NOTES #46 Kinetics IV/Reaction Mechanisms

1. Consider the following balanced reaction: $2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$

- Sure, the balanced reaction tells what the reactants are and what the products are but does NOT tell us HOW the reaction actually takes place.

- Most reactions take place in a number of simple reactions called ELEMENTARY STEPS. Put these elementary steps together and you have a reaction mechanism.

Reaction Mechanism for: $2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$

(1) $2NO\ (g) \rightarrow N_2O_2\ (g)$

(2) $N_2O_2\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

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Overall Reaction:

- The elementary steps MUST add up to equal the overall balanced equation.

- N_2O_2 (g) is an __________________________. It appears in the mechanism of the reaction but NOT in the overall balanced reaction.

- From the elementary steps, you can determine the MOLECULARITY of a reaction. Molecularity is the number of molecules reacting in an elementary step:

a. UNIMOLECULAR REACTION - elementary step in which only one reacting molecular participates. Ex:

b. BIMOLECULAR REACTION – elementary step that involves TWO molecules. The two molecules can be the same or different. Bimolecular reactions are the most common. Ex:

c. TERMOLECULAR REACTION - reactions that involve the participation of three molecules in one elementary steps. How likely do you suppose termolecular reactions are??? Why?

2. Mechanisms and Rate Laws:

a. The order for each reactant in an elementary step is EXACTLY equal to the stoichiometric coefficients and each elementary step has it's own rate of reaction and k value. EX:

$A \rightarrow$ products rate =

$A + B \rightarrow$ products rate =

$A + A \rightarrow$ products rate =

** Why can't you do the same for the overall balanced equation?

b. When we study a reaction that has more than one elementary step, the ___________________________step or the rate-determining step determines the order of the over all reaction. It's this rate law that must be proven experimentally....

EX 1: *This is what MOST examples will be like*...Consider the following equation: $2\ NO_2 + F_2 \rightarrow 2\ NO_2F$

Experimentally, the rate law for this reaction is rate = $k[NO_2][F_2]$. A suggested mechanism for this reaction is as follows:

$NO_2 + F_2 \rightarrow NO_2F + F$ *slow step*

$F + NO_2 \rightarrow NO_2F$ *fast*

Is this an acceptable mechanism? Does it meet the following conditions?

1. Do the elementary steps add up to equal the overall balanced reaction?
2. Does the rate law of the rate-determining step match the experimentally determined rate law?

EX2: The reaction between NO_2 and CO to product NO and CO_2 is believed to occur via two steps:

step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$ The experimental rate law is rate = $k[NO_2]^2$.

step 2: $NO_3 + CO \rightarrow NO_2 + CO_2$

(a) Write the equation for the overall reaction.

(b) Identify the intermediate.

(c) What can you say about the relative rates of step 1 and step 2???

EX3: *What if TWO of the elementary steps are playing a role in determining the overall rate of a reaction?*

Consider the following reaction: $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$

The experimental rate law is rate = $k\ [Cl_2]^{1/2}\ [CHCl_3]$

Proposed mechanism is: $Cl_2 \Leftrightarrow 2\ Cl$ *both directions are fast with equal rates*

$Cl + CHCl_3 \rightarrow HCl + CCl_3$ *slow*

$CCl_3 + Cl \rightarrow CCl_4$ *fast*

B. Return to CATALYSTS: 1. Purpose of a catalyst? 2. How do catalysts work? There are a couple different kinds.

a. HETEROGENEOUS CATALYSIS - the reactants and the catalyst are in ___________________________.

It is very common that a solid surface is the catalyst and the reactants are gases.

b. HOMOGENEOUS CATALYSTS – the reactants and the catalyst are in _____________________________.

EX: Makin' Ammonia. $N_2\ (g) + H_2\ (g)$ ------> $2\ NH_3\ (g)$. Even though this reaction is an exothermic reaction, it is EXTREMELY slow at room temp. Why would this be???

- So, heat it up, you may say. Well, when you do that, you start decomposing the NH_3 back to it's elements which sort of defeats the purpose. So, what to do?

- Use a catalyst If you do this reaction in the presence of a platinum catalyst at high temperatures, the reaction proceeds much faster (Why? ____). This process is called the HABER PROCESS.