

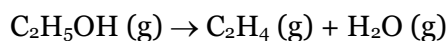
1. Experimental data for the one-step reaction $A \rightarrow B + C$ have been plotted in three different ways:

- (i) $\frac{1}{[A]}$ vs. time, which gives a straight line with a positive slope
- (ii) $[A]$ vs. time, which gives a curved line
- (iii) $\ln[A]$ vs. time, which gives a curved line

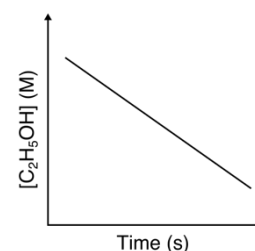
Based on this information, write the rate law for this reaction and determine the units of k .

$$\text{Rate} = k[A]^2 \quad \text{and} \quad \text{units of } k = M^{-1}s^{-1}$$

2. The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3) surface was studied at 400 K.



You plot the $[C_2H_5OH]$ vs. time and obtain a straight-line relationship (shown to the right) with a slope of $-4.00 \times 10^{-5} M/s$.



A) What is the half-life if the initial concentration of C_2H_5OH is $1.25 \times 10^{-2} M$?

From plot we know rate is zero-order with respect to $[C_2H_5OH]$:

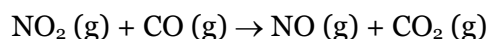
$$\text{Rate} = k \quad \text{and} \quad [C_2H_5OH]_t = -kt + [C_2H_5OH]_0$$

$$\begin{aligned} t_{1/2} &= \frac{[C_2H_5OH]_0}{2k} \\ &= \frac{1.25 \times 10^{-2} M}{2 \times (4.00 \times 10^{-5} \frac{M}{s})} \\ t_{1/2} &= 156 s \end{aligned}$$

B) Determine the time required for $1.25 \times 10^{-2} M$ C_2H_5OH to completely decompose?

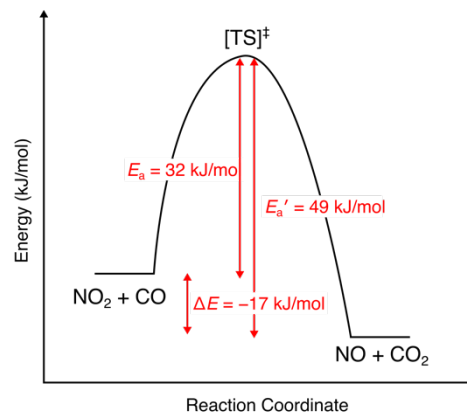
$$\begin{aligned} [C_2H_5OH]_t &= -kt + [C_2H_5OH]_0 \\ 0 M &= -\left(4.00 \times 10^{-5} \frac{M}{s}\right)t + 1.25 \times 10^{-2} M \\ t &= 312 s \end{aligned}$$

3. The activation energy for the following reaction is $E_a = 32$ kJ/mol and $\Delta E = -17$ kJ/mol.

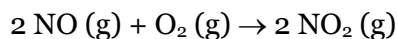


Assuming this is a single-step reaction, draw and label an energy diagram for this reaction and calculate the activation energy for the reverse reaction (E_a').

$$E_a' = E_a + |\Delta E| = 32 \frac{kJ}{mol} + 17 \frac{kJ}{mol} = 49 \frac{kJ}{mol}$$



4. Consider the following reaction again:



A) Determine the rate law for the reaction using the initial rates data collected at 298 K.

Experiment	$[\text{NO}]_0$ (M)	$[\text{O}_2]_0$ (M)	Initial Rate (M/s)
1	0.10	0.20	4.1×10^2
2	0.20	0.10	8.2×10^2
3	0.10	0.30	6.15×10^2

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k[\text{NO}]_3^a [\text{O}_2]_3^b}{k[\text{NO}]_1^a [\text{O}_2]_1^b}$$

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \left(\frac{[\text{O}_2]_3}{[\text{O}_2]_1} \right)^b$$

$$\frac{6.15 \times 10^2 \frac{\text{M}}{\text{s}}}{4.1 \times 10^2 \frac{\text{M}}{\text{s}}} = \left(\frac{0.30 \text{ M}}{0.20 \text{ M}} \right)^b$$

$$1.5 = 1.5^b$$

$$b = 1$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NO}]_2^a [\text{O}_2]_2^1}{k[\text{NO}]_1^a [\text{O}_2]_1^1}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[\text{NO}]_2}{[\text{NO}]_1} \right)^a \left(\frac{[\text{O}_2]_2}{[\text{O}_2]_1} \right)^1$$

$$2 \times \frac{8.2 \times 10^2 \frac{\text{M}}{\text{s}}}{4.1 \times 10^2 \frac{\text{M}}{\text{s}}} = \left(\frac{0.20 \text{ M}}{0.10 \text{ M}} \right)^a$$

$$4 = 2^a$$

$$a = 2$$

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$$

B) Which of the following are valid mechanisms for the reaction above?

Mechanism 1: *step 1*) $\text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{NO}_2 (\text{g}) + \text{O} (\text{g})$ (slow)
step 2) $\text{NO} (\text{g}) + \text{O} (\text{g}) \rightarrow \text{NO}_2 (\text{g})$ (fast)

Mechanism 2: *step 1*) $2 \text{NO} (\text{g}) \rightarrow \text{N}_2\text{O}_2 (\text{g})$ (fast)
step 2) $\text{N}_2\text{O}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$ (slow)

Ignore Mechanism 3. ~~Mechanism 3: *step 1*) $2 \text{NO} (\text{g}) \rightarrow \text{N}_2 (\text{g}) + \text{O}_2 (\text{g})$ (fast)
step 2) $\text{N}_2 (\text{g}) + 2 \text{O}_2 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$ (slow)~~

Mechanism 4: *step 1*) $\text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightleftharpoons \text{NO}_3 (\text{g})$ (fast)
step 2) $\text{NO}_3 (\text{g}) + \text{NO} (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$ (slow)

Mechanism 5: *step 1*) $2 \text{NO} (\text{g}) \rightarrow \text{N}_2\text{O}_2 (\text{g})$ (fast)
step 2) $\text{N}_2\text{O}_2 (\text{g}) \rightarrow \text{NO}_2 (\text{g}) + \text{N} (\text{g})$ (slow)
step 3) $\text{N} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow \text{NO}_2 (\text{g})$ (fast)

Before beginning, note that the overall experimentally-determined rate law is

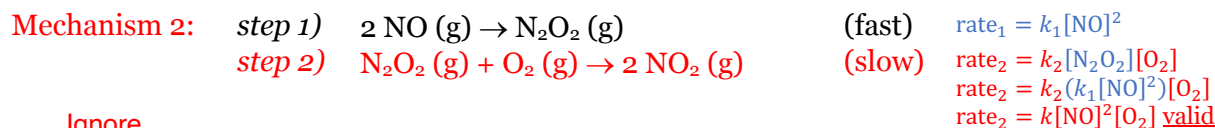
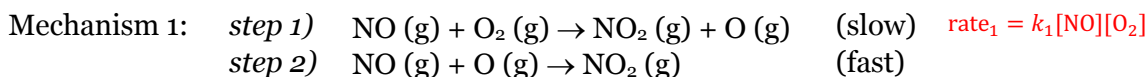
$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$$

It's critical that you understand the following regarding how we get this rate law:

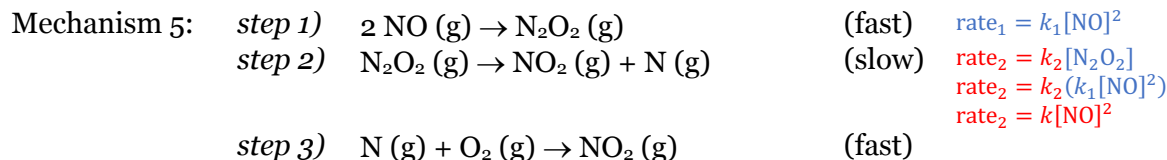
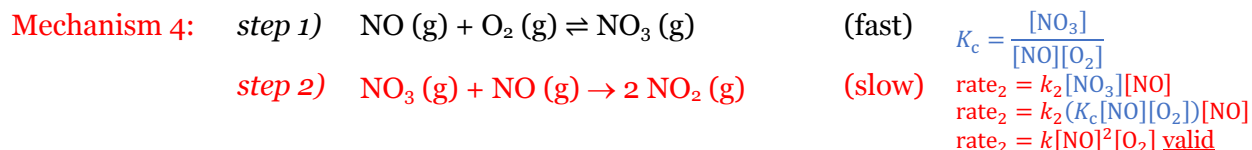
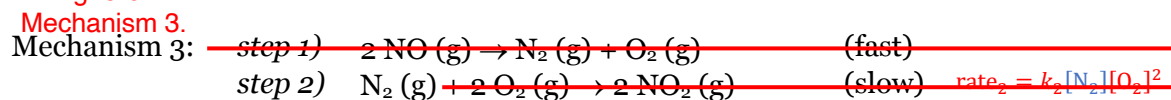
- The overall rate law is not based on the stoichiometry of the overall reaction.
- It's based on the elementary reactions comprising a reaction mechanism.
- The overall rate law is the rate of the slowest step in a reaction mechanism.
- Elementary steps are basically what happen at a molecular level step-by-step.
- Elementary rate laws can be written based off of the stoichiometry of the chemical step. (This is because elementary steps tell us about how individual molecules of reactants interact. So if you have an elementary step where $A + B \rightarrow C$, the elementary rate law must be $\text{rate} = k[A][B]$. This elementary rate law is first order with respect to A and B, indicating that a single molecule of A and single molecule of B *must* participate in this step so that elementary rate must depend on both reactants. This is different than the rate laws we wrote for the overall reaction because the overall chemical reaction relate to the overall reaction, not the individual steps.)

Strategy:

1. Write the elementary rate law for the slow elementary steps. **I will show these in red.**
2. If your elementary rate law of the slowest contains an intermediate, you must express the intermediate in terms of the reactants from the previous mechanistic step. **I will show these in blue.***
3. We only care about the slowest step in the mechanism. Does this elementary rate law match the overall rate law? If yes, this is a valid mechanism. If no, this is an invalid mechanism.

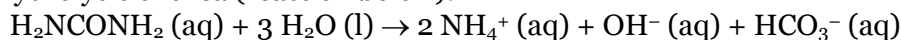


Ignore



* It is not critical that you know what the values of k_1 , k_2 , etc. are. But you should understand that they are all constants. Often, these rate constants are very complex expressions and found by solving a system of coupled differential equations.

5. Consider the hydrolysis of urea (reaction below):



A) You find the activation energy for the uncatalyzed reaction to be 138 kJ/mol. Calculate the rate constant (k_{uncat}) for the uncatalyzed reaction at 37.0 °C assuming $A = 8.66 \times 10^{12} \text{ s}^{-1}$.

$$\begin{aligned} k_{\text{uncat}} &= A e^{\frac{-E_a^{\text{uncat}}}{RT}} \\ &= (8.66 \times 10^{12} \text{ s}^{-1}) e^{\frac{-1.38 \times 10^5 \frac{\text{J}}{\text{mol}}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(310.15 \text{ K})}} \\ k_{\text{uncat}} &= 4.96 \times 10^{-11} \text{ s}^{-1} \end{aligned}$$

B) You find the activation energy for the catalyzed reaction to be 38.0 kJ/mol with the enzyme urease present. Calculate the rate constant (k_{cat}) for the catalyzed reaction at 37.0 °C assuming $A = 8.66 \times 10^{12} \text{ s}^{-1}$.

$$\begin{aligned} k_{\text{cat}} &= A e^{\frac{-E_a^{\text{cat}}}{RT}} \\ &= (8.66 \times 10^{12} \text{ s}^{-1}) e^{\frac{-3.80 \times 10^4 \frac{\text{J}}{\text{mol}}}{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(310.15 \text{ K})}} \\ k_{\text{cat}} &= 3.45 \times 10^6 \text{ s}^{-1} \end{aligned}$$

C) Calculate the temperature, theoretically, to which you would need to heat the uncatalyzed reaction to in order for the rate of the uncatalyzed reaction to be equal to the rate of the catalyzed reaction at 37.0 °C.

Assume the overall rate order, concentrations, and frequency factor (A) are constant between the catalyzed and uncatalyzed reactions.

If the overall rate law and concentrations do not change, then we can simplify:

$$\begin{aligned} \text{Rate}_{\text{uncat}} &= \text{Rate}_{\text{cat}} \\ k_{\text{uncat}}[\text{reactants}]^{\text{order}} &= k_{\text{cat}}[\text{reactants}]^{\text{order}} \\ k_{\text{uncat}} &= k_{\text{cat}} \end{aligned}$$

Substituting the Arrhenius equation into this equation, cancelling out A and R, taking the natural logarithm we can simplify further, and then solve for the temperature required:

$$\begin{aligned} k_{\text{uncat}} &= k_{\text{cat}} \\ A e^{\frac{-E_a^{\text{uncat}}}{RT_{\text{uncat}}}} &= A e^{\frac{-E_a^{\text{cat}}}{RT_{\text{cat}}}} \\ \frac{E_a^{\text{uncat}}}{T_{\text{uncat}}} &= \frac{E_a^{\text{cat}}}{T_{\text{cat}}} \\ \frac{1.38 \times 10^5 \frac{\text{J}}{\text{mol}}}{T_{\text{uncat}}} &= \frac{3.80 \times 10^4 \frac{\text{J}}{\text{mol}}}{310.15 \text{ K}} \\ T_{\text{uncat}} &= 1130 \text{ K} \end{aligned}$$