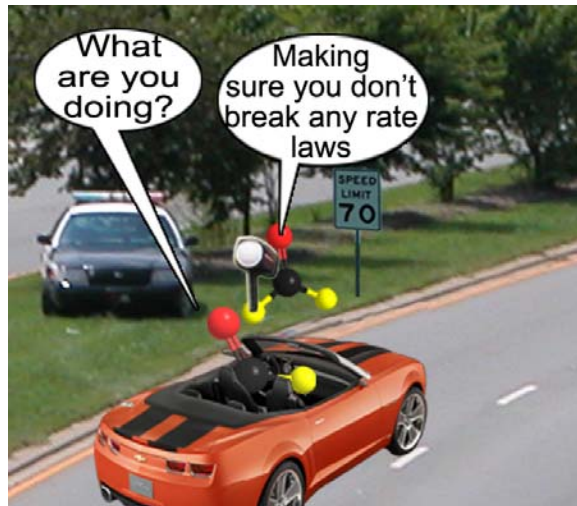


Rate Laws

Reaction rates are defined as the change in concentration of a reactant or product per unit of time. Keep in mind that chemical reactions are reversible. When reactants are first placed in the reaction vessel, initially the forward reaction is the dominant reaction. As the concentration of products increases, the reverse reaction becomes important ($\Delta_{\text{REACTANTS}} = \text{Rate}_{\text{FORWARD}} - \text{Rate}_{\text{REVERSE}}$). If conditions permit the reverse reaction to be neglected, the reaction rate depends on only the concentration of the reactants. The expression showing how the rate of the reaction depends on the concentration of the reactants is called a rate law. For the reaction $A + B \rightarrow C$, the concentration of A, [A], can be held constant while the concentration of B, [B] is changed, and the rate measured, and the concentration of B, [B], can be held constant while the concentration of A, [A] is changed, and the rate measured. This is how rate laws are determined. If doubling the concentration of A causes the reaction rate to double, while doubling the concentration of B causes it to quadruple, and doubling them both causes the reaction rate to increase eightfold, the rate law is $\text{Rate} = k[A][B]^2$. The general form of rate laws is: $\text{Rate} = k[A]^m[B]^n$. The value of m and n can only be determined experimentally. The form of the rate law depends on the reaction mechanisms. Experimental data verifying the rate law confirms the reaction mechanism.



Why molecules follow rate laws

Single Step Reactions

Concentrations of reactants are raised to their stoichiometric coefficients based on collision theory

- for $A + B \rightarrow 2C$, where one particle of A collides with one of B to form two particles of C
 - $R = k[A][B]$
- for $2C \rightarrow A + B$, where two particles of C collide to form one of A and one of B
 - $R = k[C]^2$

Multiple Step Reactions

For the reaction: $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$

- The mechanism is believed to consist of two steps
 - Step 1:** $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ slow
 - Step 2:** $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$ fast
 - Net:** $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$
- The rate law is determined from the rate determining step
 - $R = k[\text{NO}_2]^2$

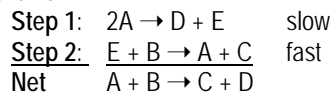
Sample Problems

For the single step reaction $A + B \rightarrow C$, what effect will tripling the concentration of both A and B have on the reaction rate?

- Write the rate law: $R = k[A][B]$
- Make a ratio of the rate laws based on the final and initial concentrations:

$$\frac{R_f}{R_i} = \frac{k[3][3]}{k[1][1]} = 9$$

For the multistep reaction $A + B \rightarrow C + D$ with the following mechanism:



What effect will doubling the concentration of A have

- Write the rate law: $R = [A]^2$
- Make a ratio of the rate laws based on the final and initial concentrations:

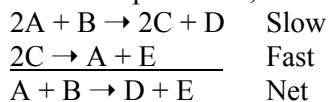
$$\frac{R_f}{R_i} = \frac{k[2]^2}{k[1]^2} = 4$$

Write the rate laws for each of the reactions below, and describe what the effect of manipulating the concentration of the reactants will be on the reaction rate.

1. A single step reaction occurs as follows: $2A + 3B \rightarrow 2C + D$

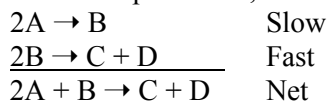
- What is the rate law?
- What is the effect of doubling both the concentrations of A and B on the reaction rate?

2. A multistep reaction, $A + B \rightarrow D + E$, occurs as follows:



- What is the rate law?
- What is the effect of doubling both the concentrations A and B on the reaction rate?

3. A multistep reaction, $2A + B \rightarrow C + D$, occurs as follows:



- What is the rate law?
- What is the effect of doubling the concentration A and tripling the concentration of B on the reaction rate?

4. A single step reaction occurs as follows: $A \rightarrow 2C + D$

- What is the rate law?
- What is the effect of tripling the concentration of A on the reaction rate?