

Chemical Kinetics

- Chemical Kinetics → the study of the rates of chemical reactions, how fast reactions occur.
- The rate of a reaction is defined as the amount of product made in a unit of time or the amount of reactant used in a unit of time.
- The rate is usually measured in M/second or M/minute.
- The **explanation** of what the molecules are doing to cause the reaction rate is often referred to as collision **theory**.

Collision Theory

In order for a reaction to occur there must be an effective collision between the molecules.

An effective collision for molecules is similar to an effective collision in a paintball game. In order to “score a hit” the paintball must be moving fast enough to break and it has to hit the opponent in a vital spot (in many paintball games a hit to the heel of a shoe or on the opponent’s gun don’t count).

Collision Theory

In similar fashion, molecules must hit each other in the correct spot (orientation) with enough speed (kinetic energy) to cause them to react.

Once there is enough energy and the correct orientation for the molecules to react the rate of the reaction will depend on factors that increase the number of these effective collisions per unit time.

Reaction Rate Factors

Concentration → The greater the concentration the more likely it is that the molecules will hit each other.

Even in reactions where a collision is not required increasing the concentration means that there are more molecules that can react resulting in a greater reaction rate.

Reaction Rate Factors

Pressure → Increasing the pressure of **gases** increases the concentration.

The gases are pushed closer together with higher pressure.

This works only on **gases**.

Solids and liquids are not affected to any significant amount by pressure.

Reaction Rate Factors

Temperature → Increasing the temperature increases the speed of the molecules.

This increases the energy of the collision and the probability that they will collide.

A general “rule of thumb” is that for every 10°C increase in temperature the reaction rate will double.

Reaction Rate Factors

Surface Area → Increasing the surface area increases the probability that the molecules will run into each other, increasing the reaction rate.

This is like having a more targets to hit.

What has more surface area - a block of wood or sawdust?

Making the particles smaller increases the reaction rate.

Reaction Rate Factors

Nature of the reactants → Some things react faster because of their makeup.

For example: Potassium reacts faster than lithium because it has a lower ionization energy - its electron is easier to remove so it requires less energy to react.

Reaction Rate Factors

Catalysts → Catalysts are substances that increase the rate of a reaction without changing themselves.

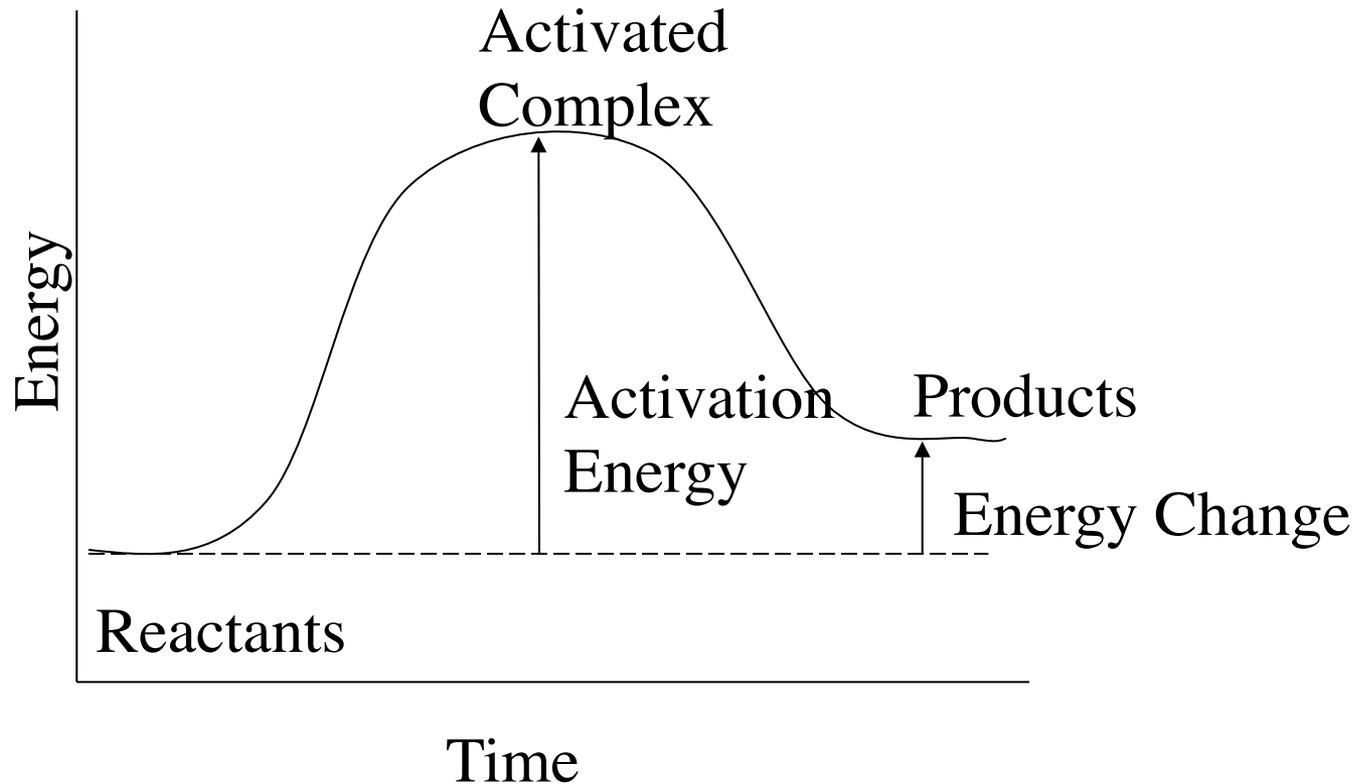
Catalysts often increase the rate of the reaction by physically bringing molecules together into a position that allows them to react.

Enzymes are biological catalysts.

Catalysts often work like the social “match maker” putting people into positions or situations where they can “get together”.

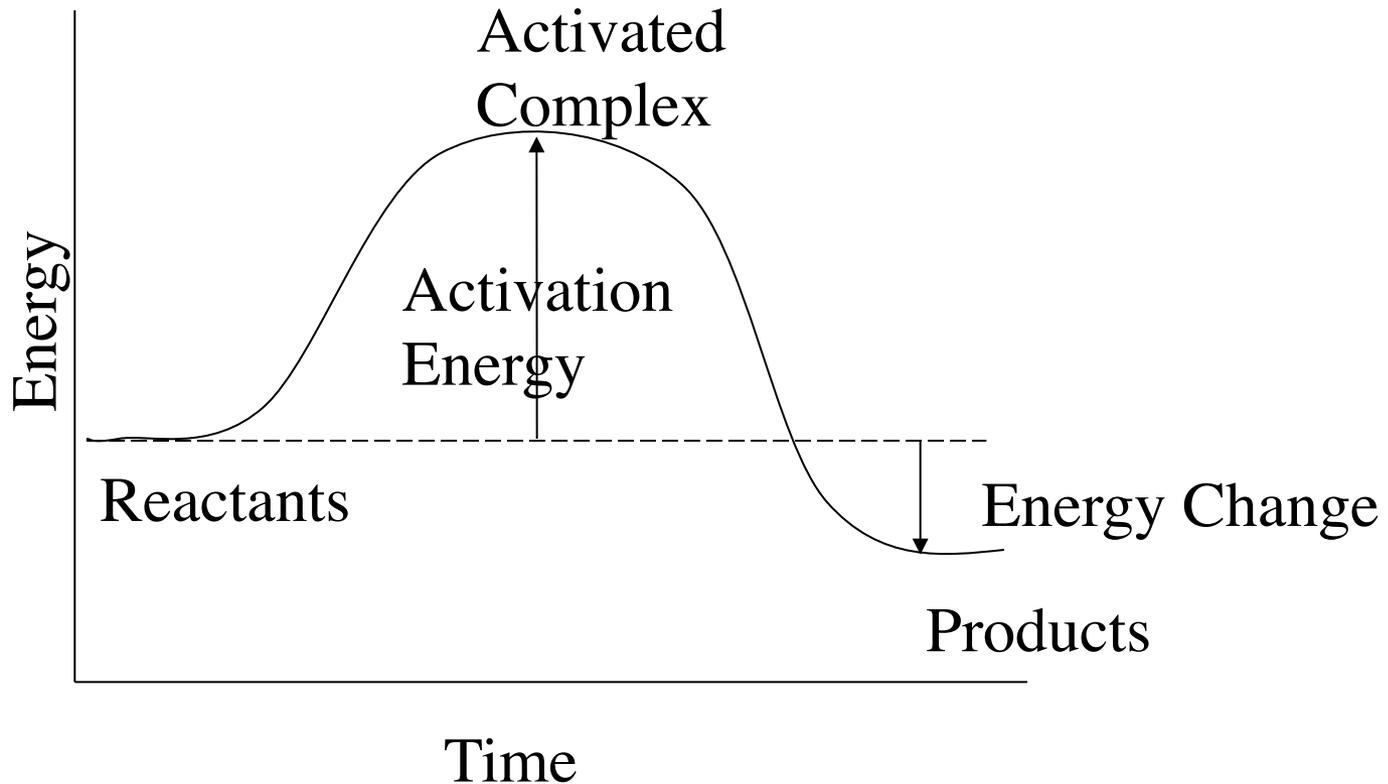
Energy Diagram

Endothermic reaction → Energy is added, the products have more energy than the reactants.



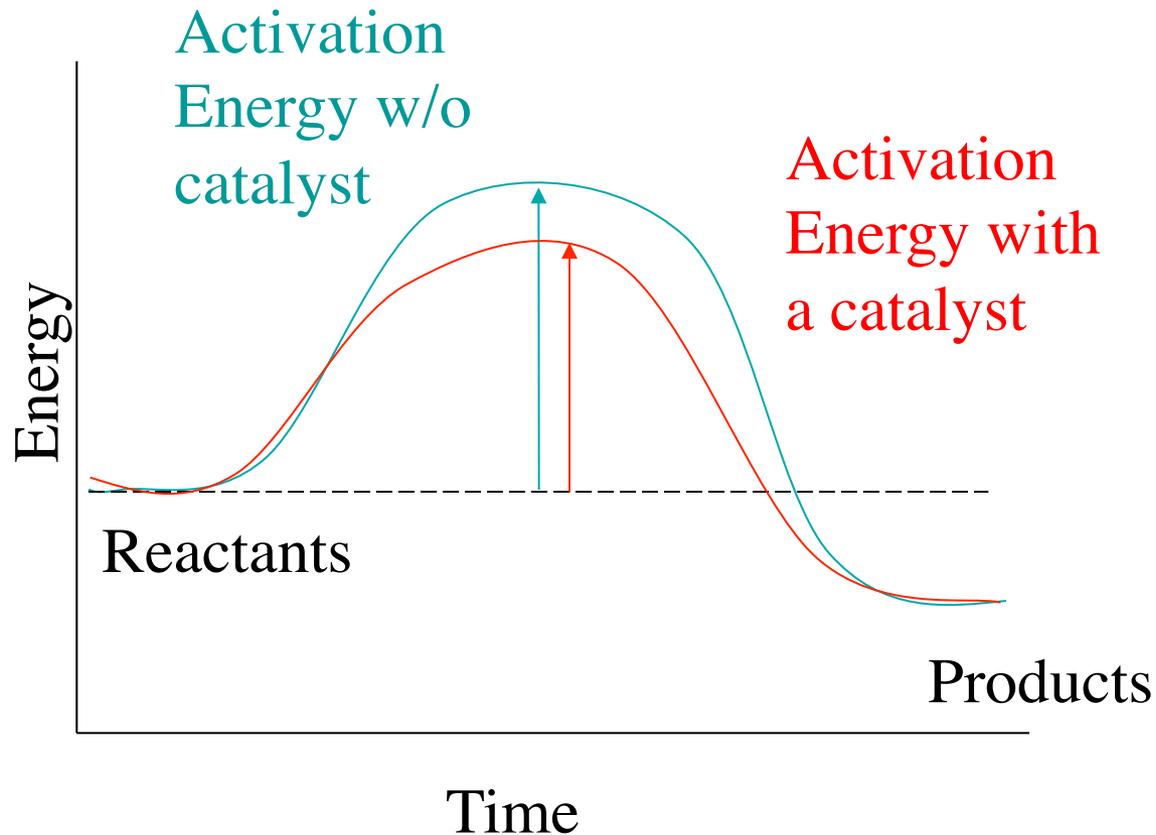
Energy Diagram

Exothermic reaction → Energy is released, the reactants have more energy than the products.



Energy Diagram

Catalysts change the reaction pathway to decrease the required activation energy



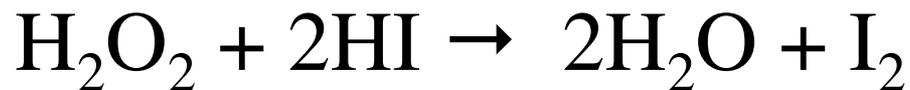
Measuring Reaction Rates

The rate of the reaction is calculated by determining the change (Δ) in concentration ($[]$) of one compound and dividing it by the time (Δt) required for the change and its coefficient in the balanced equation.

The concentration is measured in Molarity (moles/liter) and is indicated by the square brackets $[]$.

Consider the reaction between hydrogen peroxide and hydrogen iodide.

Measuring Reaction Rates



Data collected for this reaction is:

Time	[H₂O₂]	[H₂O]	Rate [H₂O₂]	Rate [H₂O]
0 seconds	0.10 M	0.00 M		
10 seconds	0.03 M	0.14 M	0.007 M/s	0.007 M/s

The change in concentration of H₂O₂ is -0.07 M

$$\Delta [\text{H}_2\text{O}_2] = 0.03 \text{ M} - 0.10 \text{ M} = -0.07 \text{ M H}_2\text{O}_2$$

Measuring Reaction Rates

The change in time (Δt) is 10 seconds (10 s - 0 s)

The rate of the reaction is $0.07 \text{ M H}_2\text{O}_2 / 10 \text{ s}$ or
 0.0070 M/s

Notice that the negative sign of the concentration change is dropped out (the absolute value is used) so that reaction rates are always positive.

Using water [H_2O] to calculate the rate should give us the same value

Measuring Reaction Rates

The change in time (Δt) is 10 seconds (10 s - 0 s)

The change in concentration ($\Delta[\text{H}_2\text{O}]$) of the water is 0.14 M (0.14 M - 0 M).

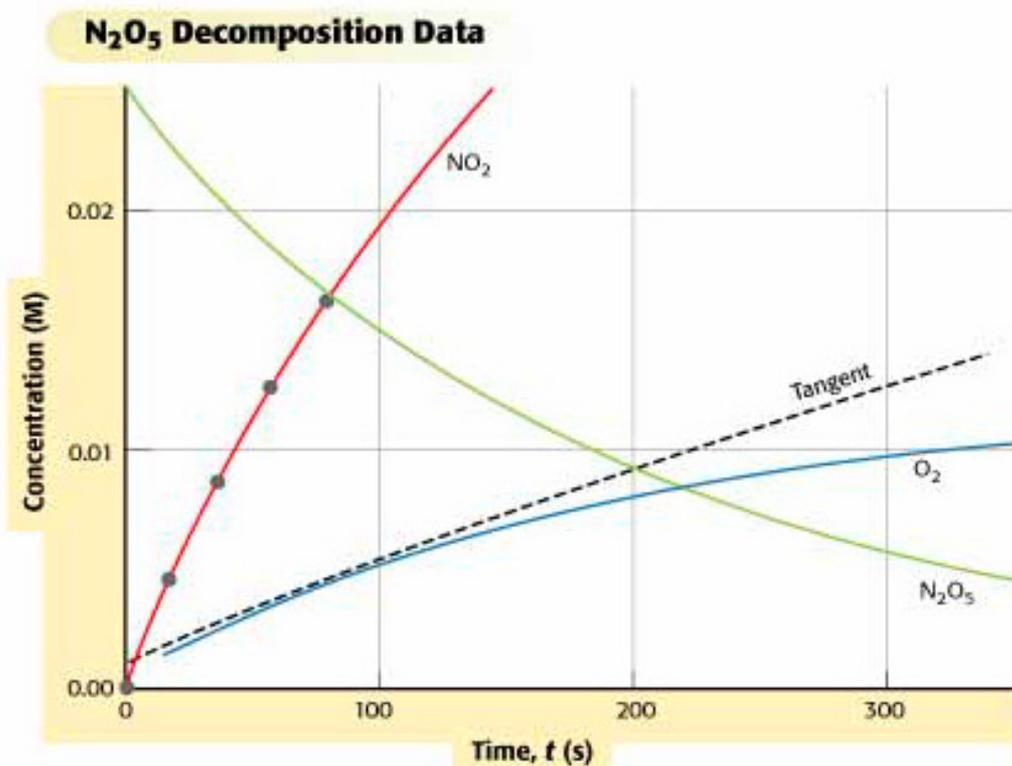
The rate of the reaction is $0.14 \text{ M H}_2\text{O} / (10 \text{ s} \times 2)$
or

$$0.0070 \text{ M/s}$$

Both sets of data give the same result for the reaction rate.

Measuring Rate Laws

Because the rate of the reaction depends on the concentration of the reactants and the concentration of the reactants decreases as the reaction proceeds the rate of the reaction will slow as time goes on.



Rate Laws

A rate law is a math equation that relates the rate of a reaction to the concentration of the reactants.

Consider the reaction $A + B \rightarrow C$

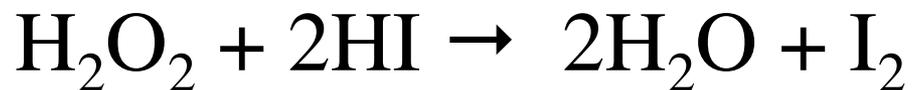
The general form of the rate law is

$$\text{Rate} = k [A]^x [B]^y$$

To determine the specific form of the rate law we must determine values for k , x and y .

Determining Rate Laws

Below we have data for the initial reaction rate for



The general form of the rate law is

$$\text{Rate} = k[\text{H}_2\text{O}_2]^x[\text{HI}]^y$$

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

Our job is to determine values for x , y and k .

To do this we have to control variables.

This means that we need to hold all the variables constant (keep them the same) except for one and see the effect of changing that one.

We then need to test each other variable in the same manner.

Determining Rate Laws

If we compare the data below we see that in trials 1 & 2 the **hydrogen peroxide concentration remained the same** - this is our control.

For the **same trials** the hydrogen iodide concentration doubled **and** the rate doubled.

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

This is a first order or linear relationship:

$2\text{Rate} = [2\text{HI}]^y$ When HI is doubled (and everything else - just hydrogen peroxide in this example - is kept constant) the rate is doubled.

This means that y must be equal to 1 ($2=2^y$ $y=1$)

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

For the next step we **need to keep the hydrogen iodide concentration constant**. This means that **for this experiment** we need to compare trials 1 & 3.

Between trials 1 & 3 the hydrogen peroxide concentration doubles and the rate doubles.

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

This means that the reaction is also first order in hydrogen peroxide

$$2\text{Rate} = [2\text{H}_2\text{O}_2]^x \quad 2=2^x$$

$$X=1$$

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

We now have values for x and y for the rate law:

$$\text{Rate} = k[\text{H}_2\text{O}_2]^1 [\text{HI}]^1$$

To complete the specific form of the rate law we need to determine a value for k.

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

First solve the rate equation for k

$$k = \text{Rate} / ([\text{H}_2\text{O}_2]^1 [\text{HI}]^1)$$

Then substitute in values from any of the three trials. If we have done the problem correctly the value of k will be the same for each trial.

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

$$k = \frac{0.0076 \text{ M/s}}{[0.10 \text{ M}]^1 [0.10 \text{ M}]^1}$$

$$k = 0.76 \text{ M}^{-1}\text{s}^{-1}$$

Trial	[H₂O₂]	[HI]	Rate
1	0.10 M	0.10 M	0.0076 M/s
2	0.10 M	0.20 M	0.0152 M/s
3	0.20 M	0.10 M	0.0152 M/s

Determining Rate Laws

We now have the **specific form of the rate law** for this equation.

$$\text{Rate} = 0.76 \text{ M}^{-1}\text{s}^{-1}[\text{H}_2\text{O}_2]^1 [\text{HI}]^1$$

The reaction is **first order** in hydrogen peroxide, **first order** in hydrogen iodide and **second order** overall.

The **order of the reaction** is the exponents in the specific rate law.