>