AP Chemistry	Name ________________________________

Ms. Ye	Date ______________________ Block ______

Balanced Chemical Equation vs. Reaction Mechanism

- A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those present at the end of the reaction. It provides no information, however, about the detailed steps that occur at the molecular level as the reactants are turned into products.
- A **reaction mechanism** ____.
  At the most sophisticated level, a reaction mechanism describes the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction.
- Remember: Rate laws can only be determined **experimentally**, NOT from coefficients in the reaction. If you know the reaction mechanism, you can determine the rate law.

Elementary Reactions

- Reactions may occur all at once or through several steps known as elementary reactions.
- An **elementary reaction** is a chemical reaction in which one or more __________________

  __________________________________ to form products in______________________
- **Molecularity**-the ____ in an elementary reaction.
  - **Unimolecular**
    - involves ________________________________
    - Overall ____________________reaction $H_3C{-}N{\equiv}C{:} \longrightarrow H_3C{-}C{\equiv}N{:}$
  - **Bimolecular**
    - involves the collision of _______________________
    - Overall ____________________ reaction $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$
  - **Termolecular**
    - involves the simultaneous collision of _____________________________; this is rare.
    - Overall ________________________ reaction.

TABLE 14.3 • Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Multistep Mechanisms

The net change represented by a balanced chemical equation often occurs by a multistep mechanism consisting of a sequence of elementary reactions.

The following reaction proceeds in two elementary reactions/steps:

Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$

Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$

The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.

Overall Reaction: ____

Because NO_3 is neither a reactant nor a product of the overall chemical reaction—it is formed in one elementary reaction and consumed in the next—it is called an ____________________

Practice:

1. It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$

   (a) Describe the molecularity of each elementary reaction in this mechanism.

   (b) Write the equation for the overall reaction.

   (c) Identify the intermediate(s)

2. For the reaction: $Mo(CO)_6 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3 + CO$

   the proposed mechanism is

$$Mo(CO)_6 \longrightarrow Mo(CO)_5 + CO$$
$$Mo(CO)_5 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3$$

   (a) Is the proposed mechanism consistent with the equation for the overall reaction?

   (b) What is the molecularity of each step of the mechanism?

   (c) Identify the intermediate(s).

Determining the Rate Law for Multi-Step Mechanisms

- In a multistep process, each elementary step of the mechanism has its own rate constant and activation energy.
- One of the steps will be slower than all others. The overall reaction cannot occur faster than this ______________________, known as the __________________________________
- The ______________ for a reaction is based on the ___________________________________

Reactions with a Slow Initial Step (these are the easier ones)

Ex: Consider the two-step mechanism:

$$\begin{array}{lllll} \text{Step 1:} & NO_2(g) + NO_2(g) & \xrightarrow{k_1} & NO_3(g) + NO(g) & \text{(slow)} \\ \text{Step 2:} & NO_3(g) + CO(g) & \xrightarrow{k_2} & NO_2(g) + CO_2(g) & \text{(fast)} \\ \hline \text{Overall:} & NO_2(g) + CO(g) & \longrightarrow & NO(g) + CO_2(g) & \end{array}$$

The rate-determining step is _________________. This step is a ____________________________ process, so the order of this reaction is ______________________. The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction and can therefore be written as __________________________________.

Experiments can be done to confirm that [CO] does not in fact affect the reaction rate (and therefore is not included in the rate law).

Practice:

1. The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$N_2O(g) \longrightarrow N_2(g) + O(g) \qquad \text{(slow)}$$

$$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) \qquad \text{(fast)}$$

   (a) Write the equation for the overall reaction.

   (b) Write the rate law for the overall reaction

2. Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

$$O_3(g) + 2\,NO_2(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction is believed to occur in two steps:

$$O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$$

$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

The experimental rate law is rate = $k[O_3][NO_2]$. What can you say about the relative rates of the two steps of the mechanism (which one is the rate determining step)?

Reactions with a Fast Initial Step (these are the trickier ones)

It is less straightforward to derive the rate law for a mechanism in which an intermediate is a reactant in the rate-determining step. This situation arises in multistep mechanisms when the first step is fast and therefore not the rate-determining step.

Ex: $2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$

Step 1: $NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2(g)$ (fast)

Step 2: $NOBr_2(g) + NO(g) \xrightarrow{k_2} 2\,NOBr(g)$ (slow)

Because ________________ is the rate-determining step, the rate law for that step governs the rate of the overall reaction and would be written as ______________________________.
However, $NOBr_2$ is an _____________________________ and not part of the overall reaction. Therefore, we need to substitute for $NoBr_2$ in the rate law equations.

You can assume step 1 is in equilibrium; the forward and reverse reactions of step 1 are occurring faster than step 2.

Set these rates equal to each other: $\underbrace{k_1[NO][Br_2]}_{\text{Rate of forward reaction}} = \underbrace{k_{-1}[NOBr_2]}_{\text{Rate of reverse reaction}}$

Rearrange to solve for $NoBr_2$: $[NOBr_2] = \frac{k_1}{k_{-1}}[NO][Br_2]$

Substitute this into the rate law that involved the intermediate:

$$\text{Rate} = k_2\frac{k_1}{k_{-1}}[NO][Br_2][NO] = k[NO]^2[Br_2]$$

Practice:

Show that the following mechanism for $2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$ also produces a rate law consistent with the experimentally observed one

Step 1: $NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ (fast, equilibrium)

Step 2: $N_2O_2(g) + Br_2(g) \xrightarrow{k_2} 2\,NOBr(g)$ (slow)

Reaction Mechanisms Problem Set

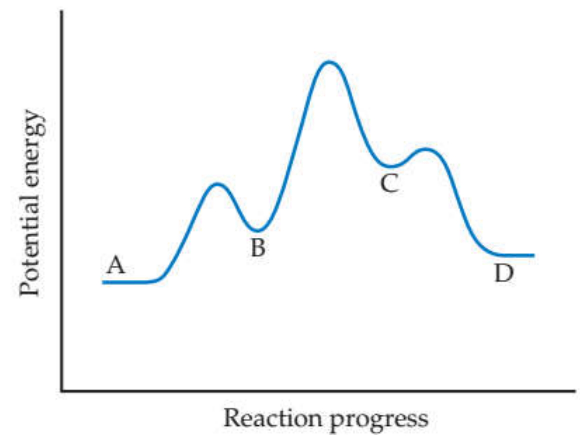
1. What is the molecularity of each of the following elementary reactions? Write the rate law for each.
   a. $Cl_2(g) \longrightarrow 2\,Cl(g)$

   b. $OCl^-(aq) + H_2O(l) \longrightarrow HOCl(aq) + OH^-(aq)$

   c. $2\,NO(g) \longrightarrow N_2O_2(g)$

2. Based on the following reaction profile,
   a. How many intermediates are formed in the reaction?

   b. How many steps are in this reaction mechanism? Which step is the rate determining step?



3. Consider the following mechanism.

$$\mathbf{A_2 + B_2 \rightarrow R + C} \qquad \textit{(slow)}$$
$$\mathbf{A_2 + R \rightarrow C} \qquad \textit{(fast)}$$

   a. Write the overall balanced chemical equation.

   b. Identify any intermediates within the mechanism.

   c. Write the rate law for the overall reaction.

4. The following mechanism has been proposed for the gas phase reaction of H_2 with ICl:

$$H_2(g) + ICl(g) \longrightarrow HI(g) + HCl(g)$$
$$HI(g) + ICl(g) \longrightarrow I_2(g) + HCl(g)$$

   a. Write the balanced equation for the overall reaction.

   b. Identify any intermediates in the mechanism.

   c. If the first step is slow and the second one is fast, which rate law do you expect to be observed for the overall reaction?

5. The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + IO^-(aq) \quad \text{(slow)}$$

$$IO^-(aq) + H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g) + I^-(aq) \quad \text{(fast)}$$

   a. Write the chemical equation for the overall process.

   b. Identify the intermediate, if any, in the mechanism.

   c. Assuming that the first step of the mechanism is rate determining, predict the rate law for the overall process.

6. Consider the exothermic reaction between reactants A and B:

   A + B → E *(fast)*

   E + B → C + D *(slow)*

Determine the rate law for the reaction.

7. The following mechanism has been proposed for the reaction of NO with H_2 to form N_2O and H_2O:

$$NO(g) + NO(g) \longrightarrow N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

   a. Show that the elementary reactions of the proposed mechanism add to provide a balanced equation for the reaction.

   b. Write a rate law for each elementary reaction in the mechanism.

   c. Identify any intermediates in the mechanism.

   d. The observed rate law is Rate = $k[NO]^2[H_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second reactions?