## Collision Theory and Mechanisms

Consider the reaction:

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

According to the collision theory, for this reaction to occur in one step, 3 particles must collide: two NO molecules and one $O_2$. It is fairly unlikely for 3 particles to combine at the right spot and with the correct energy. Think of it has playing pool and completing a combo shot.

Reactions tend to take place in steps to increase it's rate.
Each step involving a collision between **two particles** is called **bimolecular**.
The chance of a two particle collision being successful is much greater than a collision between three or more particles.

Unimolecular: $2H_2O \rightarrow O_2 + 2H_2$
Bimolecular: $O_2 + 2H_2 \rightarrow 2H_2O$
Tertiary: $A + B + C \rightarrow ABC$

Reactions which take place in one elementary step are called, appropriately, **simple reactions** or **elementary reactions** while reactions which take place in more than one step are called **complex reactions**.

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The complex reaction:

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

does not take place in one elementary step, but actually takes place in two steps:

| | |
|---|---|
| Step 1 | $2\ NO \rightarrow N_2O_2$ |
| Step 2 | $N_2O_2 + O_2 \rightarrow 2\ NO_2$ |

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Compounds such as $N_2O_2$, products of one reaction that immediately become reactants in another reaction, are called **reaction intermediates**. All complex reactions contain at least one reaction intermediate. Reaction intermediates should not be confused with the activated complex. The activated complex is a temporary particle formed during a **single** step, while the reaction intermediate is a product of a step or reaction in a mechanism.

### Net Reactions

The steps in which a reaction occurs is called that reaction's mechanism. The sum of the steps of a mechanism must equal the total or **net equation**.

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For the reaction, $NO_2 + CO \rightarrow NO + CO_2$ , the mechanism is as follows:

| | |
|---|---|
| Step 1 | $NO_2 + \cancel{NO_2} \rightarrow \cancel{NO_3} + NO$ |
| Step 2 | $\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$ |
| Net reaction: | $NO_2 + CO \rightarrow NO + CO_2$ |

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The Net reaction is the final overall reaction after the steps have been completed. Any identical intermediates that are found on both sides of the equation can be cancelled.

The $NO_3$ is the reaction intermediate, so it does not appear in the net reaction. Since $NO_2$ is found twice on the left and once on the right, we can cancel one of the $NO_2$'s just as we would adding equations in math.

**Example 2**

The decomposition of ozone using chlorine as a catalyst is illustrated in this mechanism:

| | |
|---|---|
| Step One | $Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)}$ |
| Step Two | $O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$ |
| Step Three | $ClO_{(g)} + O_{(g)} \rightarrow Cl + O_{2(g)}$ |
| Overall | $2\ O_{3(g)} \rightarrow 3\ O_{2(g)}$ |

In the above example, the Cl(g) is a catalyst and the ClO is an intermediate. ***The catalyst can be identified in the mechanism by appearing as a reactant, THEN as a product in a following step. Whereas an intermediate appears as the product THEN a reactant.*** **Treat** step one and two independent from each other because step two does not involve the Cl.

## Rate Determining Step

Not all steps in a mechanism have the same rate. The step with the slowest rate is called the **rate determining step** (**RDS**), since that step affects the rate of the reaction more than the others. Reactants in this step affect the rate more.

*Analogy*

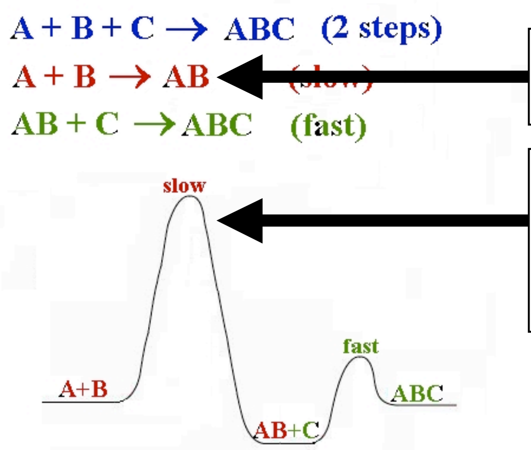
Think of a car production line. The first person puts the tires on the car, the second person installs the light bulbs, the third person installs the delicate and intricate computer system, the fourth person installs the windshield wipers and the last person drives it away. It does not matter how fast person 1, 2, 4 and 5 does their work because the rate of driving the car out of the lot still depends on person #3 in how fast he can install the delicate computer system. Persons 1 and 2 can install their products fast but it does not mean the overall rate of production will be fast. But if person 3 installs the computer systems at a faster rate, then the entire rate can be increased.

According to our last mechanism:

| | | |
|---|---|---|
| Step 1 | $NO_2 + NO_2 \rightarrow NO_3 + NO$ | (slow) |
| Step 2 | $NO_3 + CO \rightarrow NO_2 + CO_2$ | (fast) |

step 1 is the RDS because it is the slowest step.

# Rate Determining Step




AB is the catalyst cause it reappears

Rate determining Step! Cause it is the slowest one. Highest activation energy

**Example 2**

Since the RDS affects the rate of the entire reaction the most, changes to the **reactants** in the other steps will have very little effect on the rate of the reaction.

**Example 1.** Given the following mechanism:

| | | | |
|---|---|---|---|
| P + Q | → | X + T | (slow) |
| X + P | → | Y + R | (fast) |
| Y + S | → | T | (moderate) |

a) What is the net reaction?

b) What are the reaction intermediates?

c) Which is the rate determining step?

d) What would be the effect of increasing the concentration of P?

e) What would be the effect of decreasing the concentration of Q?

f) What would be the effect of increasing the concentration of S?

**Solution:**

a) by adding the three steps, eliminating the compounds common to both sides:

$$P + Q \rightarrow X + T \quad \text{(slow)}$$
$$X + P \rightarrow Y + R \quad \text{(fast)}$$
$$Y + S \rightarrow T \quad \text{(moderate)}$$
$$2P + Q + S \rightarrow R + 2T$$

b) The reaction intermediates are X and Y, since they are products in one step and become reactants in the next. They also do not appear in the net equation

c) P + Q X + T(the slowest step)

d) If the concentration of P were increased, the rate of the reaction would increase, since P is present in the RDS.

e) If the concentration of Q were decreased, the rate of the reaction would decrease, since Q is present in the RDS.

f) If the concentration of S were increased, there would be NO change in the rate of the reaction, since S is NOT present in the RDS.

By the end of these notes… you are able to do all but the rate law questions in the exercise booklet.