

PHARMACEUTICAL CHEMISTRY

Chemical Kinetics

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Keywords

Order of Reaction, Kinetics, Catalysis

Introduction

Chemical kinetics is the study and discussion of chemical reactions with respect to *reaction rates, effect of various variables, re-arrangement of atoms, formation of intermediates etc.* There are many topics to be discussed, and each of these topics is a tool for the study of chemical reactions. The study of motion is called **kinetics**, from Greek *kinesis*, meaning movement.

At the macroscopic level, the amounts reacted, formed, and the rates of their formation is taken into account. At the molecular or microscopic level, the following considerations must also be made in the discussion of **chemical reaction mechanism**.

- Molecules or atoms of reactants must collide with each other in chemical reactions.
- The molecules must have sufficient energy (discussed in terms of activation energy) to initiate the reaction.
- In some cases, the orientation of the molecules during the collision must also be considered.

In general, reaction kinetics is the study of rate of chemical change and the way in which this rate is influenced by conditions of concentration of reactants, products and other chemical species which may be present, and the factors such as solvent, pressure and temperature. Reaction kinetics permits formulation of models for the intermediate steps through which reactants are converted into other chemical compounds and is a powerful tool in elucidating the mechanism by which chemical reactions proceed.

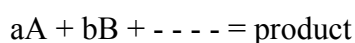
It provides a rational approach to stabilization of drug products and prediction of shelf- life and optimum storage conditions. e.g. thiamine HCl is most stable at pH 2-3 and is unstable at pH above 6. If this is combined with a buffered vehicle of say pH 8 or 9 the vitamin is rapidly inactivated. Knowing the rate at which a drug deteriorates at various hydrogen ion concentrations allows one to choose a vehicle that will retard or prevent the degradation.

Reaction Rate

The rate of reaction is the velocity with which a reactant or reactants undergo chemical change. The rate, velocity or speed of a reaction is given by the expression dc / dt where dc is increase or decrease of concentration over an infinitesimal time interval dt .

Chemical reaction takes place through collision between molecules of reactants. A chemical reaction involves breaking of bonds in reacting species and formation of new bonds in products. Since number and the nature of bonds vary in different substances therefore the rate of reaction varies. Ionic reactions are almost instantaneous e.g precipitation of AgCl takes 10^{-4} sec because no bonds are to be broken and formed.

According to the law of mass action, the rate of a chemical reaction is proportional to the product of the molar concentration of the reactant each raised to a power usually equal to the number of molecules undergoing reaction.



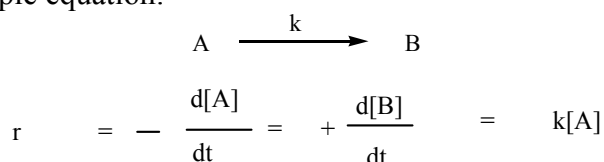
$$\begin{aligned}\text{Rate of reaction (r)} &= -\frac{1}{a} \frac{d[A]}{dt} \\ &= -\frac{1}{b} \frac{d[B]}{dt} = k[A]^a [B]^b\end{aligned}$$

k is proportionality constant known as rate constant or velocity constant. Sum of the exponents of the concentration terms involved in the rate equation is known as order of reaction.

$$r = k[A]^a [B]^b$$

Order of reaction = a + b

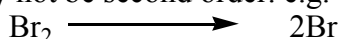
Rate of equation can be written in number of ways depending on whether we are interested in the rate of disappearance of the reactant species or in rate of appearance of the product species. Thus for a simple equation:



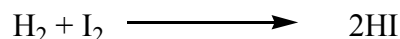
Molecularity

Molecularity is number of molecules involved in the step leading to the chemical reaction. A reaction whose overall order is measured may be considered to occur through several steps or elementary reactions. Each of elementary reaction has a stoichiometry giving the number of molecules taking part in that step. Since the order of an elementary reaction gives the number of molecules coming together to react in the step, it is common to refer to this order as the molecularity of the elementary reaction. On the other hand if a reaction proceeds through several steps, the term molecularity is not used in reference to the observed rate law because one step may involve two molecules, a second step may involve only one and a subsequent step one or two molecules and like wise.

Hence molecularity and order are ordinarily identical only for elementary reaction. Such as bimolecular reactions may or may not be second order. e.g.

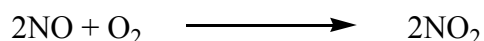


The process is unimolecular.

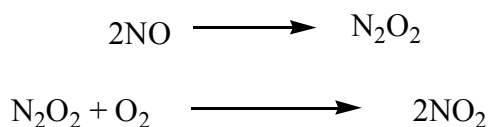


The process is bimolecular since two molecules, one of H₂ and one of I₂ must come together to form 2 molecule, of HI.

Chemical reactions that proceed through more than one step are known as complex reactions. The overall order of reaction determined kinetically may not be identical with the molecularity.



The overall order of reaction has been found experimentally to be 2. The reaction apparently looks as termolecular i.e. in which 2NO would collide simultaneously with one molecule of oxygen. Instead the mechanism is postulated to consist of two elementary steps, each being bimolar.



In complex reactions the rate of reaction is governed by the slowest steps.

Specific Rate Constant:

- The constant k appearing in the rate law associated with a single step (elementary) reaction is called the specific rate constant for that reaction.
- Any change in the conditions of the reaction e.g. temperature, solvent, slight change in reacting species will lead to a rate law having different value for specific rate constant.
- This is of great physical significance - a change in this constant necessarily represents a change at the molecular level as a result of a variation in the reaction condition. In complex reaction overall rate constant is taken in consideration.
- Any change in the nature of a step due to modification in the reaction conditions or in the properties of the molecules taking part in this step could lead to change in the value of overall rate constant.

Units of Basic Rate Constant

1. Zero order rate constant

$$k = - \frac{d[A]}{dt} = \text{moles/lit. sec}$$

2. First order rate constant

$$k = - \frac{d[A]}{dt} \frac{1}{[A]} = 1/\text{sec}$$

3. Second order rate constant

$$k = - \frac{d[A]}{dt} \frac{1}{[A]^2} = \text{lit /mol. sec}$$

$[A]$ is molar concentration of reactant

Ways of Expressing Reaction Rate

Rate means stating the amount of "progress" that occurs in a given amount of time. For example, if you drive a total distance of 80 miles in 2 hours time, your average rate of travel is 40 miles per hour. Of course, if you drive for two hours, it is unlikely that you will travel at a constant speed for the entire two hours. One way to go 40 miles per hour would be to maintain a constant speed of 40 mph for the entire 2 hour journey, but most likely your speed will change in response to road conditions. You slow down when a car changes lanes in front

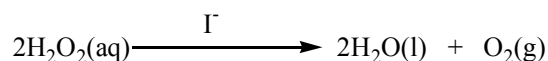
of you, and you come to a stop at a red light. You speed up when entering a multilane freeway in light traffic, and then slow down again when you exit the freeway. So the driver who travels 80 miles in 2 hours has an *average* speed of 40 miles / hour, but the *actual* speed at any moment of time could be more or less than that. The actual speed at any given point of time is the *instantaneous* speed. It's the speed that is reported by a police radar gun at the split second the officer points the device at your car. It is possible to get a speeding ticket for going 80 miles / hour even when the average speed for your journey is only 40 miles / hour.

Likewise, when we express the rate of a chemical reaction, what we really measure in the laboratory is an average rate over some observation period. The reaction has an instantaneous rate at each point in time, however. If the observation period is very short, the average rate is essentially the same as the instantaneous rate. For example, if a reaction takes about 10 minutes (600 seconds) to complete, and you monitor the reaction over the time interval 120.0 seconds to 120.1 seconds (measured from the start of the reaction), the average rate over that time interval is essentially the same as the instantaneous rate at 120.0 seconds. This is because the duration of the observation period (0.1 seconds) is very short in comparison to the total timescale for the reaction (600 seconds). Given that the reaction takes 600 seconds to complete, very little change is expected in 0.1 seconds, which amounts to only 1/6000 of the total timescale. If the reaction is going to be monitored for a very short period of time (to get an approximation of an instantaneous rate) the most useful time to make the observation is at the *beginning* of the reaction. We then get what is called the *initial* rate of the reaction. The initial rate is the instantaneous rate at time zero. What makes this so useful is that we can study a reaction in the forward direction without being concerned about a reverse reaction involving the products. We typically begin with only reactants when studying a reaction. At very early times in the reaction, the product concentrations are very low, so the reverse reaction is negligible. At later times, significant concentrations of products may exist, and if the reaction is reversible, the reverse reaction offsets the forward reaction, making it harder to determine the true rate of conversion of reactants to products.

Expressing the Rate of a Chemical Reaction

A chemical reaction takes one or more substances referred to as “reactants” and converts them to one or more other substances referred to as “products”. To determine how fast a reaction is taking place, we record how fast the “amounts” of these substances are changing. The most often reported measure of reaction rate is the amount by which the concentration of something changes in a given amount of time. Concentration is usually expressed in units of moles per liter.

As an example, let us take the iodide ion catalyzed decomposition of H_2O_2 :



Because the system is losing oxygen gas, one way to monitor the progress of the reaction is to follow the mass loss of the system over time. The decrease in mass over any time interval is the mass of oxygen that was lost in that time interval.

Suppose we start with 1.00 L of an aqueous solution known to have an H_2O_2 concentration of 0.882 M and record the following data:

TIME (seconds)	Accumulated O ₂ (g)	[H ₂ O ₂] (M)
0	0	0.882
60	2.960	0.697
120	5.056	0.566
180	6.784	0.458
240	8.160	0.372
300	9.344	0.298
360	10.336	0.236
420	11.104	0.188
480	11.680	0.152
540	12.192	0.120
600	12.608	0.094

Over the interval 0 to 60 seconds, a total of 2.960 g of O₂ is released. The number of moles of O₂ is calculated as follows:

$$2.960 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{31.9988 \text{ g O}_2} = 0.092503 \text{ mol O}_2$$

From the reaction stoichiometry, we see that 2 moles of H₂O₂ must decompose to get just 1 mole of O₂. Therefore, the number of moles of H₂O₂ that decomposed is calculated as follows:

$$0.092503 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2\text{O}_2}{1 \text{ mol O}_2} = 0.185006 \text{ mol H}_2\text{O}_2$$

The solution had an H₂O₂ concentration of 0.882 mol / L and a volume of 1.00 L. So the number of moles of H₂O₂ was 0.882 mol

Subtracting the moles of H₂O₂ that decomposed from the moles originally present should give the number of moles remaining:

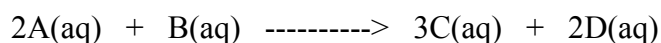
$$0.882 \text{ mol} - 0.185006 \text{ mol} = 0.696994 \text{ mol}$$

These moles are still present in the 1.00 L of solution volume:

$$\frac{0.696994 \text{ mol}}{1.00 \text{ L}} = 0.696994 \text{ mol / L} \approx 0.697 \text{ mol / L}$$

The other concentrations shown in the table were calculated using the same procedure.

Calculation of reaction rate: Not all substances in a chemical equation change their concentrations at the same rate, due to differences in the stoichiometric coefficients in the balanced equation. For example, consider the hypothetical reaction



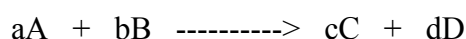
In equation, substance A is being consumed twice as fast as substance B. Substance C is being formed at a rate 3 times the rate of removal of substance B and 50% faster than substance D is being formed. As these comparisons show, two chemists could be studying the same reaction and report different rates, depending on which substance they chose to use as the basis for measuring the rate. One way to get around this difficulty is to divide the rate we would otherwise calculate by the coefficient of the substance in question. This gives the same rate for the chemical reaction regardless of which substance we monitor to measure the rate. For the above reaction, all of the following expressions would give the same numerical value:

$$\text{Rate} = -\frac{\partial[A]}{2 \partial t} = -\frac{\partial[B]}{\partial t} = \frac{\partial[C]}{3 \partial t} = \frac{\partial[D]}{2 \partial t}$$

If the substance being monitored is a reactant, we need to include a negative sign in front of the fraction in order to get a positive rate. This is because the change in concentration is a negative number for a reactant. The negative sign placed in front cancels this negative, yielding a positive rate. The change in concentration for the reactants is positive, so no negative sign is needed in front of the fraction.

Rate Law of a Chemical Reaction

A rate law allows you to play in any concentration you wish in the equation and calculate what the reaction rate should be for those concentrations. For most chemical reactions, the rate law is simply the product of a constant, called the rate constant, and the reactant concentrations, each raised to some power. The power often turns out to be an integer, though it does not have to be. That is, a reaction of the form



usually has a rate law of the form

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

where k is the rate constant and x and y are called the orders of reaction. That is, this reaction is " x^{th} order in A" and " y^{th} order in B". The overall order of a reaction is the sum of the individual orders. Thus, this reaction is $(x + y)^{\text{th}}$ order, overall.

Students are sometimes tempted to conclude that the exponents on the concentrations should be the same as the stoichiometric coefficients in the balanced equation. This is true in the case of an elementary reaction, but is not true in general. An elementary reaction is one that occurs in a single step, exactly as written. But many reactions don't occur that way. The equation that describes the reaction may be the net effect of two or more simpler or elementary reactions. If a reaction is not elementary, there is no necessary relationship between the coefficients in the balanced equation and the exponents in the rate law. They could happen to be the same, but they don't have to be. If a reaction has a rate law with orders that don't match the coefficients in the balanced equation, you know it is not an elementary reaction, because if the reaction was elementary, they would have to match. On the other hand, the fact that a reaction has a rate law with orders that match the coefficients, does not prove that it is an elementary reaction. A non-elementary reaction could happen to have orders that match the coefficients.

Unless you are told in a problem you are working, to treat the reaction as elementary, you should not assume it is elementary. In the absence of some assurance that the reaction is elementary, the only way to obtain the reaction orders is from experimental data. This is most conveniently done by conducting an initial rate study on the reaction, using reactant concentrations that differ by integer multiples from one experiment to the next.

Factors that Affect Reaction Rate

Reaction rates are affected by the following factors: concentration (for substances in solution or for gases), pressure (for gases), surface area, nature of the reactants, temperature, and presence or absence of a catalyst.

Concentration: In general, increasing reactant concentrations increases the reaction rate. This is because molecules must collide in order to react. The more concentrated the reactants, the greater the number of molecules in any given volume, and therefore, the greater the number of molecular collisions. Not every molecular collision between reactant molecules will lead to reaction, but some fraction of them will. Certainly, increasing the total number of molecular collisions will increase the number of successful collisions. "Successful collisions" are defined as those which lead to chemical reactions. The dependences of reaction rates on concentration are called rate laws. Rate laws are expressions of rates in terms of concentrations of reactants. Rate laws can be in differential forms or integrated forms. They are called differential rate laws and integrated rate laws.

Rate laws apply to **homogeneous reactions** in which all reactants and products are in one phase (solution).

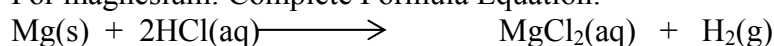
Pressure: If the substances involved in the reaction are gases, pressure will have an effect on reaction rate. For solids and liquids, the effect is negligible, because solids and liquids are essentially incompressible. Gases are readily compressible, so pressure acts as a kind of "concentration" for gases. From Boyle's law, the volume of a gas decreases as the pressure increases. For a given amount of gas, increasing the pressure means forcing the same number of gas molecules to occupy a smaller volume. In the smaller volume, the molecules will collide more often, which means there will be a greater number of successful (leading to reaction) collisions in a given period of time. The reaction rate is therefore expected to increase with pressure.

Surface Area: If a chemical reaction takes place at a boundary between two phases, the surface area will affect the reaction rate. When we consider surface area, we are usually thinking of a solid reactant in contact with a liquid solution that contains another reactant. Certainly, other cases are also possible. For illustration, let us consider the case of a solid "substance A" that reacts with an aqueous solution of "substance B". We want to compare the reaction rate when an intact "chunk" of substance A and a powdered form of substance A each react with substance B in solution. Since only the molecules at the surface of the solid are available to react, increasing the surface area increases the number of molecules available to react. With a larger surface area, there will be more molecular collisions that potentially could lead to reaction. Therefore, there will be more successful collisions in a given period of time, and we will observe a higher reaction rate. In general chemistry laboratories, this is often demonstrated by comparing the reaction rates for solid sticks of chalk (calcium carbonate, CaCO_3) and powdered chalk when dropped into an acid solution, such as hydrochloric acid (HCl).

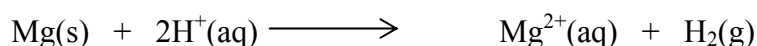
Nature of Reactants: Some substances are just naturally more reactive than others. Acid-base reactions, formation of salts, and exchange of ions are fast reactions. Reactions in which large molecules are formed or break apart are usually slow. Reactions breaking strong covalent bonds are also slow.

Consider, for example, the three metals, magnesium (Mg), zinc (Zn), and copper (Cu). If each of these metals is dropped into a concentrated hydrochloric acid solution in a separate test tube, three very different results are obtained. Magnesium is consumed within seconds, zinc is also consumed but takes considerably longer time, and copper shows no reaction. The chemical equations for these reactions (hypothetical in the case of copper) are all very similar. In each case, the metal is oxidized to the divalent cation and the hydrogen ion (H^+) from the acid is reduced to molecular hydrogen gas.

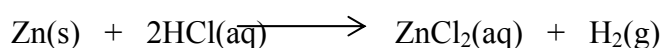
For magnesium: Complete Formula Equation:



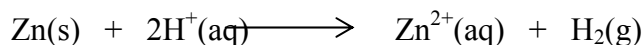
Net Ionic Equation:



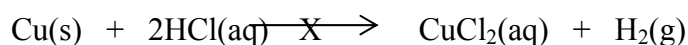
For zinc: Complete Formula Equation:



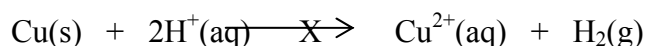
Net Ionic Equation:



For copper: Complete Formula Equation:



Net Ionic Equation:



Looking at the complete formula equations, these are all displacement reactions -- the metal displaces hydrogen from its compound. The net ionic equations show that these are also redox reactions. The metal is oxidized, while the hydrogen is reduced. In the above reactions, it is the ease or difficulty of oxidation of the metal that determines the rate of the reaction. Magnesium gets oxidized very easily, so it reacts vigorously in concentrated acid solutions. Zinc is more difficult to oxidize, so the reaction rate is slower. Finally, copper is so difficult to oxidize that it will not react in a concentrated HCl solution. Hydrogen has a higher oxidation potential than copper, so the system will remain in the state with the metal in the reduced form and the hydrogen in ionic form (H^+). It is possible to oxidize the copper to Cu^{2+} by using an "oxidizing acid", but in this case, the acid anion, rather than H^+ , is what gets reduced. Nitric acid, HNO_3 is an example of an oxidizing acid.

Complete Formula Equation:



Net Ionic Equation:



Of course, magnesium and zinc would also react with HNO_3 and would react faster than copper because they are more easily oxidized, and because both H^+ ions and NO_3^- ions could serve as oxidizing agents. In the case of copper, only NO_3^- is strong enough to serve as an oxidizing agent.

Temperature : Temperature affects the rate of a chemical reaction in two ways. The effect that usually comes to mind first is molecular velocity. The effect of concentration and pressure on reaction rate suggests that molecules must collide in order to react. Temperature is a measure of the average kinetic energy of the molecules. The higher the temperature, the higher the average kinetic energy. The kinetic energy of a moving object is equal to one half the product of its mass and the square of its velocity, that is,

$$\text{K.E.} = \frac{1}{2} m v^2$$

where m is the mass and v is the velocity. Since the molecules have a fixed mass, an increased kinetic energy means an increased velocity. That is, the molecules are moving faster in a hot system than in a cold one. For a collection of moving molecules in a fixed volume, the molecules will collide more often if they are moving faster. Therefore, one way that increasing the temperature increases reaction rate is by making the molecules collide more often. This is only a minor factor, however.

A second way that increasing the temperature increases reaction rate is through its effect on the collision energy. This is by far, the most important factor in increasing the reaction rate. Every chemical reaction has characteristic activation energy. The activation energy is the minimum energy that the reacting molecules must bring into the collision in order to react. If they collide with less than this amount of energy, they simply bounce off of each other unchanged. If the average kinetic energy of the molecules is small in comparison to the activation energy, most of the molecular collisions don't lead to reaction. Collisions may be occurring frequently, but most of them are ineffective, so the reaction rate is very low. If the system is heated, the average kinetic energy of the molecules is increased. When the average kinetic energy is comparable to the activation energy, a much greater fraction of the molecules successfully react when they collide. The percentage of successful collisions usually does not reach 100%, even when the average kinetic energy far exceeds the activation energy. This is because the molecules must collide in the correct orientation in order to react.

It has been noted that temperature's effect on collision energy is far more important than its effect on collision frequency. It has been said that the "typical" chemical reaction approximately doubles its rate when the temperature is raised by 10°C . This generalization is usually applied at 25°C . Thus, for many chemical reactions, we find the rate is approximately twice as fast at 35°C as it is at 25°C . The collision frequency at 35°C is approximately 3% higher than at 25°C . But if the reaction rate has doubled, that's a 100% increase in the

reaction rate. Only 3% of that can be attributed to the increased collision frequency. The other 97% is caused by the increased collision energy.

Arrhenius Equation: It is a well-known fact that raising the temperature increases the reaction rate. Quantitatively this relationship between the rate a reaction proceeds and its temperature is determined by the Arrhenius Equation

$$k = A e^{-\frac{E_a}{RT}} \quad (1)$$

E_a = activation energy

$R = 8.314 \text{ J/mol}\cdot\text{K}$

T = absolute temperature in Kelvins

A = frequency factor

$A = p \cdot Z$, where Z is the collision rate and p is a steric factor.

Z turns out to be only weakly dependant on temperature. Thus the frequency factor is a constant, specific for each reaction.

The Arrhenius equation is based on the collision theory which supposes that particles must collide with both the correct orientation and with sufficient kinetic energy if the reactants are to be converted into products.

The Arrhenius equation is often written in the logarithmic form:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (2)$$

A plot of $\ln k$ versus $1/T$ produces a straight line with the familiar form

$$y = -mx + b,$$

where $x = 1/T$, $y = \ln k$, $m = -E_a/R$, $b = \ln A$

The activation energy E_a can be determined from the slope m of this line:

$$E_a = -m \cdot R$$

The value of the activation energy E_a is rounded to one decimal place. The value of $\ln A$ shall be expressed with an accuracy of two decimal places.

An accurate determination of the activation energy requires at least three runs completed at different reaction temperatures. The temperature intervals should be at least 5°C .

"Two-Point" Arrhenius Equation The "Two-Point" Equation provides an algebraic method to determine the activation energy for a given reaction from the experimental data found at two different reaction temperatures. The Arrhenius equation for two temperatures (T_1 and T_2) gives two rate constants (k_1 and k_2):

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad (3)$$

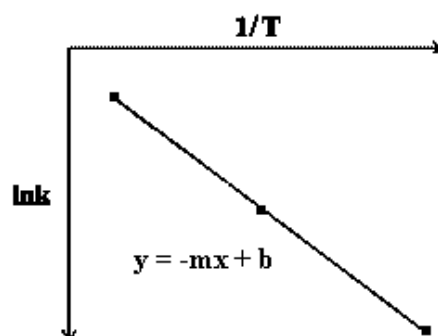
$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad (4)$$

Taking the difference of these two equations leads to

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (5)$$

Arrangement of equation (5) yields

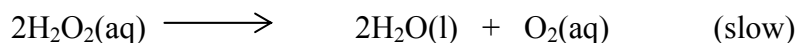
$$E_a = \frac{R T_1 T_2}{(T_1 - T_2)} \ln \frac{k_1}{k_2} \quad (6)$$



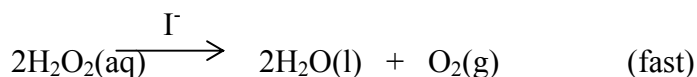
Bestimmung von E_a

Presence of Absence of a Catalyst : A catalyst is a substance that increases the rate of a chemical reaction without being consumed in the reaction. A catalyst may be either homogeneous or heterogeneous.

A homogeneous catalyst is one which is in the same state as the substances in the reaction being catalyzed. For example, hydrogen peroxide, H_2O_2 in aqueous solution slowly decomposes into water and oxygen:

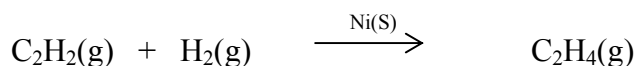


Unassisted, this reaction is very slow. However, if we add an aqueous solution containing iodide ions (I^-), the reaction is much faster.



The I^- is in aqueous solution, and so is the H_2O_2 it catalyzes. The catalyst and reactant are in the same state, making the I^- a homogeneous catalyst.

A heterogeneous catalyst is in a different state than the substances in the reaction being catalyzed. For example, the hydrogenation of acetylene (C_2H_2) to form ethylene (C_2H_4) is catalyzed by a nickel metal surface:



Here, a reaction between two gaseous substances is catalyzed by nickel, a solid. The nickel is a heterogeneous catalyst because it is in a different state than the substances whose reaction is being catalyzed.

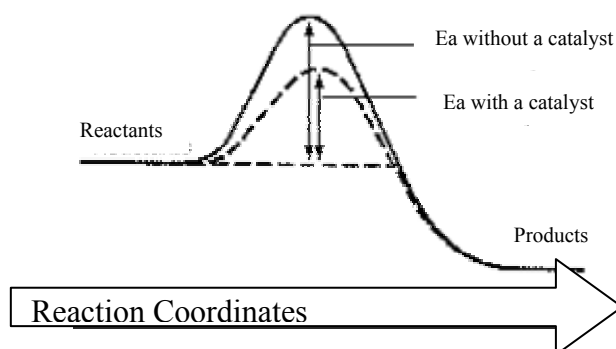
In neither of the above two cases is the catalyst "used up" by the reaction. Typically, a homogeneous catalyst undergoes some temporary change, but it is always returned at the end of the reaction. A heterogeneous catalyst usually plays a more passive role. For example, the nickel in the above reaction merely provides a surface on which the molecules can "land" (the technical word is adsorb) and encounter each other to react.

Concepts of Catalysis

All substances entering into the steps of the mechanism of a chemical reaction can, and usually do, affect the rates of those steps. When substances enter into steps of a mechanism but are regenerated in other later steps so that at the end of the reaction they are recovered unchanged, but they still affect the rate of the reaction, they are called **catalysts**. The process by which a catalyst accelerates the rate of a reaction, or **catalyzes** a reaction, is called **catalysis**. Any substance which prevents or inhibits the normal accelerating effect of a catalyst is called an **inhibitor** of the catalyst.

- Catalysts increase the rate of reaction.
- Catalysts are not consumed by the reaction.
- A small quantity of catalyst should be able to affect the rate of reaction for a large amount of reactant.
- Catalysts do not change the equilibrium constant for the reaction.

The first criterion provides the basis for defining a catalyst as something that increases the rate of a reaction. The second reflects the fact that anything consumed in the reaction is a reactant, not a catalyst. The third criterion is a consequence of the second; because catalysts are not consumed in the reaction, they can catalyze the reaction over and over again. The fourth criterion results from the fact that catalysts speed up the rates of the forward and reverse reactions equally, so the equilibrium constant for the reaction remains the same.



Catalysts increase the rates of reactions by providing a new mechanism that has a smaller activation energy, as shown in the figure below. A larger proportion of the collisions that occur between reactants now have enough energy to overcome the activation energy for the reaction. As a result, the rate of reaction increases.

Homogeneous Catalysis: When catalysts operate on reactions taking place in homogeneous gas mixtures or in homogeneous solutions, the process is called **homogeneous catalysis** i.e the reactants and the catalyst are in same phase. Many reactions taking place in the gas phase or in solution can be accelerated by homogeneous catalysis.

Example. The production of sulfuric acid from sulfur begins with the production of SO_2 according to the rapid reaction $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$. However, the oxidation of sulfur dioxide to sulfur trioxide, while thermodynamically quite feasible, is found to be extremely slow. The oxidation of sulfur dioxide to sulfur trioxide is accelerated greatly when the reaction is catalyzed by traces of the oxides of nitrogen. It is believed that these oxides produce sulfuric acid by this catalytic mechanism:

1. $\text{S(s)} + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$
2. $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
3. $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{SO}_3(\text{g})$
4. $\text{SO}_3(\text{g}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$

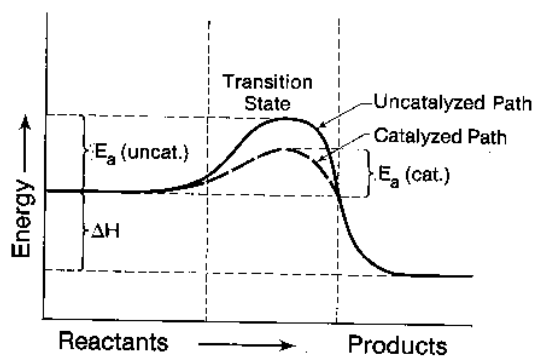
Heterogeneous Catalysis: The reactants and the catalyst are in different phase. Catalysts which operate on reactions taking place on surfaces, **heterogeneous catalysts**, are of great importance in chemical industry and in living organisms. In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical attraction called **adsorption** while the reaction takes place. Adsorption may be relatively weak (physical adsorption) or may have a strength comparable to the strengths of chemical bonds (chemisorption). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called **active sites**.

Example. The industrial synthesis of ammonia requires solid catalysts in order to obtain reasonable rates of reaction. The overall mechanism, including the adsorption steps, is believed to be:

1. $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{ads})$
2. $\text{N}_2(\text{ads}) \rightarrow 2\text{N}(\text{ads})$
3. $\text{H}_2(\text{g}) \rightarrow \text{H}_2(\text{ads})$
4. $\text{H}_2(\text{ads}) \rightarrow 2\text{H}(\text{ads})$
5. $\text{N}(\text{ads}) + 3\text{H}(\text{ads}) \rightarrow \text{NH}_3(\text{ads})$
6. $\text{NH}_3(\text{ads}) \rightarrow \text{NH}_3(\text{g})$

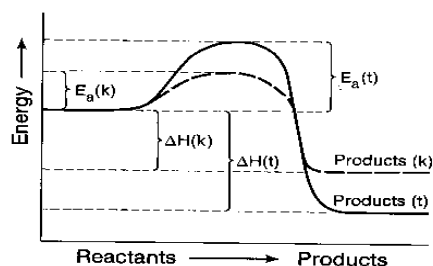
Mechanism of Catalysis

Catalysis occurs when the presence of the catalyst provides an alternate path of lower activation energy by which the reactants can proceed to form the products. In other words, a catalyst lowers the energy of the transition state significantly while the energies of the reactants and products remain the same. This is shown in the Figure below.



The transition state is a state through which the reaction must pass to obtain products from reactants. One could, incorrectly, postulate a reaction as proceeding by the mechanism $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{H}_2\text{Cl}_2 \rightarrow 2\text{HCl}(\text{g})$. In this "mechanism" the species H_2Cl_2 would be called a **transition state**, and it need have no real physical existence or duration. If a transition state has real physical significance it should be called an **intermediate** rather than a transition state.

Since a catalyst provides a path that requires a lower energy of activation, a much higher proportion of the total molecules will have sufficient energy to react effectively along the catalyzed path than could have reacted along the uncatalyzed path, and so the rate of the reaction can be greatly increased by the presence of the catalyst. However, there is no change in the free energy of the reaction since the energies of the products and reactants are not affected by the catalyst. The decrease in activation energy applies to the reverse reaction as well as to the forward reaction, and the position of equilibrium will remain unchanged on the addition of a catalyst because the rates of the forward and reverse reactions will both have been increased. These are important properties of catalysts. No catalyst will change the position of a chemical equilibrium, and any catalyst will accelerate both the forward and reverse reactions along the same path.



The above Figure shows a difference in experimental results which may arise as the result of the availability of a catalyzed route which gives a product other than the thermodynamically most stable product of the reaction.

The kinetic products are obtained because the dashed path is faster; it has lower activation energy than does the solid path which leads to the thermodynamic products. Although the solid path would yield a greater energy in reaching the thermodynamic products, it is so slow that the reaction to kinetic products is almost complete before the reaction to thermodynamic products gets under way. Only if a path with low activation energy links the kinetic products

to the thermodynamic products will the kinetic products convert to the thermodynamic products, even though the thermodynamic products are the more stable products.

Example. The overall decomposition of dinitrogen pentoxide, N_2O_5 , proceeds to oxygen and an equilibrium mixture of NO_2 and its dimer N_2O_4 both in the gas phase and in inert solvents. The overall reaction kinetics are those of a first-order reaction in which $-\text{d}[\text{N}_2\text{O}_5]/\text{dt} = k[\text{N}_2\text{O}_5]$. The reaction is not catalyzed, it is not affected by the surface of the container, and it is unaffected by the presence of a large number of possible impurities. In the gas phase, first-order kinetics hold down to very low pressures. A falloff from first-order reaction kinetics starts to appear as the pressure drops below 7 Pa, and below 0.5 Pa the reaction appears to follow second-order kinetics. The possible mechanisms which might account for this behavior are as follows.

Several mechanisms are possible. A mechanism in which the first and rate-determining step was $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_3 + \text{O}_2$, all of the subsequent steps being fast, is unlikely because both N_2O_5 and N_2O_3 have all electron spins paired while molecular oxygen has two unpaired spins and a spin change is not probable. A mechanism in which the first and rate-determining step was $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{O}$ is also unlikely because a very large amount of energy would be required to knock off a single oxygen atom from dinitrogen pentoxide.

A mechanism in which the first and rate-determining step was $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO}$, with several possible subsequent steps all being fast, is more probable.

The actual mechanism is believed to be a fourth possibility:

1. $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_2 + \text{NO}_3$; K_1 , rapid and reversible
2. $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO}$; k_2 , slow
3. $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$; k_3 , fast
4. $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$; K_2 , rapid and reversible

In this mechanism the rate-limiting step is the second one, so the observed rate law should be $-\text{d}[\text{N}_2\text{O}_5]/\text{dt} = k_2[\text{NO}_2][\text{NO}_3]$, but since $K_1 = [\text{NO}_2][\text{NO}_3]/[\text{N}_2\text{O}_5]$ the observed kinetics actually are

$$-\text{d}[\text{N}_2\text{O}_5]/\text{dt} = k_2 K_1 [\text{N}_2\text{O}_5]$$

The fall off at very low pressures arises because, as the number of collisions drops with decreasing pressure, the rapid rate of the equilibrium corresponding to K_1 can no longer be maintained. One would then postulate the mechanism:

1. $\text{N}_2\text{O}_5 + \text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_5 + \text{NO}_2 + \text{NO}_3$; k_1 , slow
2. $\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{NO}$; k_2 , fast
3. $\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$; k_3 , fast
4. $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$, K_2 , rapid and reversible

The rate constant k_2 is the same as in the previous mechanism, but it has now become relatively fast as the rate of the preceding equilibrium has fallen until the process involves a

single bimolecular collision rather than a unimolecular energy distribution and dissociation. The reaction would now appear as second-order in N_2O_5 .

Enzyme Catalysis

An **enzyme** is a protein molecule which acts as a catalyst in biochemical reactions. Enzymes are normally named after the reactions they catalyze because their molecular structure is very complex and in many cases unknown. For example, superoxide dismutase is the enzyme responsible for the destruction of the superoxide ion in living organisms. Enzymes act either in solution or attached to membranes. The material whose reaction is catalyzed by an enzyme is called a **substrate**. In some reactions catalyzed by enzymes, the reaction appears to take place on the surface of the catalyst enzyme molecules themselves, which may or may not be in homogeneous solution.

Most reactions in biological systems do not occur at any perceptible rate in the absence of an enzyme to catalyze them. Even a reaction as simple as the hydration of carbon dioxide, $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$, is catalyzed by the enzyme carbonic anhydrase in one of the fastest enzyme-catalyzed reactions known.

Enzymes are very selective catalysts. A given enzyme will catalyze only specific reactions of very specific substrate molecules. It is believed that enzyme-catalyzed reactions normally proceed by formation of an enzyme-substrate complex (ES complex) in which the substrate is bound to a specific region of the enzyme called the **active site**. The ES complex then dissociates to yield the products of the catalyzed reaction. Experimentally, it has been found that the rates of many enzyme-catalyzed reactions are directly proportional to substrate concentration when substrate concentration is low and become independent of substrate concentration as substrate concentration increases. This behavior is called **Michaelis-Menten kinetics** after Leonor Michaelis and Maud Menten, who in 1913 proposed the kinetic mechanism which accounts for this behavior. Using the usual biochemical symbols for substrate (S), enzyme (E), products (P), and ES complex (ES), this mechanism is written as:



Since the rate $dc(\text{P})/dt = k_2[\text{ES}]$ for a unimolecular step in any rate process, an equation which describes the overall process in terms of the reactants requires the preceding equilibrium. This can be used on the assumptions of microscopic reversibility and a preceding fast equilibrium:

$$k_1[\text{S}][\text{E}] = k_{-1}[\text{ES}], [\text{ES}] = K[\text{S}][\text{E}], \text{ so}$$

$$dc(\text{P})/dt = k_2K[\text{S}][\text{E}]$$

If, however, the preceding equilibrium is not fast relative to the unimolecular process governed by k_2 , and in enzymatic reactions it is often not relatively fast, then a more complex equation is found. That equation can be derived from the condition of steady state; regardless of the rates of the individual steps, most enzymatic reactions do proceed at a constant rate. At a condition of steady state the concentration of enzyme-substrate complex is steady or constant:

$$d[ES]/dt = -k_{-1}[ES] - k_2[ES] + k_1[S][E] = 0$$

$$(k_{-1} + k_2)[ES] = k_1[S][E], \text{ or } [ES] = k_1[S][E]/(k_{-1} + k_2)$$

and the overall kinetic equation is:

$$dc(P)/dt = k_2k_1[S][E]/(k_{-1} + k_2)$$

The Michaelis-Menten constant K_M is defined as $K_M = (k_{-1} + k_2)/k_1$, which leads to $dc(P)/dt = (k_2/K_M)[S][E]$.

Although this is a correct form of the Michaelis-Menten equation it has not been found useful by biochemists because the concentration of uncombined enzyme, $[E]$, is experimentally inaccessible. A more useful form of the Michaelis-Menten equation is obtained from the following argument.

All of the enzyme, or the total enzyme concentration $[E_{tot}]$, must be either part of the enzyme-substrate complex or free, so $[E] = [E_{tot}] - [ES]$. Substitution of this equation into the condition of steady state gives

$$[ES] = (k_1[S][E_{tot}] - k_1[S][ES])/(k_{-1} + k_2), \text{ or}$$

$$[ES] = K_M[S]([E_{tot}] - [ES])$$

which rearranges to a solution for $[ES]$ and its elimination:

$$[ES] = [E_{tot}][S]/([S] + K_M)$$

$$dc(P)/dt = \text{rate, rate } R = k_2[E_{tot}][S]/([S] + K_M) = \text{maximum rate } R_{max}[S]/([S] + K_M)$$

This equation is more useful because, when the enzyme is saturated with substrate and the rate $dc(P)/dt$ is the maximum rate, that maximum rate R_{max} is independent of substrate concentration and must then be equal to $k_2[E_{tot}]$. This gives the most common form of the Michaelis-Menten equation, which is useful because usually both the substrate concentration $[S]$ and the rate R are measurable.

The Michaelis-Menten equation is a form of the second-order rate law. It can be plotted in a linear form by taking the reciprocal of both sides: $1/R = 1/R_{max} + (K_M/R_{max})(1/[S])$. A plot of $1/R$ against $1/[S]$ has a slope of K_M/R_{max} and an intercept of R_{max} so that both parameters can be determined. This kind of plot is called a Lineweaver-Burk plot. Other transformations of the Michaelis-Menten equation have also been used to obtain linear plots.

The value of R_{max} , although it is actually a measure of a rate constant, $k_2[E_{tot}]$, is often expressed as a turnover number. The **turnover number** is the number of substrate molecules converted into product per unit time when the enzyme is fully saturated with the substrate. A micromolar solution of carbonic anhydrase catalyzes the formation of 0.6 mol/litre- s of " H_2CO_3 " solution when fully saturated, so its turnover number is $600,000 \text{ s}^{-1}$. This is one of the largest turnover numbers known; one of the smaller ones is that of lysozyme, which is only 0.5 s^{-1} . In fact, the turnover number is the pseudo-first-order rate constant for the dissociation of the ES complex and for carbonic anhydrase would be $600,000 \text{ s}^{-1}$.

The value of the Michaelis-Menten constant K_M is the value of the equilibrium constant for the formation of the ES complex when, and only when, k_2 is small relative to k_{-1} . Experimentally, this is often observed at very low concentrations of the substrate relative to the enzyme. For carbonic anhydrase, the value of the Michaelis-Menten constant is 0.008 mol/litre under physiological conditions; the form of this constant is $[E][CO_2]/[ECO_2]$. Kinetic studies of R_{max} and of K_M have led to considerable understanding of the nature of complex biological reactions and are a significant area of biochemical research.

Zero Order Reaction

A reaction is of zero order when the rate of reaction is independent of the concentration of materials. The rate of reaction is a constant. When the limiting reactant is completely consumed, the reaction stops abruptly.

The zero order rate law for the general reaction



is written as the equation

$$-\frac{d[A]}{dt} = k \quad (1)$$

which on integration of both sides gives

$$[A] = -kt + C \quad (2)$$

When $t = 0$ the concentration of A is $[A]_0$. The constant of integration must be $[A]_0$. Now the integrated form of zero-order kinetics can be written as follows

$$[A] = -kt + [A]_0 \quad (3)$$

Plotting $[A]$ versus t will give a straight line with slope $-k$.

First Order Reaction

A general unimolecular reaction



where A is a reactant and P is a product is called a first-order reaction.

The rate is proportional to the concentration of a single reactant raised to the first power.

The decrease in the concentration of A over time can be written as:

$$v = -\frac{d[A]}{dt} = k[A] \quad (1)$$

$$-\frac{d[A]}{[A]} = k dt \quad (2)$$

Equation (2) represents the differential form of the rate law. Integration of this equation and determination of the integration constant C produces the corresponding integrated law.

Integrating equation (2) yields:

$$\ln[A] = -kt + C \quad (3)$$

The constant of integration **C** can be evaluated by using boundary conditions. When **t = 0**, **[A] = [A]₀**. **[A]₀** is the original concentration of **A**.

Substituting into equation (3) gives:

$$\ln[A]_0 = -k(0) + C \quad (4)$$

Therefore the value of the constant of integration is:

$$C = \ln[A]_0 \quad (5)$$

Substituting (5) into (4) leads to:

$$\ln \frac{[A]}{[A]_0} = -kt \quad (6)$$

Plotting $\ln[A]$ or $\ln[A] / [A]_0$ against time creates a straight line with slope $-k$. The plot should be linear up to about 90%-conversion.

Equation (6) can also be written as:

$$[A] = [A]_0 e^{-kt} \quad (7)$$

This means that the concentration of **A** decreases exponentially as a function of time.

The rate constant **k** can also be determined from the half-life **t_{1/2}**. Half-life is the time it takes for the concentration to fall from **[A]₀** to **[A]₀ / 2**.

Equation (6) can be rewritten as:

$$k t_{1/2} = \ln \frac{[A]_0}{[A]_0 / 2} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}} \quad (8)$$

Pseudo First Order Reaction

A and **B** react to produce **P**:



If the initial concentration of the reactant **A** is much larger than the concentration of **B**, the concentration of **A** will not change appreciably during the course of the reaction. The concentration of the reactant in excess will remain almost constant. Thus the rate's dependence on **B** can be isolated and the rate law can be written

$$v = -\frac{d[B]}{dt} = k'[B] \quad \text{where} \quad k' = k \cdot [A] \quad (1)$$

Equation (1) represents the differential form of the rate law. Integration of this equation and evaluation of the integration constant **C** produces the corresponding integrated law.

Substituting **[B] = c** into equation (1) yields:

$$-\frac{dc}{c} = k' \cdot dt \quad (2)$$

Integrating equation (2) gives:

$$\ln c = -k' \cdot t + C \quad (3)$$

The constant of integration **C** can be evaluated by using boundary conditions. At **t = 0** the concentration of **B** is **c₀**.

Therefore

$$C = \ln c_0 \quad (4)$$

Accordingly is obtained:

$$\ln c = \ln c_0 - k' \cdot t \quad \text{or} \quad c = c_0 \cdot e^{-k' \cdot t} \quad (5)$$

If the decrease in concentration of **B** is followed by photometric measurement the **Beer' Law** must be taken into account.

Beer' Law can be written as:

$$A = \log \frac{P_0}{P} = -\log T = \varepsilon \cdot c \cdot d \quad (6)$$

A = absorbance, ε = molar absorptivity with units of $L \cdot \text{mol}^{-1} \text{cm}^{-1}$
 c = concentration of the compound in solution, expressed in $\text{mol} \cdot L^{-1}$
 d = path length in cm

P_0 = radiant power for radiation entering; P = radiant power for radiation leaving
 gives the relationship between **k'** and **lnA**:

$$\begin{aligned} \ln A &= -k' \cdot t + \ln c_0 + \ln(\varepsilon \cdot d) \\ \text{or} \quad \ln A &= -k' \cdot t + C \end{aligned} \quad (7)$$

Equation (7) is analogous to equation (3) or equation (5)

One needs only monitor the relative concentration of **B** as a function of time to obtain the **pseudo-first order rate constant k'**. The value of **k'** can then be divided by the known, constant concentration of the excess compound to obtain the true constant second order **k**:

$$k = \frac{k'}{[A]} \quad (8)$$

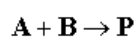
The **pseudo-first order rate constant k'** can also be determined from the **half-life t_{1/2}**.

$$k' \cdot t_{1/2} = \ln \frac{c_0}{c_0/2} \quad \text{or} \quad k' = \frac{\ln 2}{t_{1/2}} \quad (9)$$

Second Order Reaction

The rate of a second order reaction is proportional to either the concentration of a reactant squared, or the product of concentrations of two reactants.

For the general case of a reaction between **A** and **B**, such that



the rate of reaction will be given by

$$-\frac{d[A]}{dt} = k \cdot [A][B] \quad (1)$$

1. Initial concentrations of the two reactants are equal:

Equation (1) can be written as:

$$-\frac{d[A]}{dt} = k \cdot [A]^2 \quad (2)$$

Separating the variables and integrating gives:

$$\frac{1}{[A]} = kt + C \quad (3)$$

Provided that $[A] = [A]_0$ at $t = 0$ the constant of integration C becomes equal to $1 / [A]_0$.

Thus the second order integrated rate equation is

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

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (4)$$

A plot of $1 / [A]$ vs t produces a straight line with slope k and intercept $1 / [A]_0$. The plot should be linear up to about 50%-conversion.

2. Starting concentrations of the two reactants are different:

If $[A]_0$ and $[B]_0$ are different the variable x is used.

Equation (1) becomes

$$\frac{dx}{([A]_0 - x)([B]_0 - x)} = k dt \quad (5)$$

where $[A]_0 - x = [A]$, $[B]_0 - x = [B]$ and x is the decrease in the concentration of **A** and **B**.

Taking into account that the left side of equation (5) can be written as

$$\frac{1}{[B]_0 - [A]_0} \left(\frac{1}{[A]_0 - x} - \frac{1}{[B]_0 - x} \right) \quad (6)$$

Integrating equation (5) gives

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0 - x}{[B]_0 - x} = kt + C \quad (7)$$

where C is the constant of integration.

Using the condition that $x = 0$, when $t = 0$, the value of C can be found

$$C = \frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0}{[B]_0} \quad (8)$$

and equation (7) becomes

$$\ln \frac{[A]_0 - x}{[B]_0 - x} = kt ([B]_0 - [A]_0) + \ln \frac{[A]_0}{[B]_0} \quad (9)$$

A plot of

$$\ln \frac{[A]_0 - x}{[B]_0 - x} \quad (10)$$

against t should be a straight line.

If the experimental method yields reactant concentrations rather than x , the equivalent form of the equation is

$$\ln \frac{[B]_0 [A]}{[A]_0 [B]} = kt ([B]_0 - [A]_0) \quad (11)$$

If equimolar amounts of **A** and **B** are converted, then **[A]** can be expressed by the concentration of **B**.

If **[B] = x** , **[A] = [A]₀ - (x₀ - x)**

Provided that the initial concentration of **A** is twice the concentration of **B** equation (11) becomes

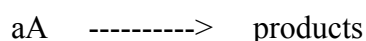
$$\ln \left[\frac{1}{2} \left(\frac{x_0}{x} + 1 \right) \right] = x_0 \cdot kt \quad (12)$$

Summary

Reaction Order	Differential Rate Law	Integrated Rate Law	Linear Plot	Slope of Linear Plot	Units of Rate Constant
0	$-d[A] / dt = k$	$[A] = [A]_0 - kt$	$[A]$ vs t	$-k$	$\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1 st	$-d[A] / dt = k [A]$	$[A] = [A]_0 e^{-kt}$	$\ln[A]$ vs t	$-k$	s^{-1}
2 nd	$-d[A] / dt = k [A]^2$	$1/[A] = 1/[A]_0 + kt$	$1/[A]$ vs t	k	$\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

Concentration as a Function of Time

For simplicity, we will only consider reactions in which there is a single reactant. That is, reactions of the form



where a is a stoichiometric coefficient and A is a chemical formula. Such a reaction would have a rate law in terms of that single reactant, A . We would expect the rate law to have the form

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

where x will equal 0, 1, or 2, because we are only going to consider zero, first, and second order reactions. The equation we obtain for the time dependence of concentration depends on the order of the reaction. The equations are often presented in a form that makes it obvious that a linear plot can be constructed. These plots are useful to test whether or not a reaction is of a particular order, and also allow us to determine the reaction rate constant. Here are the integrated rate laws for reactions of zero, first, and second order in a single reactant:

$$\text{Zero Order: } [A]_t = [A]_0 - kt$$

$$\text{First Order: } \ln [A]_t = \ln [A]_0 - kt$$

$$\text{Second Order: } \frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

In the above equations, $[A]_0$ is the initial concentration of substance A (the concentration at the start of the reaction or "time zero"), $[A]_t$ is the concentration of substance A after a period of time t has elapsed, and k is the rate constant. If we compare the above three integrated rate laws to the equation for a straight line,

$$Y = m \cdot X + b$$

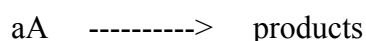
Each of them suggests a linear plot as follows:

Zero Order: If the reaction is zero order, a plot of $[A]_t$ on the Y-axis against t on the X-axis gives a straight line that has a slope of $-k$ and a Y-axis intercept of $[A]_0$.

First Order: If the reaction is first order, a plot of $\ln [A]_t$ on the Y-axis against t on the X-axis gives a straight line that has a slope of $-k$ and a Y-axis intercept of $\ln [A]_0$.

Second Order: If the reaction is second order, a plot of $1 / [A]_t$ on the Y-axis against t on the X-axis gives a straight line with a slope of k and a Y-axis intercept.

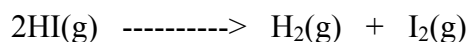
How initial rate studies (multiple experiments with different initial reactant concentrations) can be used to determine the rate law of a chemical reaction. But if the reaction involves only a single reactant, that is, one of the form



the integrated rate laws presented above allow a means of determining the rate law in a single experiment. A convenient starting concentration of substance A is used, and the concentration of substance A is measured at regular time intervals. The concentration is then plotted against time as a linear plot ($[A]_t$ vs. t), a logarithmic plot ($\ln [A]_t$ vs. t), and a reciprocal plot ($1 / [A]_t$ vs. t). The plot that comes closest to a straight line indicates the order of the reaction. If it is the linear plot, the reaction is zero order; if it is the logarithmic plot, the reaction is first order; and if it is the reciprocal plot, the reaction is second order. In all cases, the slope of the line is used to get the rate constant. For the zero and first order plots, the line will have a negative slope. We simply ignore the negative sign. The rate constant is the magnitude of the slope, taken as a positive number. For the second order plot, the line has a positive slope, and the slope is equivalent to the rate constant, with no modification being required.

In addition to their utility in constructing graphical plots, the integrated rate laws are also useful for algebraic calculations. The following examples illustrate their use:

Example: The decomposition of hydrogen iodide is described by the following equations:



$$\text{Rate} = k [\text{HI}]^2$$

At 427 °C, the rate constant k has the value $1.20 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$. If the initial concentration of HI is 0.560 mol L^{-1} , what will the HI concentration be after 2.00 hours of reaction time?

Solution: Since the rate constant has the time units in seconds, we must convert the 2.00 hour of reaction time to seconds:

$$2.00 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} = 7200 \text{ s}$$

The other quantities we need are $[\text{HI}]_0 = 0.560 \text{ mol L}^{-1}$ and $k = 1.20 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1}$. From these, we can calculate $[\text{HI}]_t$. The rate law indicates that this is a second order reaction, so we use the second order integrated rate law. Substituting HI for the generic substance A in that equation, we have

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

Substituting our numerical values into this equation, we have

$$\frac{1}{[\text{HI}]_t} = \frac{1}{0.560 \text{ mol L}^{-1}} + 1.20 \times 10^{-3} \text{ mol}^{-1} \text{ L s}^{-1} (7200 \text{ s})$$

$$\frac{1}{[\text{HI}]_t} = 1.7857 \text{ mol}^{-1} \text{ L} + 8.64 \text{ mol}^{-1} \text{ L}$$

$$\frac{1}{[\text{HI}]_t} = 10.4257 \text{ mol}^{-1} \text{ L}$$

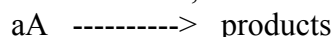
The above is still the *reciprocal* concentration, however. We must take the reciprocal of both sides of this equation to get the actual concentration. The reciprocal of $1 / [\text{HI}]_t$ is $[\text{HI}]_t$. To get the reciprocal of the number on the right hand side, we enter the number in our calculator and press the key that says $1/x$ or x^{-1} . If the answer is not immediately displayed, the = or EXE key needs to be pressed. To get the reciprocal of the units, change the sign of the exponents. The reciprocal of $\text{mol}^{-1} \text{ L}$ is mol L^{-1} .

$$[\text{HI}]_t = 0.09592 \text{ mol L}^{-1}$$

Half Life

One way to gauge the speed of a reaction is to specify the amount of time required for a reactant concentration to be reduced to half its original value. The faster the reaction, the less time required for the concentration to be cut in half. We use the symbol $t_{1/2}$ to refer to the half

life. The $\frac{1}{2}$ serves as a *label* here. We should not interpret it as being multiplied by the time t . Since the concentration at the half life time ($t_{1/2}$) is half the starting concentration, we can represent it as $\frac{1}{2}[A]_0$. In Section 3.1, we consider reactions of the form



which were either zero, first, or second order. If we take the integrated rate laws for each of these reactions (as presented in Section 3.1) and make the substitutions $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$ we obtain the equations for half life for each of these reaction orders.

For the zero order, start with

$$[A]_t = [A]_0 - kt$$

and substitute $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$ to get

$$\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$$

By transposing the $[A]_0$ from the right side to the left side (subtracting $[A]_0$ from both sides) we get

$$\frac{1}{2}[A]_0 - [A]_0 = -kt_{1/2}$$

The subtraction on the left gives $-\frac{1}{2}[A]_0$ so we now have

$$-\frac{1}{2}[A]_0 = -kt_{1/2}$$

Dividing both sides of this equation by $-k$ gives

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

The above is final equation for the half life of a zero order reaction. Two forms have been presented because the $\frac{1}{2}$ in the numerator can be re-expressed as a 2 in the denominator.

Features of the zero order half life equation. Since the initial reactant concentration ($[A]_0$) is in the numerator, the half life will increase with the initial concentration. The greater the concentration of the reactant, the longer it will take for half of it to be consumed. We can explain this feature as follows:

The rate law for a reaction that has a single reactant (referred to generically as A) and is zero order in that reactant is

$$\text{Rate} = k[A]^0 = k(1) = k$$

Since any quantity raised to the zero power is equal to 1, the concentration factor simply drops out of the equation and is replaced by 1. Then, since any quantity multiplied by 1 is equal to itself, the reaction rate is equal to the rate constant. That is,

$$\text{Rate} = k$$

The rate of a zero order reaction does not depend on the reactant concentration! At first glance, this seems strange, considering that it was pointed out in Section 1 that molecules must collide in order to react. A reaction is zero order when a factor other than collision frequency and collision energy (activation energy) controls the rate. For example, if a reaction must absorb light in order to occur, the availability of photons of the proper energy might be what limits the rate of the reaction. Increasing the concentration does not increase the rate in this case. You will have a greater concentration of reactant molecules, but they all must "wait" for an incoming photon to energize them.

Since the rate of a zero order reaction does not depend on the reactant concentration, it will continue at a constant rate as the reactant is consumed. This is in contrast to reactions of other orders, for which the rate decreases as the reactant is consumed, due to the decreasing collision frequency. If the reaction proceeds at a constant rate, then of course, the greater the amount of reactant you have, the longer it will take to use it up. This same argument applies if we consider the time required to use up half of it. Therefore, half life should increase with the initial concentration of the reactant. This is exactly what our half life equation shows us.

The half life equation also shows that the half life decreases with the rate constant. The rate constant is in the denominator, so the larger it is, the smaller (i.e., shorter) the half life will be. This is logical. A larger rate constant means a faster reaction. The faster the reaction, the more quickly the reactant is used up, and therefore, the more quickly half of it is used up.

Now let's consider the first order reaction. We start with the integrated rate law

$$\ln [A]_t = \ln [A]_0 - kt$$

and substitute $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$ to get

$$\ln (\frac{1}{2}[A]_0) = \ln [A]_0 - kt_{1/2}$$

On the left hand side, we can use the fact that the log of a product is the sum of the logs. This allows us to split up the $\frac{1}{2}$ and the $[A]_0$ and write

$$\ln \frac{1}{2} + \ln [A]_0 = \ln [A]_0 - kt_{1/2}$$

Since $\ln [A]_0$ appears on both sides, it can be canceled out (mathematically what we do is subtract it from both sides). This leaves

$$\ln \frac{1}{2} = -kt_{1/2}$$

Another way to think of $\frac{1}{2}$ is 2^{-1} . Our equation can now be written

$$\ln 2^{-1} = -kt_{1/2}$$

Since the log of a number raised to a power is equal to the power multiplied by the log of the number, we can take the power of -1 on 2 and place it in front of the ln. This merely puts a negative sign in front of it. We now have

$$-\ln 2 = -kt_{1/2}$$

The negative sign appears on both sides and can be cancelled. Mathematically, what we are doing is multiplying both sides by -1. We now have

$$\ln 2 = kt_{1/2}$$

Now, dividing both sides by k, and reversing the order in which we write the equation, so that $t_{1/2}$ appears on the left side, we have

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

This is final result for the half life of a first order reaction. It is an interesting result in that the initial reactant concentration, $[A]_0$ does not appear. This means that the half life of a first order reaction is independent of the starting concentration. No matter how much or how little you have, it still takes the same amount of time to get rid of half of it. How can this be? To understand this phenomenon, let us look at the rate law for a reaction that is first order in a single reactant.

$$\text{Rate} = k [A]^1 = k [A]$$

Since any quantity raised to the first power is equal to itself, the rate is equal to the product of the rate constant and the reactant concentration. If you double the reactant concentration, you will double the rate. This is why the half life is independent of initial concentration. If you increase the reactant concentration -- which might seem like it should make it take longer to use it up -- you also increase the rate by the same factor. As a result, you always break even, no matter how much you increase the concentration.

The rate constant again appears in the denominator, just as it did in the zero order reaction. Therefore, once again, a higher rate constant will give a shorter half life. The explanation here is the same as before. A higher rate constant means a faster reaction, and if the reaction is faster, it should not take as long to consume half of the reactant.

Now let's consider the reaction that is second order in a single reactant. We take the integrated rate law

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

and substitute $t = t_{1/2}$ and $[A]_t = \frac{1}{2}[A]_0$ to get

$$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

On the left hand side, we see a fraction within a fraction. If we multiply the numerator and denominator of the "big" fraction by 2, we can clear the "little" fraction in the denominator, because 2 times $\frac{1}{2}$ is 1. This does not change the value of the "big" fraction because in

multiplying the numerator and denominator by the same number (both get multiplied by 2), we have multiplied the "big" fraction by 1. Our equation now looks like this:

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

If we subtract $1 / [A]_0$ from both sides, we have

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

On the left side, the two fractions have a common denominator ($[A]_0$) so we can simply subtract the numerators. We now have

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

Dividing both sides by k (or multiplying by $1/k$ if you prefer to think of it that way) and reversing the order of writing the equation so that $t_{1/2}$ appears on the left, we now have

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

This is the final result for the half life of a second order reaction. Notice that the initial concentration of the reactant ($[A]_0$) now appears in the denominator. This means that the greater the reactant concentration is, the shorter the half life will be! How can this be? You have more of it, and it takes less time to get rid of half of it than if you had less of it. As we have seen with the reaction orders we considered earlier, we look to the rate law to understand the characteristics of the half life. For a reaction that is second order in a single reactant, the rate law is

$$\text{Rate} = k[A]^2$$

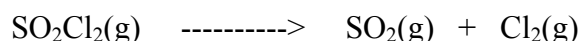
Since the rate depends on the *square* of the concentration rather than the concentration itself, if we double the concentration, the rate is increased by a factor of 4. This is because the factor of 2 increase in concentration gets squared to produce a factor of 4 increase in the rate. So the reaction rate increases faster than the concentration. That is why larger concentrations have shorter half lives than smaller concentrations.

As usual, the rate constant is in the denominator, meaning that the larger the rate constant is, the shorter the half life will be. As we have seen, this is because a larger rate constant means a faster reaction, and the faster the reaction, and less time it should take to consume half of the reactant.

In summary then, the following features pertain to half lives:

- Half life always decreases as the rate constant increases. This is true regardless of the reaction order.
- For zero order reactions, the greater the reactant concentration, the longer the half life.
- For first order reactions, the half life is independent of reactant concentration
- For second order reactions, the greater the reactant concentration, the shorter the half life.

Example: The decomposition of sulfuryl chloride, SO_2Cl_2 is described by the following equations:



$$\text{Rate} = k [\text{SO}_2\text{Cl}_2]$$

At 320°C , the rate constant k has the value $2.20 \times 10^{-5} \text{ s}^{-1}$. If the reaction begins with SO_2Cl_2 at an initial concentration of $1.00 \times 10^{-4} \text{ mol L}^{-1}$, how long will it take for the SO_2Cl_2 concentration to be reduced to $2.50 \times 10^{-5} \text{ mol L}^{-1}$?

Solution via a Half Life Approach: Notice that the ending concentration is $\frac{1}{4}$ of the initial concentration:

$$\frac{1.00 \times 10^{-4} \text{ mol L}^{-1}}{4} = 2.50 \times 10^{-5} \text{ mol L}^{-1}$$

To reduce a reactant to $\frac{1}{4}$ of its original concentration should require 2 half lives. This is because in the first half life, the reactant concentration will be reduced to half of its original value, and in the second half life, that "new" concentration (half of the original) will again be cut in half so it now amounts to only $\frac{1}{4}$ of the original value. Since the half life of a first order reaction does not depend on concentration, the second half life will be the same duration as the first. In fact, every half life in a first order reaction will be the same duration as the first. So if we need an integer number of half lives (i.e., 2 half lives, 3 half lives, 4 half lives, etc), we can calculate the half life just once and then multiply by the number of half lives we need. In this case, we need 2 half lives so we calculate the first order half life and multiply that result by 2.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{2.20 \times 10^{-5} \text{ s}^{-1}} = 31507 \text{ s}$$

Every 31507 seconds, the concentration is reduced to half of what it was at the beginning of that time interval. So if we start with a concentration of $1.00 \times 10^{-4} \text{ mol L}^{-1}$, we will find that 31507 seconds later, the concentration will be only $5.00 \times 10^{-5} \text{ mol L}^{-1}$. That is,

$$\frac{1.00 \times 10^{-4} \text{ mol L}^{-1}}{2} = 5.00 \times 10^{-5} \text{ mol L}^{-1}$$

If we now take the $5.00 \times 10^{-5} \text{ mol L}^{-1}$ as the "new" starting concentration and wait another 31507 seconds, that concentration will also be cut in half:

$$\frac{5.00 \times 10^{-5} \text{ mol L}^{-1}}{2} = 2.50 \times 10^{-5} \text{ mol L}^{-1}$$

We had to wait for 2 half lives and they were each 31507 seconds in duration. Our total waiting time has been

$$2 (31507 \text{ s}) = 63014 \text{ s} \quad 6.30 \times 10^4 \text{ s}$$

The above is our answer to the problem. If we prefer the answer in minutes or hours, we can convert the units.

$$63014 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 1050 \text{ min}$$

$$1050 \text{ min} \times \frac{1 \text{ h}}{60 \text{ min}} = 17.5 \text{ h}$$

The shortcut we took advantage of here does not always work. So, let's discuss when it will work. First, we must be seeking a "good" fraction of the original concentration. The fraction $\frac{1}{4}$ is one of those "good" fractions. A "good" fraction is one that is obtained after an integer number of half lives. As we have seen, we have $\frac{1}{2}$ the original concentration in 1 half life, and $\frac{1}{4}$ the original concentration in 2 half lives. If we continue taking half of what we had before, we find that $\frac{1}{2}$ of $\frac{1}{4}$ is $\frac{1}{8}$, $\frac{1}{2}$ of $\frac{1}{8}$ is $\frac{1}{16}$, $\frac{1}{2}$ of $\frac{1}{16}$ is $\frac{1}{32}$, and so on. In general, the fraction remaining after n half lives is $\frac{1}{2^n}$ where n is a positive integer (whole number). So if we wanted to know how long it would take for the concentration to be reduced to $\frac{1}{3}$ of its original value, we would have to solve the problem using the longer method illustrated in Section 3.1. The fraction $\frac{1}{3}$ is not a "good" fraction -- that is, it does not correspond to an integer number of half lives.

Also, the shortcut is most convenient for first order reactions, because their half life do not change as the reactant gets used up in the reaction. While we could, in principle, apply the shortcut to reactions of zero or second order, it would not be as much of a shortcut. We could not just calculate the half life once and then multiply by the number of half lives we need, because the half life would keep changing. We would need to determine the time interval required for each half life and then add all of these times together. To illustrate the difference in half life characteristics for reactions of zero, first, and second order, consider these three reaction orders all starting out with a half life of 32 minutes. We can construct the following table showing number of elapsed half lives, fraction of reactant remaining, and total reaction time.

# of Half Lives	Fraction Remaining	Zero Order Reaction Time	First Order Reaction Time	Second Order Reaction Time
0	1	0 min	0 min	0 min
1	$\frac{1}{2}$	32 min	32 min	32 min
2	$\frac{1}{4}$	48 min	64 min	96 min
3	$\frac{1}{8}$	56 min	96 min	224 min
4	$\frac{1}{16}$	60 min	128 min	480 min
5	$\frac{1}{32}$	62 min	160 min	992 min

Notice that the fraction of reactant remaining after any number of half lives is the same for all reaction orders. However, the total reaction times are quite different when we compare the different reaction orders.

The first order is the easiest to understand, in terms of half lives. In the table above, all the half lives for this order are 32 minutes long. This is because the half life is independent of concentration, so if the first half life is 32 minutes, they all will be. Looking down the column for First Order Reaction Time, notice that each time is 32 minutes more than the one before it. If you multiply the number of half lives by 32 minutes, you get the total reaction time in the first order reaction.

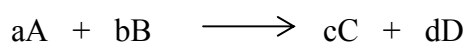
For the zero order reaction, the half life decreases with the concentration. When the concentration is only half what it used to be, the half life will only be half as long. So if the first half life is 32 minutes, the second half life will be only 16 minutes. The total reaction time over the first 2 half lives will be 48 minutes (32 minutes plus 16 minutes). The third half life will be only half as long as the second half life (16 minutes) meaning it will be only 8 minutes long. The total reaction time over the first 3 half lives will be 56 minutes (32 minutes plus 16 minutes plus 8 minutes). The fourth half life will be only half as long as the third (8 minutes) meaning it will be only 4 minutes long. The total reaction time over the first 4 half lives will be 60 minutes (32 minutes plus 16 minutes plus 8 minutes plus 4 minutes). The fifth half life will be only half as long as the fourth (4 minutes) meaning it will be only 2 minutes long. The total reaction time over the first 5 half lives will be 62 minutes (32 minutes plus 16 minutes plus 8 minutes plus 4 minutes plus 2 minutes).

For the second order reaction, the half life increases as the concentration decreases. When the concentration is only half what it used to be, the half life will be twice as long. So if the first half life is 32 minutes, the second half life will be 64 minutes. The total reaction time over the first 2 half lives will be 96 minutes (32 minutes plus 64 minutes). The third half life will be twice as long as the second half life (64 minutes) meaning it will be 128 minutes long. The total reaction time over the first 3 half lives will be 224 minutes (32 minutes plus 64 minutes plus 128 minutes). The fourth half life will be twice as long as the third (128 minutes) meaning it will be 256 minutes long. The total reaction time over the first 4 half lives will be 480 minutes (32 minutes plus 64 minutes plus 128 minutes plus 256 minutes). The fifth half life will be twice as long as the fourth (256 minutes) meaning it will be 512 minutes long.

minutes long. The total reaction time over the first 5 half lives will be 992 minutes (32 minutes plus 64 minutes plus 128 minutes plus 256 minutes plus 512 minutes).

Temperature Dependence of Reaction Rate

The temperature affects a reaction's rate -- the higher the temperature, the faster the reaction rate. In this section, we consider the manner in which the reaction rate increases with temperature. The temperature dependence of reaction rate is found in the rate constant. To see this, consider the generic reaction and rate constant



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

This reaction will have a higher rate at a higher temperature, even if we use the *same* reactant concentrations as we did at the lower temperature. Assuming the reaction orders (x and y) are the same at the higher temperature (and they should be unless the reaction somehow follows different kinetics at the higher temperature), the only way we can get a higher Rate is if the value of k is larger. Therefore, the rate constant k must be temperature dependent. The manner in which the rate constant depends on temperature is given by the Arrhenius equation:

$$k = A \cdot \exp \left[- \frac{E_a}{RT} \right]$$

In the above equation, A is a pre-exponential factor, not to be confused with [A] with brackets around it, which refers to the concentration of "substance A". The A in the above equation is called the frequency factor, because it accounts for the collision frequency of the reactant molecules. The exp part of the equation is the energy factor, and accounts for the fraction of reactant molecules that will have enough energy to react. The variable E_a is the activation energy, R is the gas constant (which has the value 8.314510 J / mol K) and T is temperature, which MUST be expressed in Kelvin units. The function exp is the inverse of the natural logarithm ln. That is, exp(x) is another way of writing e^x . It is useful when the argument of the inverse natural logarithm is a complicated function, because you can avoid having to write that function as a superscript. The pre-exponential factor or "frequency factor" is slightly temperature dependent, because at higher temperatures the molecules are moving faster and collide more often. However, the changes in collision frequency contribute only about 3% of the change in reaction rate. By far, the inverse natural logarithm term is the major contributor to the change in reaction rate as temperature is changed. Therefore, we will simplify matters and derive an approximate equation by treating A as a constant, ignoring its slight temperature dependence.

We can re-write the Arrhenius equation presented above in a form that suggests a linear plot. From this plot, we can determine the activation energy of the reaction. We begin by taking the natural logarithm of both sides of the equation. We then have

$$\ln k = \ln \left[A \cdot e \left[- \frac{E_a}{RT} \right] \right]$$

Since the log of a product is equal to the sum of the logs, we can split the frequency factor and the energy factor on the right hand side.

$$\ln k = \ln A + \left[\ln \exp \left[-\frac{E_a}{RT} \right] \right]$$

In the second term on the right hand side, the ln and exp cancel each other out because they are inverse functions. This leaves the following expression:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Now factor the fraction E_a/RT into two fractions as follows:

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

Comparing the above equation to the equation for a straight line,

$$Y = mX + b$$

we see that $\ln k$ plays the role of Y , $1/T$ plays the role of X , $-E_a/R$ plays the role of m , and $\ln A$ plays the role of b . The rate constant that is determined in those experiments only applies to the temperature at which the experiment is conducted, because rate constants are temperature dependent. If the experiments are repeated at several different temperatures, we can compile a list of temperatures and corresponding rate constants at those temperatures. We then take the natural logarithm of all the rate constants and the reciprocal of all the temperatures (which must be expressed in Kelvin units). If we then plot $\ln k$ on the Y -axis against $1/T$ on the X -axis, hopefully the points will approximately fall on a straight line. The slope of this line is $-E_a/R$. Since R is a known constant, the activation energy E_a can be calculated if the slope is measured.

$$E_a = -R \cdot \text{Slope} \quad \text{where } R = 8.314510 \text{ J / mol K}$$

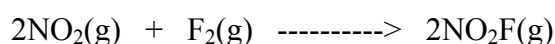
Activation energies are never negative. The line on this plot will have a negative slope, and this will cancel the negative sign in front of R , leaving a positive value for the activation energy.

The graphical method described above for determining activation energies is most useful when the rate constant has been measured at several different temperatures. If the rate constant has only been determined at two different temperatures, we might as well just calculate the activation energy algebraically. Certainly, any two points will determine a straight line. One of the principal benefits of constructing a graphical plot is that a "bad" experiment (that is, one in which errors have been made) stands out as a data point that falls out of line with the other points on the plot. The erroneous experiment can then be excluded from the calculations. Activation energies obtained from the slope of the line tend to be more

reliable than those calculated algebraically from a pair of measured temperatures and rate constants.

Reaction Mechanisms

In the concept of the rate law and reaction orders we noted that reactions can be either elementary (occur in one step) or non-elementary. For elementary reactions, the reaction orders had to match the coefficients in the balanced equation, but for non-elementary reactions, there was no necessary relationship. As an example, consider the reaction



If this reaction is elementary, its rate law would have to be

$$\text{Rate} = k [\text{NO}_2]^2 [\text{F}_2]$$

because of the requirement that reaction orders and coefficients match. However, experimental data indicate that the rate law of this reaction is

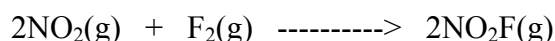
$$\text{Rate} = k [\text{NO}_2] [\text{F}_2]$$

That is, the reaction is first order in NO_2 , even though the coefficient of NO_2 is 2 in the balanced equation. This mismatch between a reaction order and a stoichiometric coefficient means that the reaction is definitely NOT elementary. If it is not elementary, then it must be the net effect of two or more other reactions that *are* elementary. With some chemical intuition, we can propose a reasonable set of chemical reactions (assumed to be elementary) by which the overall reaction might occur. Such a set of elementary reactions is called a **reaction mechanism**. To be accepted as a possibility, any reaction mechanism proposed must pass two tests:

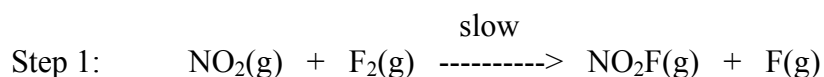
1. When added together, the individual reactions in the mechanism must produce the overall reaction in question.
2. The rate law predicted by the mechanism must agree with the experimentally determined rate law.

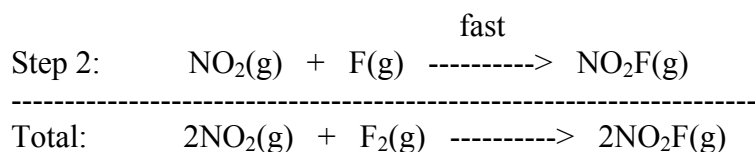
If a proposed mechanism passes both of the above tests, it *may* be the correct mechanism -- but then again, it may not be. We can never prove with absolute certainty that we have the right mechanism, though in some cases we can show that a proposed mechanism can NOT be correct, and therefore, can be ruled out. This is the scientific method in action. Because a hypothesis or theory can never be proved with absolute certainty, though in some cases, they can be disproved.

For the reaction



chemists have proposed the following 2-step mechanism





In the above mechanism, the monatomic fluorine, $\text{F}(\text{g})$ cancels out because it is both a reactant (Step 2) and a product (Step 1). Chemical species like these, that arise naturally in the course of a reaction sequence, but cancel out when the reactions are added, are called **reaction intermediates**. Thus, the $\text{F}(\text{g})$ is a reaction intermediate in this mechanism. Often, there is a big difference in reaction rates for different steps in the mechanism. In this mechanism, Step 1 has been identified as slow and Step 2 as fast. This can be justified on the basis of the unstable and highly reactive nature of monatomic fluorine. Fluorine is the most reactive of all the elements, especially when it is in monatomic form. Because fluorine is so highly reactive, we would expect to find it somewhat difficult to form it in the monatomic state, in which the F atom is not bonded to anything. Once formed, however, it would be reasonable to conclude that it will rapidly react with anything it encounters with which it is capable of reacting. It is on this basis that Step 1 has been labeled slow and Step 2 has been labeled fast.

To predict the rate law from a reaction mechanism, we need only look at the slowest step. The overall reaction, which depends on completing all the steps in the mechanism, can not be completed any faster than that slowest step can be completed. Therefore, the rate law for the slowest step will be the rate law for the overall reaction. We can write the rate law for the slowest step by inspection, because it, like all steps in the mechanism, is assumed to be elementary. In Step 1 of the proposed mechanism, the reactants are NO_2 and F_2 . Each of these substances has a coefficient of 1, so Step 1 must be first order in each. That is, the rate law predicted by the mechanism is

$$\text{Rate} = k [\text{NO}_2] [\text{F}_2]$$

This is in agreement with experimental data. While this does not absolutely prove that the reaction occurs by this mechanism, it certainly seems plausible that it might occur this way, and it explains our experimental observations. This mechanism will likely continue to be accepted by chemists unless someone uncovers new data that suggests a different mechanism for the reaction.

Suggested Readings:

- K.J.Laidler Physical Chemistry with biological application, Benjamin
- Samuel Glasston and David Lewis, Elements of Physical Chemistry, Macmilan Press, London
- Puri, Sharma Pathania Principles of Physical Chemistry Shoban Lal Nagin Chand & Co Jhalander