Reaction Mechanisms

- A reaction mechanism is step or series of steps that make up a reaction.
- The steps in a reaction mechanism are referred to as **elementary steps**.
- **Molecularity** refers to the number of reactant molecules involved in an elementary step.
  Unimolecular:
  Bimolecular:
  Termolecular:
- Lower molecular steps tend to be faster than ones with more molecules.
- The rate determining step is the slowest step in the reaction mechanism and will have the largest activation energy.

Using Reaction Mechanisms to Determine the Rate Law Equation

- The rate law expression can be determined from the reaction mechanism.
- The rate determining step is the elementary step that determines the rate law expression.
- The rate of a reaction is proportional to the concentrations of the reactants in the rate determining step raised to their molar coefficients.
- If any reaction intermediates appear in this expression, you must use the other steps to eliminate these species.

Example 1

The reaction, $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$ occurs by the mechanism below. Use that mechanism to determine the rate law expression.

$A + B \rightleftharpoons [AB]$ (fast)
$[AB] + B \rightarrow C + D$ (slow)

Example 2

The reaction between NO and H_2 is believed to occur in the following three-step process. Write the overall equation for this reaction and the rate law expression.

$2\ NO \rightleftharpoons N_2O_2$ (fast)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

Worksheet

1. The reaction between nitrogen dioxide and carbon monoxide occurs in the 2 step process below.

   Step 1 $2\ NO_2 \rightarrow NO_3 + NO$ (slow) bimolecular

   Step 2 $NO_3 + CO \rightarrow NO_2 + CO_2$ (fast) bimolecular

   a) State the molecularity of each step.

   b) Write the equation for the overall reaction and identify and reaction intermediates.

   $NO_2 + CO \rightarrow NO + CO_2$ Intermediates: NO_3 and 1 mole of NO_2

   c) Write the rate law expression.

   Use Step 1 as it is the rate determining step

   $r= k[NO_2]^2$

2. The reaction between hydrogen bromide and oxygen gas, occurs in the 4 step process below.

Step 1:	$HBr + O_2 \rightarrow HOOBr$	Slow	bimolecular
Step 2:	$HOOBr + HBr \rightarrow 2\ HOBr$	Fast	bimolecular
Step 3:	$HOBr + HBr \rightarrow H_2O + Br_2$	Fast	bimolecular
Step 4:	$HOBr + HBr \rightarrow H_2O + Br_2$	Fast	bimolecular

   a) State the molecularity of each step.

   b) Write the equation for the overall reaction and identify and reaction intermediates.

   $4\ HBr + O_2 \rightarrow 2\ H_2O + 2\ Br_2$ Intermediates: HOOBr, HOBr

   c) Write the rate law expression.

   Use Step 1 as it is the rate determining step

   $R=k[HBr][O_2]$

3. Given the following mechanism:

   step 1 $2\ NO \rightleftharpoons N_2O_2$ (fast) bimolecular

   step 2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow) bimolecular

   step 3 $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast) bimolecular

   a) State the molecularity of each step.

   b) Write the equation for the overall reaction and identify and reaction intermediates.

   $2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O$ Intermediates: N_2O_2, N_2O

   c) Write the rate law expression.

   Use Step 2 as it is the Rate determining step

   $r=k[N_2O_2][H_2]$

   ** N_2O_2 is a reaction intermediate so it must be replaced using step 1

   $[N_2O_2]$ can be replaced by $[NO]^2$ since step 1 is a reversible reaction

   $r=k[NO]^2[H_2]$

4. The kinetics of the reaction: $2\ X + Y \rightarrow Z$ was studied and the results are:

Trial	[X]	[Y]	Rate (mol/Ls)
1	0.20	0.10	7.00×10^{-4}
2	0.20	0.20	1.40×10^{-3}
3	0.40	0.20	1.40×10^{-3}

a) Use the data above to determine the rate law equation, including the value of k with correct units.

For X, compare 2 and 3 [X] x 2 rate x 1 therefore zero order in X
For Y, compare 1 and 2 [Y] x2 rate x2 therefore first order in Y
r=k[Y]
to find k sub in trial 1
$7.00 \times 10^{-4} = k(0.10)$
$k = 7.00 \times 10^{-3}$
$r = 7.00 \times 10^{-3}[Y]$

Below are 3 proposed mechanisms for this reaction.

b) What is the overall reaction for each mechanism?
c) What is the molecularity of each step?
d) What is the rate law derived from each mechanism?
e) Which mechanism is consistent with the rate law from part a?

Mechanism I
$X + Y \rightarrow M$ (slow) bimolecular
$X + M \rightarrow Z$ (fast) bimolecular
Overall: $2\ X + Y \rightarrow Z$
r=k[X][Y]

Mechanism II
$Y \rightarrow M$ (slow) unimolecular
$X + M \rightarrow Z$ (fast) bimolecular
Overall: $X + Y \rightarrow Z$
r=k[Y]

Mechanism III
$Y \rightarrow M$ (slow) unimolecular
$M + X \rightarrow N$ (fast) bimolecular
$N + X \rightarrow Z$ (fast) bimolecular
Overall: $2\ X + Y \rightarrow Z$
r=k[Y]

Mechanism III is consistent with the rate law from part a