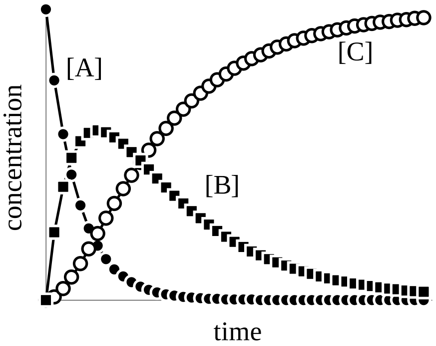
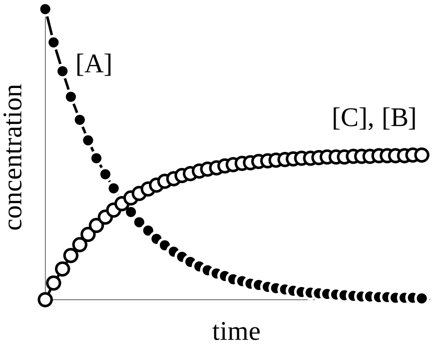
ChemE 2200 - Physical Chemistry II for Engineers
Solutions to Exercises for Calculation Session 12

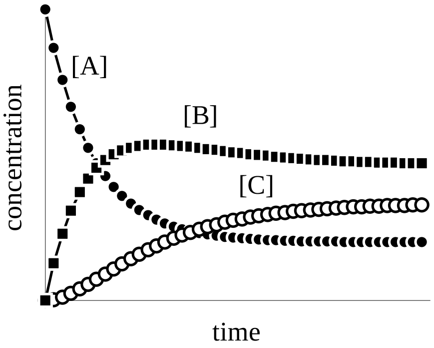
1. It is useful to sketch the time dependence of [B] on each plot. A mass balance on the reactor yields $[B] = [A]_0 - [A] - [C]$.



The first graph corresponds to reaction (1). At long times the reaction goes entirely to C, so the conversion of B to C is not reversible. The possibilities are reactions (1), (2), and (3). [A] decreases more rapidly than [C] increases, so [B] is finite during the reaction. This eliminates reaction (2), which imposes the steady-state approximation on B. Because [A] decreases to zero as a single exponential, it must be reaction (1). That is, it is *not* the case that A first equilibrates with B, then B reacts to C as in reaction (3). If (3) were the reaction, then [B]/[A] would be constant, after a short induction period of length ~$1/(k_1 + k_{-1})$.

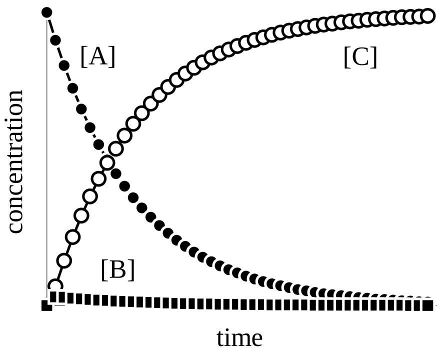


The second graph corresponds to reaction (4). [C] goes to 0.5 at long times, so the conversion of B to C is reversible. [A] goes to zero at long times, so the conversion of A to B is not reversible, or A to B is reversible and $k_{-1} \ll k_1$. The only choice is reaction (4).

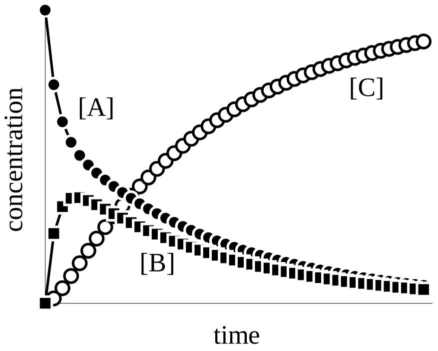


The third graph corresponds to reaction (5). [A] goes to 0.25 at long times, so the conversion of A to B is reversible. [C] goes to 0.5 at long time, so the conversion of B to C is also reversible. Finally, because the ratios [B]/[A] and [C]/[B] are finite, we know $k_1 \approx k_{-1}$, $k_2 \approx k_{-2}$. The only choice is reaction (5).

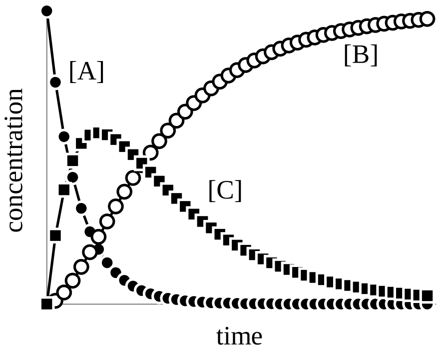
It is useful to consider the graphs that obtain for the other mechanisms. Reaction (2) is similar to reaction (1), but intermediate B does not accumulate. The steady-state approximation applies to B and the graph is



Reaction 3 is pre-equilibrium of A and B. [A] and [B] rapidly approach an equilibrium ratio and the ratio is maintained as C is formed. The graph of reaction 3 is



Reaction 6 is similar to reaction 1, but [B] and [C] are switched:



2. Begin with the qualitative features of each mechanism. Note that the reaction rate is second order in $[N_2O]$ at low concentrations of N_2O. This suggests the mechanism will have a step that involves two N_2O molecules, such as the first steps in mechanisms B and C. The $[N_2O]$ term in the denominator suggests that N_2O opposes the overall reaction, likely by reacting with an intermediate to prevent the intermediate from forming product.

Mechanism B has both these features. Try mechanism B. Write a rate equation.

$$\frac{d[O_2]}{dt} = k_3[N_2O][\cdot O\cdot] \qquad (1)$$

We need an expression for $[\cdot O\cdot]$. Apply the steady-state approximation to the free radical, $\cdot O\cdot$.

$$\frac{d[\cdot O\cdot]}{dt} = 0 = k_2[N_2O^*] - k_3[N_2O][\cdot O\cdot]$$

$$k_2[N_2O^*] = k_3[N_2O][\cdot O\cdot] \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[O_2]}{dt} = k_2[N_2O^*] \qquad (3)$$

Now we need an expression for the concentration of the activated complex, $[N_2O^*]$. Apply the steady-state approximation to N_2O^*.

$$\frac{d[N_2O^*]}{dt} = 0 = k_1[N_2O]^2 - k_{-1}[N_2O^*][N_2O] - k_2[N_2O^*]$$

$$[N_2O^*] = \frac{k_1[N_2O]^2}{k_2 + k_{-1}[N_2O]} \qquad (4)$$

Substitute eqn (4) into eqn (3).

$$\frac{d[O_2]}{dt} = k_2\frac{k_1[N_2O]^2}{k_2 + k_{-1}[N_2O]} = \frac{k_1[N_2O]^2}{1 + (k_{-1}/k_2)[N_2O]} = \frac{\alpha[N_2O]^2}{1 + \beta[N_2O]}$$

Mechanism B yields the correct form of the rate equation.

Aside: Mechanism A yields a rate equation whose denominator contains two terms that depend on concentrations.

$$\text{Mechanism A: } \frac{d[O_2]}{dt} = \frac{k_1k_2[N_2O]^2}{k_{-1}[N_2] + k_2[N_2O]}$$

Mechanism C has no steps in which N_2O opposes the overall reaction. Consequently, $[N_2O]$ does not appear in the denominator.

$$\text{Mechanism C: } \frac{d[O_2]}{dt} = \frac{k_1k_2[N_2O]^2}{k_{-1} + k_2}$$

3. The two criteria for a viable mechanism are (1) each step is an elementary reaction and (2) a sum of the elementary steps agrees with the overall reaction.

Mechanism 1: The first reaction breaks two bonds and makes one bond. This exceeds the guideline of "breaks one bond, or makes one bond, or breaks one bond and makes one bond," but it is a minor infraction. The mechanism agrees with the overall reaction.

$$\begin{array}{c} 2\times(HNO_3 \rightarrow \cdot OH + NO_2) \\ 2\times(\cdot OH + HNO_3 \rightarrow H_2O + NO_3) \\ NO_3 + NO_2 \rightarrow NO_2 + O_2 + NO \\ NO_3 + NO \rightarrow 2NO_2 \\ \hline 4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2 \end{array}$$

Mechanism 2: Both steps meet the guidelines for elementary steps, but the mechanism does not agree with the overall reaction. This reaction never produces O_2, which is one of the products. This mechanism is not viable.

Mechanism 3: Both steps meet the guidelines for elementary steps, but the mechanism does not agree with the overall reaction. NO, which is not a product, is produced in the last reaction, but there is no reaction to consume NO.

Mechanism 4: This is a viable mechanism. Both steps meet the guidelines for elementary steps and the reactions can be summed to the overall reaction.

$$3\times(\mathrm{HNO_3} \rightarrow {\cdot}\mathrm{OH} + \mathrm{NO_2})$$

$$2\times({\cdot}\mathrm{OH} + \mathrm{HNO_3} \rightarrow \mathrm{H_2O} + \mathrm{NO_3})$$

$$\mathrm{NO_3} + {\cdot}\mathrm{OH} \rightarrow \mathrm{NO_2} + {\cdot}\mathrm{OOH}$$

$$\underline{{\cdot}\mathrm{OOH} + \mathrm{NO_3} \rightarrow \mathrm{HNO_3} + \mathrm{O_2}}$$

$$4\mathrm{HNO_3} \rightarrow 4\mathrm{NO_2} + 2\mathrm{H_2O} + \mathrm{O_2}$$

Overall, Mechanism 4 is the better choice. If thermodynamic data reveal that the intermediates in Mechanism 1 are significantly lower than the intermediates in Mechanism 4, the elementary-reaction infraction in Mechanism 1 would be overlooked.

4. The rate equation suggests NO reacts with O_2. Assume one product of this reaction is the intermediate NO_2. To balance the chemical equation, the other product must be atomic oxygen.

$$\mathrm{NO} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{NO_2} + {\cdot}\mathrm{O}{\cdot}$$

Use the atomic oxygen to react with the other reactant and produce the product, SO_3.

$$\mathrm{SO_2} + {\cdot}\mathrm{O}{\cdot} \xrightarrow{k_2} \mathrm{SO_3}$$

The mechanism is incomplete because the overall reaction (so far) produces NO_2. Assume NO_2 is consumed by unimolecular dissociation to NO and $\cdot$O$\cdot$.

$$\mathrm{NO_2} \xrightarrow{k_3} \mathrm{NO} + {\cdot}\mathrm{O}{\cdot}$$

Use the second elementary reaction to write a rate equation for SO_3.

$$\frac{d[\mathrm{SO_3}]}{dt} = k_2[\mathrm{SO_2}][{\cdot}\mathrm{O}{\cdot}] \qquad (1)$$

We need an expression for [$\cdot$O$\cdot$]. Apply the steady-state approximation to $\cdot$O$\cdot$.

$$\frac{d[{\cdot}\mathrm{O}{\cdot}]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_2[\mathrm{SO_2}][{\cdot}\mathrm{O}{\cdot}] + k_3[\mathrm{NO_2}] \qquad (2)$$

Clearly the expression above will contain [NO_2]. We will thus need an expression for [NO_2]. Apply the steady-state approximation to NO_2.

$$\frac{d[\mathrm{NO_2}]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_3[\mathrm{NO_2}]$$

$$k_3[\mathrm{NO_2}] = k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (3)$$

Substitute equation (3) into equation (2).

$$0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_2[\mathrm{SO_2}][{\cdot}\mathrm{O}{\cdot}] + k_1[\mathrm{NO}][\mathrm{O_2}]$$

$$k_2[\mathrm{SO_2}][{\cdot}\mathrm{O}{\cdot}] = 2k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (4)$$

Substitute equation (4) into equation (1).

$$\frac{d[\mathrm{SO_3}]}{dt} = 2k_1[\mathrm{NO}][\mathrm{O_2}]$$

In summary, a valid mechanism is

$$\mathrm{NO} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{NO_2} + \cdot\mathrm{O}\cdot \qquad \text{rate} - \text{limiting step}$$

$$\mathrm{SO_2} + \cdot\mathrm{O}\cdot \xrightarrow{k_2} \mathrm{SO_3}$$

$$\mathrm{NO_2} \xrightarrow{k_3} \mathrm{NO} + \cdot\mathrm{O}\cdot$$

Other mechanisms yield the observed rate equation. For example, assume NO_2 is consumed by reacting with SO_2, as follows.

$$\mathrm{NO} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{NO_2} + \cdot\mathrm{O}\cdot \qquad \text{rate} - \text{limiting step}$$

$$\mathrm{SO_2} + \cdot\mathrm{O}\cdot \xrightarrow{k_2} \mathrm{SO_3}$$

$$\mathrm{NO_2} + \mathrm{SO_2} \xrightarrow{k_3} \mathrm{NO} + \mathrm{SO_3}$$

Use the second and third elementary reactions to write a rate equation for SO_3.

$$\frac{d[\mathrm{SO_3}]}{dt} = k_2[\mathrm{SO_2}][\cdot\mathrm{O}\cdot] + k_3[\mathrm{NO_2}][\mathrm{SO_2}] \qquad (5)$$

We need an expression for $[\cdot\mathrm{O}\cdot]$. Apply the steady-state approximation to $\cdot\mathrm{O}\cdot$.

$$\frac{d[\cdot\mathrm{O}\cdot]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_2[\mathrm{SO_2}][\cdot\mathrm{O}\cdot]$$

$$k_2[\mathrm{SO_2}][\cdot\mathrm{O}\cdot] = k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (6)$$

We need an expression for $[NO_2]$. Apply the steady-state approximation to NO_2.

$$\frac{d[\mathrm{NO_2}]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_3[\mathrm{NO_2}][\mathrm{SO_2}]$$

$$k_3[\mathrm{NO_2}][\mathrm{SO_2}] = k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (7)$$

Substitute equations (6) and (7) into equation (5).

$$\frac{d[\mathrm{SO_3}]}{dt} = k_1[\mathrm{NO}][\mathrm{O_2}] + k_1[\mathrm{NO}][\mathrm{O_2}]$$

$$\frac{d[\mathrm{SO_3}]}{dt} = 2k_1[\mathrm{NO}][\mathrm{O_2}]$$

A third mechanism yields the observed rate equation, as follows. Assume the atomic oxygen is consumed by reacting with NO. Assume SO_3 is produced by SO_2 reacting with NO_2.

$$\mathrm{NO} + \mathrm{O_2} \xrightarrow{k_1} \mathrm{NO_2} + \cdot\mathrm{O}\cdot \qquad \text{rate} - \text{limiting step}$$

$$\mathrm{NO} + \cdot\mathrm{O}\cdot \xrightarrow{k_2} \mathrm{NO_2}$$

$$\mathrm{NO_2} + \mathrm{SO_2} \xrightarrow{k_3} \mathrm{NO} + \mathrm{SO_3}$$

Start with a rate equation for the production of SO_3, which we obtain from the third reaction in the mechanism.

$$\frac{d[\mathrm{SO_3}]}{dt} = k_3[\mathrm{NO_2}][\mathrm{SO_2}] \qquad (8)$$

We need an expression for $[NO_2]$. Apply the steady-state approximation to NO_2.

$$\frac{d[\mathrm{NO_2}]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] + k_2[\mathrm{NO}][\cdot\mathrm{O}\cdot] - k_3[\mathrm{NO_2}][\mathrm{SO_2}] \qquad (9)$$

Clearly the expression above will contain [·O·]. We will thus need an expression for [·O·]. Apply the steady-state approximation to ·O·.

$$\frac{d[\cdot\mathrm{O}\cdot]}{dt} = 0 = k_1[\mathrm{NO}][\mathrm{O_2}] - k_2[\mathrm{NO}][\cdot\mathrm{O}\cdot]$$

$$k_2[\mathrm{NO}][\cdot\mathrm{O}\cdot] = k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (10)$$

Substitute equation (10) into equation (9).

$$0 = k_1[\mathrm{NO}][\mathrm{O_2}] + k_1[\mathrm{NO}][\mathrm{O_2}] - k_3[\mathrm{NO_2}][\mathrm{SO_2}]$$

$$k_3[\mathrm{NO_2}][\mathrm{SO_2}] = 2k_1[\mathrm{NO}][\mathrm{O_2}] \qquad (11)$$

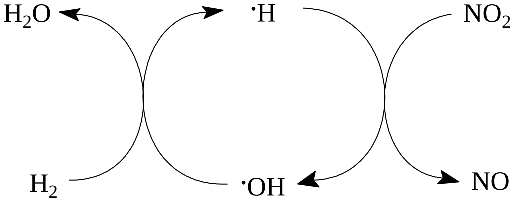
Substitute equation (11) into equation (8).

$$\frac{d[\mathrm{SO_3}]}{dt} = 2k_1[\mathrm{NO}][\mathrm{O_2}]$$

Again, the observed rate equation is obtained.

5.(A) Reaction 1 is initiation. Reactions 2 and 3 are propagation. Reaction 4 is termination.

(B) The propagating radicals are ·H and ·OH, so they should be inside the cycle. The first propagation reaction converts NO_2 to NO. The second propagation reaction converts H_2 to H_2O.



(C) The rate of formation of H_2O is given by step 3.

$$\frac{d[\mathrm{H_2O}]}{dt} = k_3[\cdot\mathrm{OH}][\mathrm{H_2}] \qquad (1)$$

We need an expression for [·OH]. Assume the rate of initiation of radicals in reaction 1 equals the rate of termination of radicals in reaction 4.

$$k_1[\mathrm{H_2}][\mathrm{NO_2}] = k_4[\cdot\mathrm{OH}][\mathrm{NO_2}]$$

$$[\cdot\mathrm{OH}] = \frac{k_1[\mathrm{H_2}]}{k_4} \qquad (2)$$

Substitute eqn (2) into eqn (1),

$$\frac{d[\mathrm{H_2O}]}{dt} = \frac{k_1k_3}{k_4}[\mathrm{H_2}]^2$$

(D) NO_2 participates in the initiation reaction *and* the termination reaction. Increasing the concentration of NO_2 increases the rate of both initiation and termination.

The factor of [NO_2] is present on both sides of the equation preceding eqn (2). Because NO_2 is a reactant in both the initiation and the termination steps, it cancels from the equation.

6.(A) To analyze a chain reaction, it is useful to identify the reactions. The first is initiation; the reaction creates two propagating radicals. The second and third are propagation; each consumes one propagating radical and a reactant molecule and each creates a propagating radical and a product molecule. The three options for the fourth reaction are termination; each consumes two propagating radicals.

The third elementary reaction provides an equation for the rate of formation of CH_3Br.

$$\frac{d[\mathrm{CH_3Br}]}{dt} = k_3[\cdot\mathrm{CH_3}][\mathrm{Br_2}] \qquad (1)$$

Set the rate of propagation reaction 1 equal to the rate of propagation reaction 2.

$$k_2[\mathrm{Br}\cdot][\mathrm{CH_4}] = k_3[\cdot\mathrm{CH_3}][\mathrm{Br_2}] \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{CH_3Br}]}{dt} = k_2[\mathrm{Br}\cdot][\mathrm{CH_4}] \qquad (3)$$

We need an expression for $[\mathrm{Br}^\cdot]$. Set the rate of initiation equal to the rate of termination. Arbitrarily use the first of the three termination reactions.

$$k_1[\mathrm{Br_2}][\mathrm{M}] = k_4[\mathrm{Br}\cdot]^2[\mathrm{M}]$$

$$[\mathrm{Br}\cdot] = \left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{Br_2}]^{1/2} \qquad (4)$$

Substitute eqn (4) into eqn (2).

$$\frac{d[\mathrm{CH_3Br}]}{dt} = k_2[\mathrm{Br}\cdot][\mathrm{CH_4}] = k_2\left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{Br_2}]^{1/2}[\mathrm{CH_4}] \qquad (5)$$

This is not the correct form of the rate equation. Try the second option for the termination reaction and set the rate of initiation equal to the rate of termination.

$$k_1[\mathrm{Br_2}][\mathrm{M}] = k_4[\mathrm{Br}\cdot][\cdot\mathrm{CH_3}]$$

$$[\mathrm{Br}\cdot] = \frac{k_1}{k_4}\frac{[\mathrm{Br_2}][\mathrm{M}]}{[\cdot\mathrm{CH_3}]} \qquad (6)$$

We need an expression for $[^\cdot\mathrm{CH_3}]$. Use eqn (2) and solve for $[^\cdot\mathrm{CH_3}]$.

$$[\cdot\mathrm{CH_3}] = \frac{k_2}{k_3}\frac{[\mathrm{Br}\cdot][\mathrm{CH_4}]}{[\mathrm{Br_2}]} \qquad (7)$$

Substitute eqn (7) into eqn (6).

$$[\mathrm{Br}\cdot] = \frac{k_1}{k_4}\frac{[\mathrm{Br_2}][\mathrm{M}]}{[\cdot\mathrm{CH_3}]} = \frac{k_1}{k_4}\frac{[\mathrm{Br_2}][\mathrm{M}]}{\dfrac{k_2}{k_3}\dfrac{[\mathrm{Br}\cdot][\mathrm{CH_4}]}{[\mathrm{Br_2}]}} = \frac{k_1k_3}{k_2k_4}\frac{[\mathrm{Br_2}]^2[\mathrm{M}]}{[\mathrm{Br}\cdot][\mathrm{CH_4}]}$$

$$[\mathrm{Br}\cdot] = \left(\frac{k_1k_3}{k_2k_4}\right)^{1/2}\frac{[\mathrm{Br_2}][\mathrm{M}]^{1/2}}{[\mathrm{CH_4}]^{1/2}} \qquad (8)$$

Substitute eqn (8) into eqn (3).

$$\frac{d[\mathrm{CH_3Br}]}{dt} = k_2[\mathrm{Br}\cdot][\mathrm{CH_4}] = k_2\left(\frac{k_1k_3}{k_2k_4}\right)^{1/2}\frac{[\mathrm{Br_2}][\mathrm{M}]^{1/2}}{[\mathrm{CH_4}]^{1/2}}[\mathrm{CH_4}] = \left(\frac{k_1k_2k_3}{k_4}\right)^{1/2}[\mathrm{Br_2}][\mathrm{CH_4}]^{1/2}[\mathrm{M}]^{1/2} \qquad (10)$$

This is the correct form of the rate equation. Note that we disregarded the rate CH_3Br is created by the termination reaction; we did not add a term to the rate equation, eqn (1) or eqn (3). This contribution is negligible relative to the propagation reaction, step 3.

If the third option for the termination reaction is assumed, one again sets the rate of initiation equal to the rate of termination.

$$k_1[\mathrm{Br}_2][\mathrm{M}] = k_4[\cdot\mathrm{CH}_3]^2$$

$$[\cdot\mathrm{CH}_3] = \left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{M}]^{1/2} \qquad (11)$$

Substitute eqn (11) into eqn (1).

$$\frac{d[\mathrm{CH}_3\mathrm{Br}]}{dt} = k_3[\cdot\mathrm{CH}_3][\mathrm{Br}_2] = k_3\left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{Br}_2]^{1/2}[\mathrm{M}]^{1/2}[\mathrm{Br}_2] = k_3\left(\frac{k_1}{k_4}\right)^{1/2}[\mathrm{Br}_2]^{3/2}[\mathrm{M}]^{1/2}$$

This is not the correct form of the rate equation. In summary, the chain reaction is

$$\begin{array}{ll}
\mathrm{Br}_2 + \mathrm{M} \xrightarrow{k_1} 2\mathrm{Br}\cdot + \mathrm{M} & \text{initiation} \\
\mathrm{Br}\cdot + \mathrm{CH}_4 \xrightarrow{k_2} \mathrm{HBr} + \cdot\mathrm{CH}_3 & \text{propagation} \\
\cdot\mathrm{CH}_3 + \mathrm{Br}_2 \xrightarrow{k_3} \mathrm{CH}_3\mathrm{Br} + \mathrm{Br}\cdot & \text{propagation} \\
\mathrm{Br}\cdot + \cdot\mathrm{CH}_3 \xrightarrow{k_4} \mathrm{CH}_3\mathrm{Br} & \text{termination}
\end{array}$$

An occasional error was to reject termination reactions 2 and 3 because a mechanism with either reaction did not sum to the overall reaction. Both provide the correct sum, when the frequency of the reactions is considered. For example, assume initiation occurs once, termination occurs once, and propagation occurs about a million times.

$$1\times(\mathrm{Br}_2 + \mathrm{M} \xrightarrow{k_1} 2\mathrm{Br}\cdot + \mathrm{M})$$

$$1{,}000{,}001\times(\mathrm{Br}\cdot + \mathrm{CH}_4 \xrightarrow{k_2} \mathrm{HBr} + \cdot\mathrm{CH}_3)$$

$$1{,}000{,}000\times(\cdot\mathrm{CH}_3 + \mathrm{Br}_2 \xrightarrow{k_3} \mathrm{CH}_3\mathrm{Br} + \mathrm{Br}\cdot)$$

$$1\times(\mathrm{Br}\cdot + \cdot\mathrm{CH}_3 \xrightarrow{k_4} \mathrm{CH}_3\mathrm{Br})$$

$$\text{sum}:\ 1{,}000{,}001\,\mathrm{Br}_2 + 1{,}000{,}001\,\mathrm{CH}_4 \rightarrow 1{,}000{,}001\,\mathrm{CH}_3\mathrm{Br} + 1{,}000{,}001\,\mathrm{HBr}$$

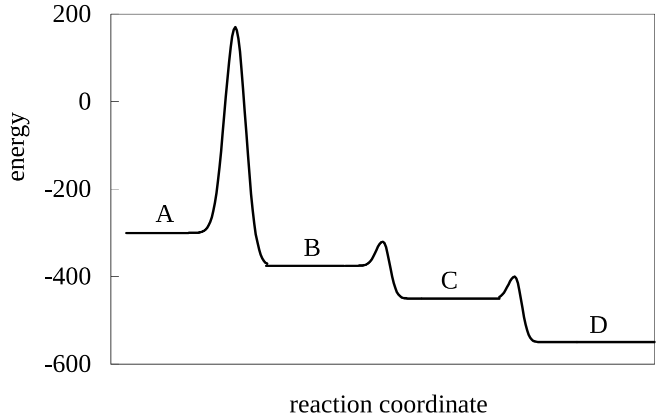
The sum with the third termination reaction is also consistent with the overall reaction, albeit with a trace of CH_3CH_3 (about 1 part per million). This is similar to the trace CH_4 produced in the Rice-Herzfeld mechanism for the dehydrogenation of ethane.

But recall that to check if a chain reaction agrees with an overall reaction, we consider the propagating reactions *only*. That is, we draw a propagation cycle and verify the cycle consumes the reactants, creates the products, and cycles the propagating radicals. The initiation and termination reactions are not considered when checking for agreement with the overall reaction.

Another occasional error was to reject the first and third termination reactions because they did not remove *both* propagating radicals. For a propagation cycle, it is not necessary to remove both propagating radicals. In this case, removing either $\mathrm{Br}\cdot$ or $\cdot\mathrm{CH}_3$ breaks the propagation cycle.

Some discarded the second and third termination reactions on the mistaken belief that a third body is needed for two radicals to combine to a form a molecule. A reaction between two *atoms* is nearly impossible; only a rare spontaneous photon emission during the atom-atom collision will allow a diatomic to form. But molecular fragments have additional vibrational modes to absorb the collision energy. Both the second and third reactions are viable.

(B) For a series reaction, such as $A \rightarrow B \rightarrow C \rightarrow D$, with a large activation barrier for the first reaction in the series, such as shown in the reaction-coordinate energy-level diagram below, the overall activation energy must be greater than or equal to the activation energy of the first reaction.



In this case, the overall rate equals the rate of the rate-limiting step, the rate of the first reaction. Rate = k_1[A] and the overall activation energy equals the activation energy of the first step in this approximation.

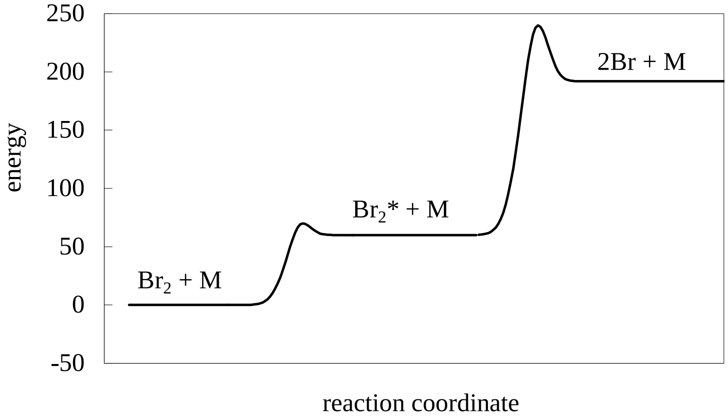
But $CH_4 + Br_2 \rightarrow CH_3Br + HBR$ is a chain reaction, not four reactions in series. Because this is a chain reaction, reactions 2 and 3 (propagation) occur many times for each occurrence of reaction 1. The apparent activation energy is given by the ratio of rate constants in eqn (10). Assume an Arrhenius form for each elementary rate constant.

$$k = \left(\frac{k_1 k_3 k_2}{k_4}\right)^{1/2} = \left(\frac{A_1 e^{-E_{a,1}/RT} A_2 e^{-E_{a,2}/RT} A_3 e^{-E_{a,3}/RT}}{A_4 e^{-E_{a,4}/RT}}\right)^{1/2}$$

$$= \left(\frac{A_1 A_3 A_2}{A_4}\right)^{1/2} \exp\left(-\frac{E_{a,1} + E_{a,2} + E_{a,3} - E_{a,4}}{2RT}\right)$$

The overall activation energy is ½($E_{a,1} + E_{a,2} + E_{a,3} - E_{a4}$). Reactions 2, 3, and 4 involve radicals, so the activation energies are likely to be small, around 10-40 kJ/mol. Assuming 20 kJ/mol for each, one obtains an apparent activation energy of 106 kJ/mol.

A plausible, but insufficient, explanation is that the initiation reaction is not elementary as written. Rather, the dissociation of Br_2 is a Lindemann mechanism, in which the Br_2 is first activated, and then the rate-limiting step is dissociation of activated Br_2, as shown in the reaction-coordinate energy-level diagram below.



With this mechanism, the apparent activation energy could be less than the dissociation energy of Br_2.

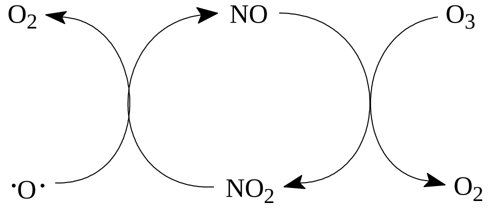
7.(A)

$O_3 + h\nu \rightarrow O^* + O_2$ initiation

$O^* + N_2O \xrightarrow{k_2} 2NO$ initiation

$\mathrm{NO} + \mathrm{O_3} \xrightarrow{k_3} \mathrm{NO_2} + \mathrm{O_2}$	propagation
$\mathrm{NO_2} + \cdot\mathrm{O}\cdot \xrightarrow{k_4} \mathrm{NO} + \mathrm{O_2}$	propagation
$\mathrm{O^*} + \mathrm{M} \xrightarrow{k_5} \cdot\mathrm{O}\cdot + \mathrm{M}$	This step is difficult to classify. This step is not initiation or propagation. It is not quite termination or inhibition because it does not eliminate a primary propagator. It is a step that terminates the initiation process by removing $\mathrm{O^*}$.
$\mathrm{NO_2} + \cdot\mathrm{OH} \xrightarrow{k_6} \mathrm{HNO_3}$	termination.

(B)



(C) We can assume $\mathrm{O_3}$ is consumed chiefly in the propagation step.

$$\frac{d[\mathrm{O_3}]}{dt} = k_3[\mathrm{NO}][\mathrm{O_3}] \qquad (1)$$

We need an expression for the intermediate NO. Assume steady-state concentration of the intermediates, which for chain reactions requires the rate of initiation equals the rate of termination. That is, the rate propagators are produced in an initiation step must equal the rate propagators are consumed in a termination step. Reaction 2 produces NO and reaction 6 consumes $\mathrm{NO_2}$.

$$-\left[\frac{d[\mathrm{NO}]}{dt}\right]_{\text{rxn 2}} = \left[\frac{d[\mathrm{NO_2}]}{dt}\right]_{\text{rxn 6}}$$

$$2k_2[\mathrm{O^*}][\mathrm{N_2O}] = k_6[\mathrm{NO_2}][\cdot\mathrm{OH}]$$

$$[\mathrm{NO_2}] = \frac{2k_2[\mathrm{O^*}][\mathrm{N_2O}]}{k_6[\cdot\mathrm{OH}]} \qquad (2)$$

We have an expression for $[\mathrm{NO_2}]$, but we seek an expression for [NO]. Note that at steady state, the rates of propagation are equal.

$$\text{rate of propagation rxn 3} = \text{rate of propagation rxn 4}$$

$$k_3[\mathrm{NO}][\mathrm{O_3}] = k_4[\mathrm{NO_2}][\cdot\mathrm{O}\cdot]$$

$$[\mathrm{NO}] = \frac{k_4[\mathrm{NO_2}][\cdot\mathrm{O}\cdot]}{k_3[\mathrm{O_3}]} \qquad (3)$$

Substitute eqn (2) into eqn (3).

$$[\mathrm{NO}] = \frac{k_4[\cdot\mathrm{O}\cdot]}{k_3[\mathrm{O_3}]}[\mathrm{NO_2}] = \frac{k_4[\cdot\mathrm{O}\cdot]}{k_3[\mathrm{O_3}]}\frac{2k_2[\mathrm{O^*}][\mathrm{N_2O}]}{k_6[\cdot\mathrm{OH}]}$$

$$[\mathrm{NO}] = \frac{2k_2k_4[\cdot\mathrm{O}\cdot][\mathrm{O^*}][\mathrm{N_2O}]}{k_3k_6[\mathrm{O_3}][\cdot\mathrm{OH}]} \qquad (4)$$

Eqn (4) is not quite ready to substitute into eqn (1). We need an expression for the intermediate [O*]. Apply the steady-state approximation to O*. This is equivalent to setting the rate of initiation equal to the sum of the two reactions that terminate the O*.

$$\frac{d[\mathrm{O}^*]}{dt} = 0 = I_{\mathrm{abs}}\phi - k_2[\mathrm{O}^*][\mathrm{N_2O}] - k_5[\mathrm{O}^*][\mathrm{M}]$$

$$[\mathrm{O}^*] = \frac{I_{\mathrm{abs}}\phi}{k_2[\mathrm{N_2O}] + k_5[\mathrm{M}]} \qquad (5)$$

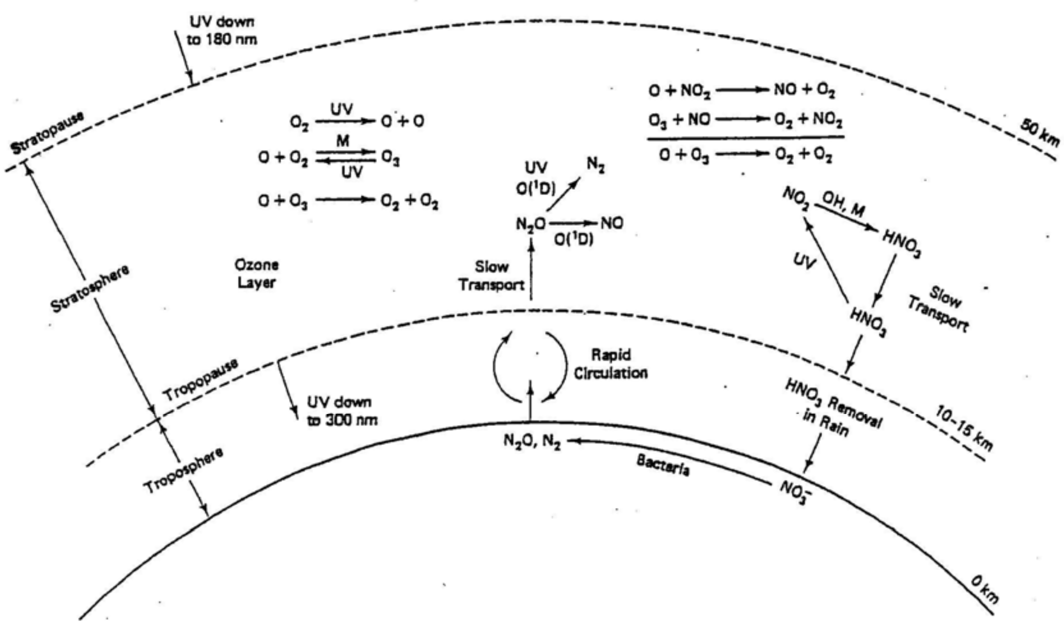
Substitute eqn (5) into eqn (4).

$$[\mathrm{NO}] = \frac{2k_2k_4[\cdot\mathrm{O}\cdot][\mathrm{N_2O}]}{k_3k_6[\mathrm{O_3}][\cdot\mathrm{OH}]}[\mathrm{O}^*] = \frac{2k_2k_4[\cdot\mathrm{O}\cdot][\mathrm{N_2O}]}{k_3k_6[\mathrm{O_3}][\cdot\mathrm{OH}]}\frac{I_{\mathrm{abs}}\phi}{(k_2[\mathrm{N_2O}] + k_5[\mathrm{M}])} \qquad (6)$$

Finally, substitute eqn (6) into eqn (1).

$$\frac{d[\mathrm{O_3}]}{dt} = k_3[\mathrm{NO}][\mathrm{O_3}] = k_3[\mathrm{O_3}]\frac{2k_2k_4[\cdot\mathrm{O}\cdot][\mathrm{N_2O}]I_{\mathrm{abs}}\phi}{k_3k_6[\mathrm{O_3}][\cdot\mathrm{OH}](k_2[\mathrm{N_2O}] + k_5[\mathrm{M}])}$$

$$\frac{d[\mathrm{O_3}]}{dt} = \frac{2k_2k_4[\cdot\mathrm{O}\cdot][\mathrm{N_2O}]I_{\mathrm{abs}}\phi}{k_6[\cdot\mathrm{OH}](k_2[\mathrm{N_2O}] + k_5[\mathrm{M}])}$$



The main features of the NO$_x$ atmospheric cycle, from *Chemical Kinetics and Dynamics*, J. I. Steinfeld, J. S. Francisco, and W. L. Hase (Prentice Hall, 1989), p. 500.

Team Competition Champion for Calculation Session 12:

Team “Join Mafia Club”

Anirudh Tenneti

Team Score: 24/26.

(next highest team score was 16/26)

Solution to the Team Competition

Circle the specifications necessary to obtain the rate equation.

rate equation	elementary reactions	rxn reversible?	if reversible, in equil?	steady-state approximation on intermed?
$N_2O_5 + NO \rightarrow 3NO_2$ $\frac{d[NO_2]}{dt} = k[N_2O_5]$	$N_2O_5 \rightarrow NO_2 + NO_3$ $NO + NO_3 \rightarrow 2NO_2$	**no** **no**		**yes**
$2NO + H_2 \rightarrow N_2O + H_2O$ $\frac{d[N_2O]}{dt} = k[NO]^2[H_2]$	$NO + H_2 \rightarrow NOH_2$ $NOH_2 + NO \rightarrow N_2O + H_2O$	**yes** **no**	**yes**	**no**
$NO_2 + CO \rightarrow NO + CO_2$ $\frac{d[CO_2]}{dt} = \frac{k_a[NO_2]^2[CO]}{k_b[NO] + k_c[CO]}$	$NO_2 + NO_2 \rightarrow NO_3 + NO$ $NO_3 + CO \rightarrow NO_2 + CO_2$	**yes** **no**	**no**	**yes**
$2NO + Cl_2 \rightarrow 2NOCl$ $\frac{d[NOCl]}{dt} = k[NO][Cl_2]^{1/2}$	$Cl_2 + M \rightarrow 2Cl\cdot + M$ $NO + Cl\cdot \rightarrow NOCl$	**yes** **no**	**yes**	**no**
$2H_2 + 2NO \rightarrow N_2 + 2H_2O$ $\frac{d[N_2]}{dt} = k[H_2][NO]^2$	$NO + NO \rightarrow N_2O_2$ $H_2 + N_2O_2 \rightarrow N_2O + H_2O$ $H_2 + N_2O \rightarrow N_2 + H_2O$	**yes** **no** **no**	**yes**	N_2O_2: **no** N_2O: **yes**