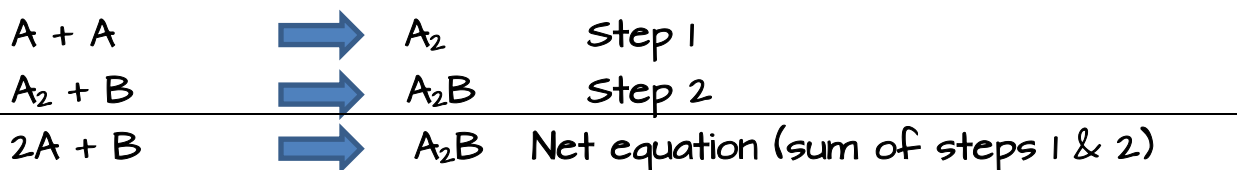Chemistry Lecture #86: Reaction Mechanism and Rate Law

Most reactions occur in a series of steps or collisions. A balanced equation may show something like 3 atoms or molecules as reactants and a single substance as a product, but it is unlikely that all 3 reactant particles collided simultaneously and produced a single product. For example, suppose we have reactants A and B producing product A_2B
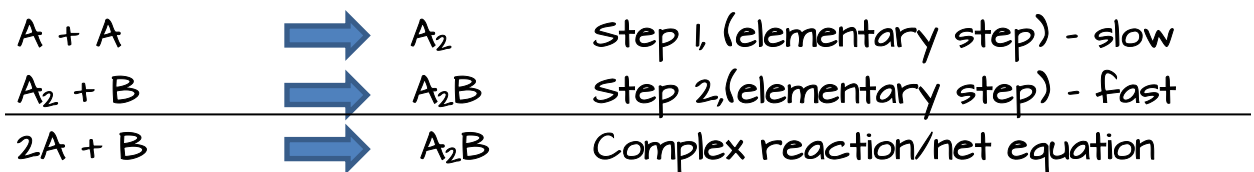
$2A + B \longrightarrow A_2B$

We have a total of three reactant particles on the left (2 + 1 = 3). It is highly unlikely that 2A's and a B all smacked into each other at exactly the same time to produce A_2B

Instead, it is more likely that collisions occurred between two particles to make a new particle. This new particle would then collide with the other reactants and form another new particle. These steps would continue until the final product is reached.

What are the steps that produce the final products? We don't know - we have to make an educated guess. Here's a proposed series of steps that might lead to the production of A_2B from 2A's and a B.

$A + A$	$\longrightarrow$	A_2	Step 1
$A_2 + B$	$\longrightarrow$	A_2B	Step 2
$2A + B$	$\longrightarrow$	A_2B	Net equation (sum of steps 1 & 2)

Notice that if you add steps 1 & 2, you get the net reaction.

A + A	→	A$_2$	Step 1, (elementary step) - slow
A$_2$ + B	→	A$_2$B	Step 2, (elementary step) - fast
2A + B	→	A$_2$B	Complex reaction/net equation

Steps 1 and 2 are called elementary steps. A complex reaction is made of two or more elementary steps.

The complete sequence of elementary steps that make up a complex reaction is called the reaction mechanism.

In the above reaction mechanism, A$_2$, is called an intermediate. An intermediate is a substance that is produced during one step of a complex reaction, and is then consumed in a subsequent step. In the above example, A$_2$ is produced in step 1, but is then consumed or reacted with B in the second step to produce A$_2$B. Intermediates do not appear in the net chemical equation.
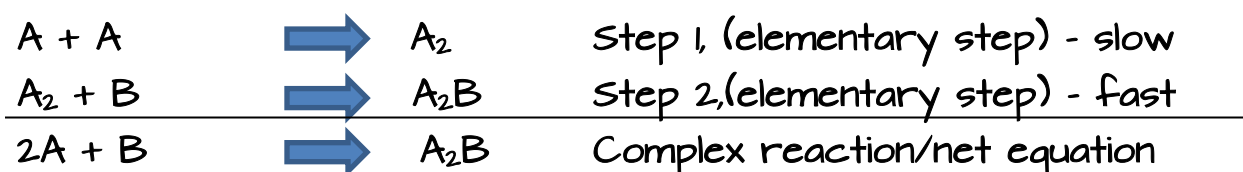
In a reaction mechanism, one step will be slower than all of the others. This is called the rate determining step. The speed of the reaction is completely dependent on this step - the other steps have no influence on the reaction rate. In the above reaction, we're guessing that the first step is the slowest and is therefore the rate determining step.

How do we know if the above reaction mechanism is correct? How do we know if the first step is the slow step? We'll never really know for sure, but we can compare it to data from actual experiments to find evidence that our guesses might be correct.

Specifically, we derive a rate law from the reaction mechanism and compare it to the rate law that was found by experiment. If the rate laws match, the reaction mechanism might actually exist.

The rate law is derived from the reaction mechanism by multiplying the concentration of the reactants in the rate determining step. Let's go back to our previous example and derive a rate law.

A + A	⟹	A_2	Step 1, (elementary step) - slow
A_2 + B	⟹	A_2B	Step 2,(elementary step) - fast
2A + B	⟹	A_2B	Complex reaction/net equation

Step 1 is the rate determining step. The reactants are A and A. So, the derived rate law would be

Rate = k[A][A] or
Rate = $k[A]^2$

Suppose that we perform an experiment and find that doubling the concentration of A quadruples the rate $(4 = 2^2)$ and doubling the concentration of B has no effect $(1 = 2^0)$. The experimental rate law would be
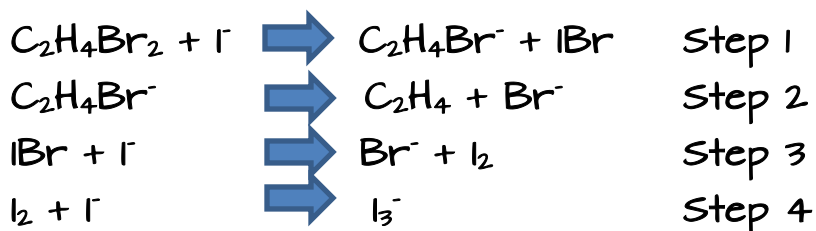
Rate = $k[A]^2[B]^0$ or
Rate = $K[A]^2$

The experimental rate law matches the rate law derived from the reaction's slowest step, so there is evidence that our proposed reaction mechanism might be correct.

For the reaction

$$C_2H_4Br_2 + 3I^- \implies C_2H_4 + 2Br^- + I_3^-$$

The experiment rate law is rate = $k[C_2H_4Br_2][I^-]$. From the reaction mechanism below, identify the rate determining step, and derive the rate law from the mechanism.

$C_2H_4Br_2 + I^-$ $\implies$ $C_2H_4Br^- + IBr$	Step 1
$C_2H_4Br^-$ $\implies$ $C_2H_4 + Br^-$	Step 2
$IBr + I^-$ $\implies$ $Br^- + I_2$	Step 3
$I_2 + I^-$ $\implies$ I_3^-	Step 4

Answer

The reactants in the rate law are in the rate determining step. The experimental rate law has $C_2H_4Br_2$ and I^-, which are found in step 1. Thus, step 1 is the rate determining step.

The rate law derived from the reaction mechanism is found by multiplying the concentration of the reactants from step 1. Thus, the derived rate law is
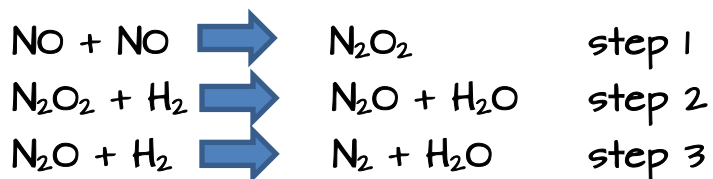
Rate = $k[C_2H_4Br_2][I^-]$

which is the same as the experimental rate law. The reaction mechanism is possible.

Rate laws only contain the starting reactants. But how do we derive a rate law if an intermediate is in the rate determining step? If the intermediate is made from a starting reactant, we can substitute the concentration of the starting reactant for the intermediate.

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

The experimental rate law for the above reaction is rate = $k[NO]^2[H_2]$. The proposed reaction mechanism is

$NO + NO \longrightarrow$	N_2O_2	step 1
$N_2O_2 + H_2 \longrightarrow$	$N_2O + H_2O$	step 2
$N_2O + H_2 \longrightarrow$	$N_2 + H_2O$	step 3

In step 1, NO is converted to N_2O_2 very quickly. It is also known that N_2O_2 rapidly converts back to NO at the same rate that NO is converted to N_2O_2.

$$N_2O_2 \longrightarrow NO + NO$$

Derive the rate law from the reaction mechanism.

Answer
The experimental rate law contains H_2, which is found in steps 2 and 3 but not step 1. Let's make a guess that step 2 is the slow, rate determining step. The derived rate law for the reaction would then be

Rate = $k_2[N_2O_2][H_2]$ derived from step 2

But N_2O_2 is an intermediate, so we can't use it in the rate law. But we can find a way to substitute NO in place of N_2O_2.

NO + NO $\Longrightarrow$ N_2O_2 (step 1), and N_2O_2 $\Longrightarrow$ NO + NO

We first write the rate law for step 1 as

Rate = k_1[NO][NO] or rate = k_1[NO]^2

The rate at which N_2O_2 is converted back to NO is expressed as

Rate = k_3[N_2O_2].

The rate at which N_2O_2 is made is equal to the rate at which is decomposes back to NO, so we can write

k_1[NO]^2 = k_3[N_2O_2]

We rearrange this equation to solve for [N_2O_2] and get

[N_2O_2] = $\dfrac{k_1[NO]^2}{k_3}$. We can substitute this in place of N_2O_2 in our derived rate law.

Rate = k_2[N_2O_2][H_2]   derived from step 2

Rate = $\dfrac{k_2 k_1 [NO]^2 [H_2]}{k_3}$ k_1, k_2 and k_3 are just numbers, so we substitute k for all 3 of them and get

rate = k[NO]^2[H_2] which matches the experimental rate law. The reaction mechanism is plausible.