Chemical Kinetics

The rusting of iron and the explosion of TNT are both chemical reactions. However, the speed at which they occur is very different.

Chemical Kinetics is the area of chemistry that deals with the speeds, or rates, at which reactions occur.

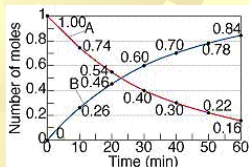Rates are affected by many factors, including concentration, temperature, catalysts and surface area.

Reaction rate and time

As can be seen from a graph of concentration versus time for a reaction, the rate of the reaction varies depending on the concentration of the reactants.

Reaction Rate

The speed of a chemical reaction is called its reaction rate.

The reaction rate is a measure of how quickly the reactants are consumed or how quickly the products are produced.

For the general equation A --> B, the average rate can be written:

$$\text{Average rate} = \frac{\Delta(\text{moles of B})}{\Delta t} = -\frac{\Delta(\text{moles of A})}{\Delta t}$$

Reaction Rates & Concentrations

Reaction rates are usually written in terms of the concentration of reactants and products of the reaction.

For the reaction 2 HI (g) --> H_2 (g) + I_2 (g), the reaction rates would be:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Reaction rate and time

Because the speed or rate of a reaction depends so heavily on how much reactant is present to react, the concentration dependence is figured into an expression called a rate law.

Every equation has it's own rate law. For the reaction H_2 (g) + I_2 (g) --> 2 HI (g), the rate law expression is

Rate = $k[H_2] [I_2]$

The constant k is called the rate constant. Every equation has its own k value determined through experimental results

Rate Laws & Initial Rates

● The rate law cannot be determined by just looking at the reaction. It is necessary to determine the rate law and rate constant for a reaction from actual data.

Experiment Number	Initial [A] (M)	Initial [B] (M)	Initial [C] (M)	Initial Rate (M/s)
1	0.100	0.100	0.100	1.6×10^{-2}
2	0.200	0.100	0.100	3.2×10^{-2}
3	0.200	0.300	0.100	2.9×10^{-1}
4	0.100	0.100	0.300	1.6×10^{-2}
5	0.100	0.400	0.100	2.6×10^{-1}

Reaction Orders

Reaction orders are classifications for how changing the concentration affects the rate:

Zero order - changing concentration does not effect rate.

First order - doubling concentration doubles the rate

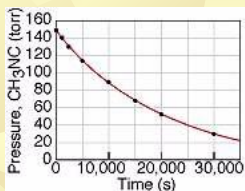Second order - doubling concentration increases the rate by a factor of 4 (2^2)

Concentration & Time

As we have seen earlier, as time increases, the concentration of the reactant goes down.

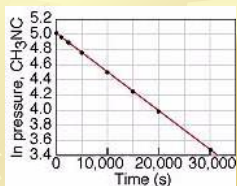For first order reactions, the graph of this type of reaction looks similar to this:

Concentration & Time

Calculus can convert the curve to a straight line:

The reaction now has a slope and y-intercept:

$\ln[A]_t = -kt + \ln[A]_o$

(for first order rxns)

Concentration & Time

For second order reactions, the rate depends on the square of the reactant concentration or both reactants if there is two dependent reactants.

As a result, calculus proves that the rate law produces a straight line and the slope-intercept form of this line is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

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Half-life of a reaction

The time required for the concentration to drop to one half of its initial value.

For first order:

$$t_{1/2} = \frac{0.693}{k}$$

For second order:

$$t_{1/2} = \frac{1}{k[A]_0}$$

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Temperature & Rate

The rates of most chemical reactions increase as the temperature rises.

The faster rate is due to an increase in the rate constant at higher temperatures.

Three factors are theorized to have an affect on the rate constant:

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Collision Model

Molecules must collide to react. When more molecules collide per second, the greater the reaction rate.

As the concentration of reactant increases, collisions increase which increases the rate.

As temperature increases, the reactants move faster, which means more collisions and a higher rate.
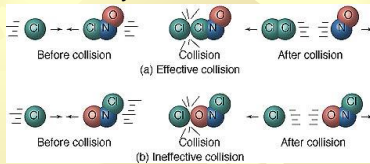
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Orientation

Another factor that can affect the rate is the orientation of the collision. If reactants do not collide just right, a reaction may not occur.

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Activation Energy

Some reactions will not occur without some energy being added to the chemicals. The theory is the reactants do not collide hard enough to break bonds.

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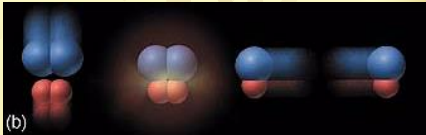
Activation Energy

Upon adding some energy to the reactant, the molecules can then move faster and collide with sufficient energy to break bonds and recombine. The amount of energy added is called the activation energy.
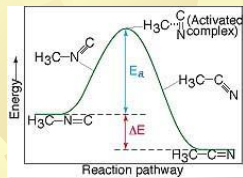

Activation energy

Graphically, we can visualize the activation energy with a plot of energy versus time. From a graph like this we can also determine the net change in energy of the reaction.

Arrhenius formula transformed

Activation energy is not always a value that can be easily determined, so the Arrhenius formula can be rearranged:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln [A]$$

In this form, the E_a/R is the slope of the line formed by the graph of ln k vs. 1/T

Another way of writing this equation is:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Elementary Steps

Most chemical reactions occur in single steps. The number of molecules that participate in an elementary step defines the molecularity of the step.

If a single molecule is involved, the step is said to be unimolecular.

If a reaction occurs due to the collision of 2 molecules, it is bimolecular

If a reaction occurs due to the collision of 3 molecules simultaneously, it is termolecular.

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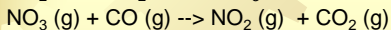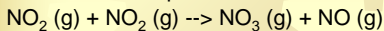
Multistep Mechanisms

Many times a chemical change occurs due to a sequence of elementary steps. The addition of the steps must give the chemical equation for the overall process.

NO_2 (g) + NO_2 (g) --> NO_3 (g) + NO (g)

NO_3 (g) + CO (g) --> NO_2 (g) + CO_2 (g)

For this multistep process, the NO_3 (g) is an intermediate and the overall reaction is:

NO_2 (g) + CO (g) --> NO (g) + CO_2 (g)

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Slow and Fast Elementary Steps

When one step of a multistep mechanism is slower than the other(s), the slowest step is said to be the rate determining factor.

If the slow step is the first step, then we assume the rate law is based off of the first reaction.

If the slow step is not the first step, and involves an intermediate, we must use the first step to rearrange and remove the intermediate from the rate law.

Remember, predictions and true rate laws may be different!

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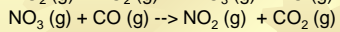
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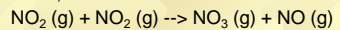
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Catalysts

Catalysts are substances that change the speed of a reaction without undergoing a permanent change in the reaction.

Catalysts usually lower the overall activation energy for a chemical reaction.

Some catalysts adsorb the reactants and align the reactants so that they can react.

Catalysts are sometimes reacted in the first step of a mechanism, then remade later in the mechanism:

$$NO_2 (g) + NO_2 (g) \rightarrow NO_3 (g) + NO (g)$$
$$NO_3 (g) + CO (g) \rightarrow NO_2 (g) + CO_2 (g)$$