Collision Theory of Chemical Reactions

Do you ever wonder how reactions actually happen? What are the conditions necessary for a reaction to happen? Is it certain that a reaction will take place even after the conditions are fulfilled? The answer to all these questions is Collision Theory. Let’s understand what collision theory is and learn about the conditions mentioned in the collision theory.

Collision Theory

Collision theory basically explains how reactions occur and why different reactions have different reactions rates. It states that:

- Molecules must collide in order to react.
- In order to effectively initiate a reaction, the molecules in the collisions must have sufficient energy to bring about disruptions in the bonds of molecules.
- A rise in temperature will cause the molecules to move faster and collide more vigorously, increasing the likelihood of bond cleavages and rearrangements greatly.

- The reactions containing neutral molecules cannot take place at all until they have acquired the activation energy needed to stretch, bend or distort one or more bonds.

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- Factors Influencing Rate of a Reaction
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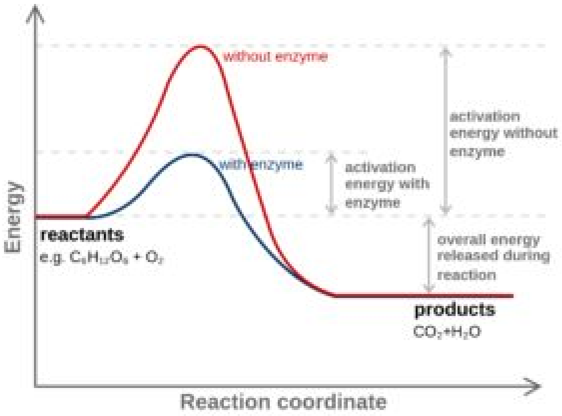
Activation Energy

Activation energy is the energy that must be overcome in order for a reaction to occur. It is the minimum energy that is required to start a chemical reaction.



Explanation of Collision Theory

As we discussed, collision theory qualitatively explains how chemical reactions occur and why different reactions have different rates. Consider a simple biomolecular step:

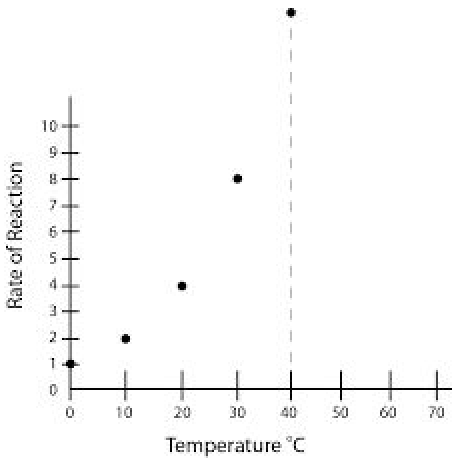
- Clearly, if two molecules A and B are to react, they must approach closely enough to disrupt some of their existing bonds and to permit the creation of new bonds that are required to form products. We call this a collision. The frequency of collision between A and B in a gas will be proportionate to the concentration of each. If we double the concentration of A, the frequency of A-B collision will double. Doubling the concentration of B will have the same effect.

- It is not enough that the molecules just collide. They need to be oriented in a specific manner that is appropriate for the process to occur. The molecules must collide with one another from the correct side. If they do not do so, the collision will not lead to the reaction.
- The molecules *must* collide with energies greater than or equal to the activation energy of the reaction. If this does not happen the reaction will not take place. The molecules need the energy to break their existing bonds and form new bonds. This is the kinetic energy that the molecules possess. If this energy is not equal to or greater than the activation energy, the reaction will not proceed.

Temperature dependence of Collison theory

Thermal energy relates direction to motion at the molecular level. As the temperature rises, the molecules move faster and collide more vigorously, therefore causing more collisions and increasing the likelihood of bond cleavages. In most cases, the activation energy is supplied in the form of thermal energy.

As the reaction is completing and products are being formed, the activation energy is returned in the form of vibrational energy which is quickly released as heat. Therefore, it very important for the molecules to collide with energies greater than or equal to the activation energy of the reaction.



Rate of Reaction according to Collison theory

For a bimolecular elementary reaction, A + B → Products, the rate of reaction is,

$$\text{Rate} = Z_{AB}\, e^{-Ea/RT}$$

where Z_{AB} represents the collision frequency of reactants A and B and $e^{-Ea/RT}$ represents the fraction of molecules with energies equal to or greater than the activation energy of the reaction. This is why different reactions have different reactions rates. Different reactions have different frequencies of reactants and different activation energies.

A collision that satisfies all the conditions in the collision theory and succeeds in forming a new product is known as an effective collision. Thus, the two important criteria in collision theory are the activation energy and proper orientation of molecules.

A Solved Question for You

Q: Mention the important criteria in order for a reaction to occur.

Solution:

- The molecules must collide.
- The molecules must have correct orientation, that is, they must collide from the correct side.
- The colliding molecules must collide with energies greater than or equal to the activation energy of the reaction.

- The molecules can be given kinetic energy in the form of thermal energy in order to increase the chance of bond cleavages.

Therefore, if all the criteria are fulfilled, the collision will lead to fruition.

Rate of a Chemical Reaction

In a chemical reaction, a substance converts into another substance under certain given conditions in a given time. It is important to know the rate of a chemical reaction to completely understand the reaction. Which are the slowest and the fastest reactions in the world? The study of the rate of a reaction is helpful in our day to day life as well. Let's learn how to calculate the rate of a chemical reaction.

Inside a Chemical Reaction

It is very important to find out the rate of a chemical reaction and the factors controlling the rate of reaction. This information is useful in our daily life as well. For example, we need to the know the rate at which food cooks to know when we have to stop the cooking process and prevent burning of food. Doctors need to design a rapidly filling setting material for a dental filling. We need to know at what rate the fuel in a vehicle burns.

The branch of chemistry which deals with the study of reaction rates and their mechanisms is called Chemical Kinetics. Thermodynamics can only tell the feasibility of a chemical reaction whereas chemical kinetics tells about the rate of a chemical reaction. Chemical kinetics not only helps in finding the rate of a chemical reaction but also the factors influencing the rate such as concentration, temperature, pressure and a catalyst.

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- Factors Influencing Rate of a Reaction
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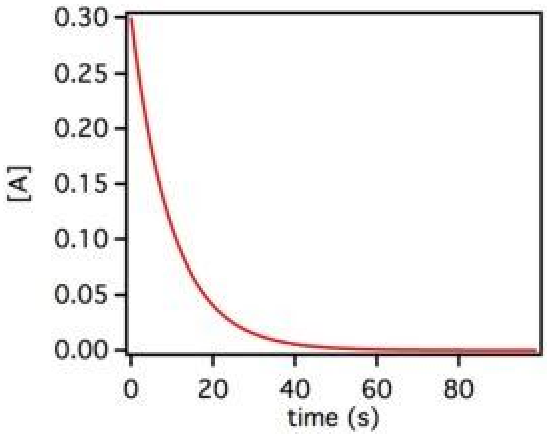
Rate of a Chemical Reaction

Some reactions happen very fast like the precipitation of silver chloride. It occurs immediately after mixing aqueous solutions of silver nitrate and sodium chloride. On the other hand, some reactions are very slow like the rusting of iron in the presence of air and moisture. Some chemical reactions are neither slow nor fast but take place at a moderate rate.



The speed or rate of a chemical reaction is the change in concentration of a reactant or product per unit time. To be specific, it can be expressed in terms of:

- the rate of decrease in concentration of any of the reactants
- the rate of increase in the concentration of any of the products

Let's understand the rate of a chemical reaction better. Consider a reaction in which the total volume of the system remains constant. Let R be the reactants and P be the products i.e. R → P

Thus, one mole of reactant R produces one mole of product P. Let the initial concentration of R be $[R]_1$ and the concentration of P be $[P]_1$ at time t_1. Therefore at time t_2, the concentrations of R and P are $[R]_2$ and $[P]_2$ respectively. Therefore,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$$\Delta[P] = [P]_2 - [P]_1$$

(The square brackets represent the molar concentrations)

Equation of Rate of a Chemical Reaction

Rate of disappearance of R = Decrease in concentration of R/time taken = $-\Delta[R]/\Delta t$

and, rate of appearance of P = Increase in concentration of P/time taken = $+ \Delta[P]/\Delta t$

$\Delta[R]$ is a negative quantity because the concentration of the reactants is decreasing while $\Delta[P]$ is a positive quantity because the concentration of the products is increasing. While performing calculations on the rate of a chemical reaction, we multiply $\Delta[R]$ by -1 to make it a positive quantity. The above equations give the average rate of a chemical reaction which is, r_{av}.

Therefore, the average rate of a reaction depends upon the change in concentrations of the reactants or products and the time taken for that change to occur.

Unit of Rate of a Chemical Reaction

It is clear from equations I and II that the unit of rate of a reaction is concentration time^{-1}. But if the concentration is in mol L^{-1} and time is in second then the unit will be mol L$^{–1}$ s$^{–1}$. In case of gases, the rate of a chemical reaction will be atm s^{-1} when the concentration of gases is expressed in their partial pressures.

Solved Questions For You

Q1: Define average rate of a chemical reaction.

Solution: The average rate of a chemical reaction is the change in the concentration of the reactant or product divided by the time taken for that reaction to occur.

Q2: Derive formula of the rate of reaction for the reaction given below:

$$2Na + Cl_2 \rightarrow 2NaCl$$

Solution: The rate of a reaction is the change in concentration of the reactant or product divided by the change in time.Therefore, the formula of rate of reaction for the above reaction would be:

$$\text{Rate of reaction} = -(1/2)\Delta[Na]/\Delta t = -\Delta[Cl]/\Delta t = +(1/2)[NaCl]/\Delta t$$

Integrated Rate Equations

You must already know that calculating the rate of a reaction is extremely important to understand the reaction. But it also necessary to infer the rate law of a reaction to find out the order of the reaction. But what is the order of a reaction you ask? Let’s find out below and also learn about the different types of reactions.

Rate Law

We know that the rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be equal to the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Consider a general reaction, aA + bB → cC + dD where a, b, c, d are the stoichiometric coefficients of the reactants and the products. Therefore, the rate law for the above reaction is,

Rate

$\propto$

$$[A]_x\ [B]_y$$

where x and y may or may not be equal to the stoichiometric coefficients of the reactants. Therefore, the rate of the reaction is equal to k $[A]_x\ [B]_y$, where k is the rate constant.

$$\therefore\ -d[R]/dt = k\ [A]_x\ [B]_y$$

Order of Reaction

The order of a reaction is the sum of the powers of the concentrations of the reactants in the rate law expression. In the above general reaction, x and y are the powers. The sum of them will give the order of the reaction. Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero-order reaction means that the rate of the reaction is *independent* of the concentration of reactants.

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Zero Order Reaction

So we already know that in a zero order reaction, the rate is independent of the concentration of the reactants. Thus, it means the sum of the powers of the concentrations is zero. It can only be zero when the all the powers are zero. Consider a reaction, R → P. Therefore, the rate law of this reaction is,

Rate

$\propto$

$$[R]_0$$

$$\therefore \text{Rate} = -d[R]/dt = k[R]_0 = k \times 1$$

$$\therefore \text{Rate} = -d[R]/dt = k$$

$$\therefore d[R] = -kdt$$

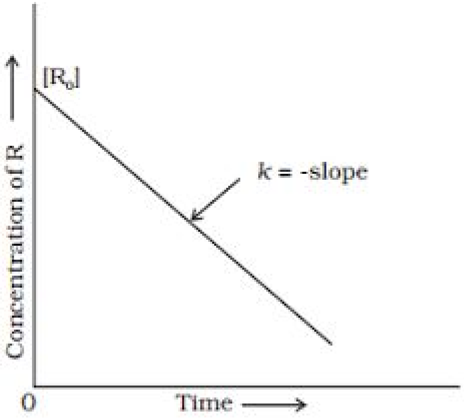
Integrating both sides, $[R] = -kt + I$……………….(I) where I is the constant if integration. At t = 0, the concentration of the reactant R = $[R]_0$. Where $[R]_0$ is the initial concentration of the reactant. Substituting this value in the equation I,

$$[R]_0 = -k \times 0 + I = I$$

Substituting this value of I in the equation (I), we get

$$[R] = -kt + [R]_0 \ldots\ldots\ldots\ldots\ldots\ldots(II)$$

Comparing equation II with the equation of a straight line y= mx +c, if we plot [R] against t, we get a straight line with slope = -k and intercept = $[R]_0$



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Therefore, on simplifying equation II, we get

$$k = \{[R]_0 - [R]\}/t \ldots\ldots\ldots\ldots\ldots\ldots (III)$$

Example of Zero Order Reaction

Zero-order reactions are very uncommon but they occur under certain condition. An example of a zero-order reaction is decomposition of ammonia, $2NH_3 \rightarrow N_2 + 3H_2$

$$Rate = k[NH_3]_0 = k$$

First Order Reaction

In this type of reaction, the sum of the powers of concentrations of reactants in rate law is equal to 1, that is the rate of the reaction is proportional to the first power of the concentration of the reactant. Consider the reaction R → P again. Therefore, the rate law for this reaction is,

Rate

$\propto$

[R]

We know that $[R] = -kt + [R]_0$ (from equation II). Taking log of both sides, we get

$\ln[R] = -kt + \ln[R]_0$ …………………………….(IV)

$\therefore \ln[R]/[R]_0 = -kt$ ……………………………….(V)

$\therefore k = (1/t) \ln [R]_0 /[R]$ ……………………….(VI)

Now, consider equation II again. At time t_1 and time t_2, the equation II will be $[R]_1 = -kt_1 + [R]_0$ and $[R]_2 = -kt_2 + [R]_0$ respectively, where $[R]_1$ and $[R]_2$ are concentrations of the reactants at time t_1 and t_2 respectively. Subtracting second equation from first one, we get

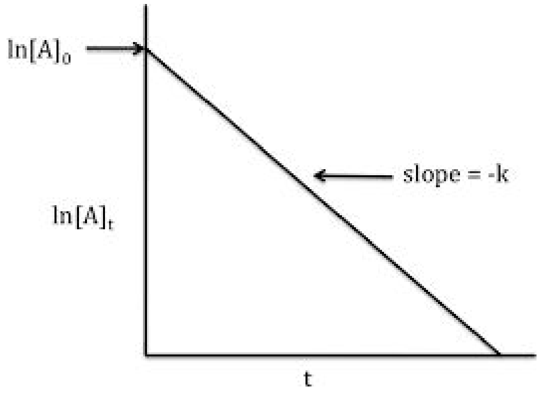
$$\ln [R]_1 - \ln[R]_2 = -kt_1 - (- kt_2)$$

$$\therefore \ln[R]_1 /[R]_2 = k (t_2 - t_1)$$

$$\therefore k = [1/(t_2 - t_1)] \ln[R]_1 /[R]_2$$

Now, taking antilog of both sides of equation V, we get $[R] = [R]_0e^{-kt}$

Comparing this equation with equation of a straight line y = mx + c, if we plot ln [R] against t, we get a straight line with slope = -k and intercept = $\ln[R]_0$



(Source: nonsibihighschool.org)

On removing natural logarithm from equation VI, the first-order reaction can also be written as,

$$k = 2.303/t \log[R]_0/[R] \ldots\ldots\ldots\ldots.(VII)$$

If we plot a graph of $\log[R]_0/[R]$ against t, we get slope = k/2.303

Example of First Order Reaction

An example of a first-order reaction is the hydrogenation of ethene.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

Therefore the rate of reaction for the above is k [C_2H_4]. Hence, equations III and VII are the equations of rate constants of zero and first order reactions respectively. We can find rate constants, initial and final concentrations and the time taken for the reaction to occur using these reactions.

A Solved Question for You

Q: The order of a reaction is:

a) can never be zero b) can never be a fraction

c) must be a whole number only d) can be a whole number or a fraction or zero

Solution: d) can be a whole number or a fraction or zero. It depends on the dependency of the rate of reaction on the reactants. If the rate is independent of the reactants, then the order of reaction is zero. Therefore, the rate law of a zero order reaction would be rate α $[R]_0$ where [R] is the concentration of the reactant.

Pseudo First Order Reaction

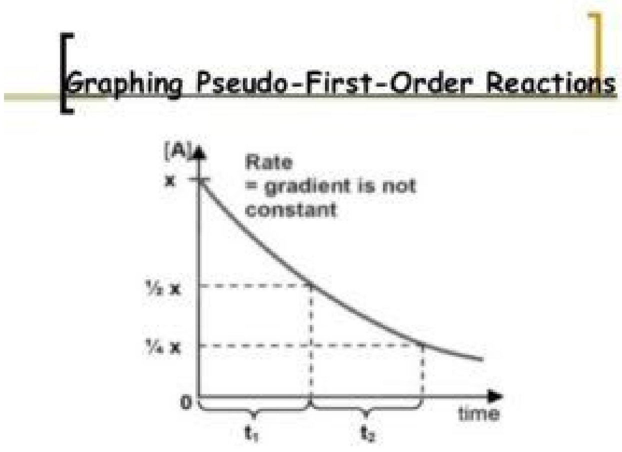
Sometimes adults ‘fake’ being younger when they’re actually way older. Isn’t it? Did you know we can ‘fake’ in chemistry as well? Yes, a reaction whose order of reaction is actually more than one can ‘fake’ being a first order reaction. This type of reaction is known as a pseudo first order reaction. Let’s understand what a pseudo first order reaction is and how it ‘fakes’ being a first order reaction.

Pseudo First Order Reaction

We know that order of reaction depends on the dependency of the rate of reaction on the concentration of reactants. That is if the rate is independent of the concentrations of reactants, the order of reaction is zero. Similarly, if the rate of reaction is proportional to the first power of the concentration of the reactant, then the order of reaction is one.

But sometimes the order of a reaction can be made to alter by changing the concentration of the reactants, that is, increasing or decreasing the concentration of one or the other reactant.

Learn about the Temperature dependence of the Rate of reaction.



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A reaction which is not first-order reaction naturally but made first order by increasing or decreasing the concentration of one or the other reactant is known as Pseudo first order reaction. Pseudo means ‘fake’.

Therefore, it is clear from the name itself that it is not first-order reaction by nature. The order of reaction is made one by altering certain conditions. Let’s understand more about pseudo-first order reactions with some examples.

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Learn 5 Main types of Organic Reaction here.

Examples of Pseudo First Order Reaction

- Consider a reaction in which one reactant is in excess, say hydrolysis of ethyl acetate. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, the reaction goes like this,

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

Time	$CH_3COOC_2H_5$	H_2O	CH_3COOH	C_2H_5OH
t = 0	0.01 mol	10 mol	o mol	0 mol
t	0 mol	9.9 mol	0.01 mol	0.01 mol

As the concentration of water does not get altered much during the process (because it is in excess), we can take it as constant. So in the rate equation, Rate = k′ $[CH_3COOC_2H_5]$ $[H_2O]$ the term $[H_2O]$ can be taken constant. Thus, the equation becomes

$$\text{Rate} = k\,[CH_3COOC_2H_5] \text{ where } k = k'[H_2O]$$

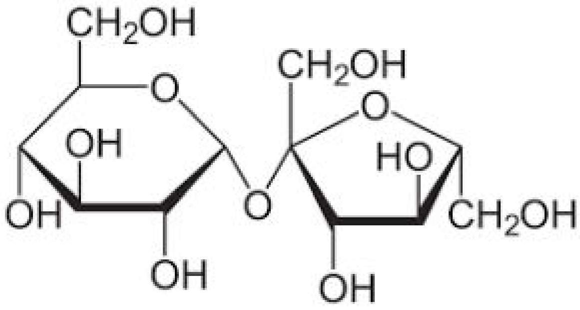
Therefore, the order of reaction now becomes one, that is the reaction is now first order reaction. Such reactions are called pseudo-first order reactions.

- Another example of pseudo first-order reaction is the inversion of cane sugar.

$C_{12}H_{22}O_{11}$ + H_2O → $C_6H_{12}O_6$ + $C_6H_{12}O_6$

Cane sugar Glucose Fructose

Rate = $k[C_{12}H_{22}O_{11}]$



(Source: en.wikipedia.org)

In pseudo-first order reactions, we are basically isolating a reactant by increasing the concentration of the other reactants. When the other reactants are in excess, change in their concentrations does not affect the reaction much, Therefore, now the reaction only depends on the concentration of the isolated reactant. The concentrations of all the other reactants are taken as constant in the rate law. Thus, the order of reaction becomes one.

Difference Between Pseudo First Order Reaction and First Order Reaction

The main difference is obviously that, in a first order reaction, the order of reaction is one by nature. A pseudo first-order reaction is second order reaction by nature but has been altered to make it a first order reaction.

The second difference is that in a first order reaction, the rate of reaction depends on all the reactants whereas, in a pseudo-first-order reaction, the rate of reaction depends only on the isolated reactant since a difference in concentration of the reactant in excess will not affect the reaction.

A Solved Question for You

Q: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

The rate law for the above equation is:

a) $r = k[C_{12}H_{22}O_{11}]\,[H_2O]$ b) $r = k[C_{12}H_{22}O_{11}]$

c) $r = k[H_2O]$ d) $r = k[C_{12}H_{22}O_{11}]\,[H_2O]^2$

Solution: b) r = k[$C_{12}H_{22}O_{11}$]. In the reaction, $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$, water is present in large excess. Hence, it will not appear in the rate law expression. Thus, it is an example of pseudo first order reaction.

Factors Influencing Rate of a Reaction

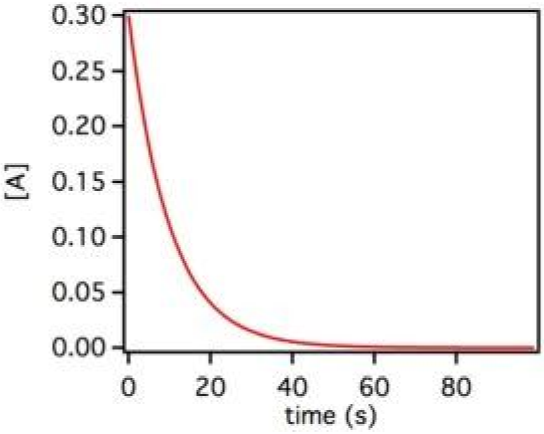
We all know how to warm milk, right? When the gas stove is at low temperature, the milk heats very slowly but as soon as we increase the temperature, the milk starts heating up quickly, that is, the rate increases. In this case, temperature is the factor influencing the rate of reaction. Let's learn about all the other factors that influence the rate of a reaction and how they affect the rate.

Rate of Reaction

The study of the rate of reaction and factors affecting the rate of reaction is known as Chemical Kinetics. We can measure the rate of a chemical reaction by measuring either:

- how quickly a reactant is consumed
- how quickly a product is formed

Therefore, the rate of a reaction is the change in concentration of a reactant or a product over a certain period of time.



Factors influencing the Rate of Reaction

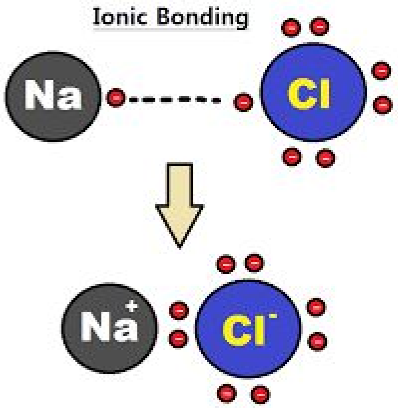
Chemical reactions only happen when the reactant molecules collide with one another. This is known as the Collision theory of Chemical Kinetics. The collision states that, in order for a reaction to happen, the reactants must collide with sufficient energy that is greater than the activation energy E_a.

But there are some factors which can influence the rate of reaction, that is, increase the fraction of molecules with energies more than activation energy E_a. There are four factors that influence the rate of a reaction. These are:

1) The Nature of the Reactants

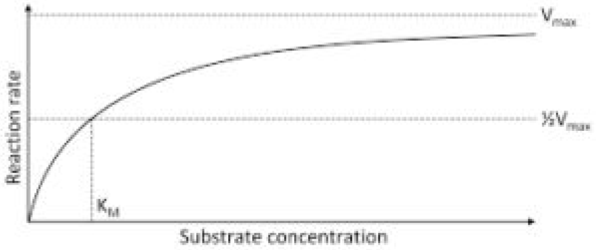
Chemical reactions in an aqueous solution take place almost immediately. It is because the molecular bonds in the molecules of reactants are broken down. The attractive forces between the ions are broken and the ions become hydrated by the water molecules.

Additionally, most ions exert attractive forces equally in all directions. Usually, no covalent bonds need to be broken in these cases. In contrast, reactions between molecules that require covalent bonds to be broken tend to proceed very slowly. Therefore, certain structural characteristics of the reactant molecules, such as bond polarity, geometry, overall size and orientation *influence* the rate of reaction.



2) The Concentration of the Reactants

We know that for most reactions, the rate of reaction will *increase* as the concentration of the reactants *increases*. Increasing the concentration of a reactant means increasing the number of reactant molecules that are in that same volume.

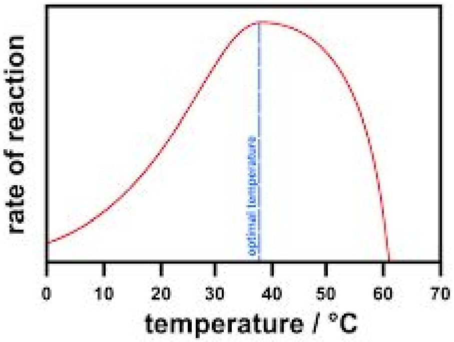


For many reactions (not all), there is a direct relationship between the concentration and rate of reaction. Therefore, when the concentration doubles, the rate of reaction also doubles. We can explain this using the collision theory which says that if we double the number of reactant molecules, there will be twice as many collisions occurring at the same time.

3) The Temperature of the Reactants

In nearly all cases, the rate of a reaction increases with increasing temperature. Each time the temperature is increased by 10°, the rate of reaction doubles! This effect is extremely powerful. For instance, for a rise in temperature from 20° to 80°(which is six 10° increments), the rate of reaction will occur $2^6 = 64$ times faster. That is a great change in rate.

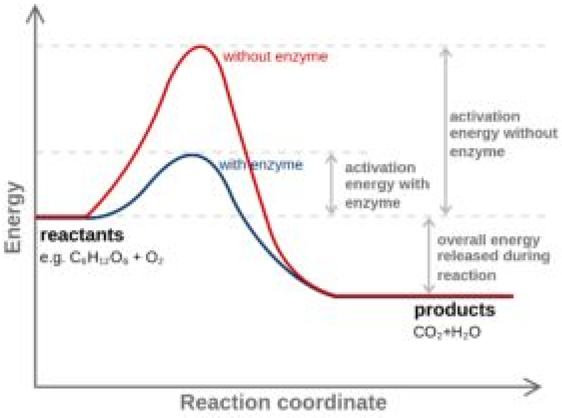
We can also explain this with the Collision theory: the average kinetic energy of all molecules is a direct function of temperature. The molecules collide with a greater energy, that is, their activation energy decreases.



We already know the dependence of the rate of reaction on temperature can be explained by Arrhenius equation which is, $k = A e^{-Ea/RT}$ where $e^{-Ea/RT}$ is the number of molecules with energies greater than the activation energy.

4) The Presence of a Catalyst

A Catalyst is a substance that increases the rate of reaction without actually participating in the reaction. Catalysts work by providing an alternate pathway for the reaction. It is the one which requires less energy for the reactants to convert into products. Some catalysts increase the rate of more than one type of reactions whereas catalyst like the enzymes in our bodies is specific to just one reaction or even one single type of reactant molecule. Therefore, a catalyst increases the rate of reaction.



A Solved Question for You

Q: How does concentration affect the rate of reaction?

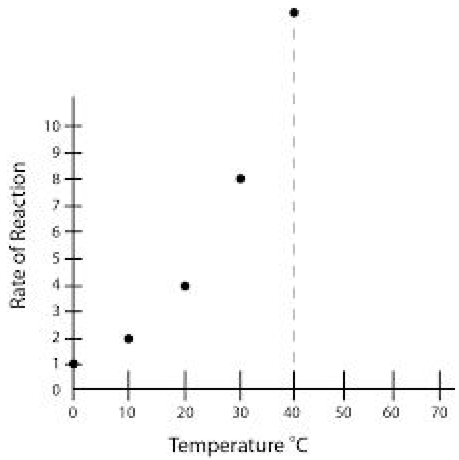
Solution: According to Collision theory, increasing the number of reactant molecules will increase the number of collisions taking place for a reaction to happen. In the same way, increasing the concentration, that is, increasing the number of reactant molecules in the solution will increase the number of collisions taking place in the solution. Thus, the rate of the reaction will increase.

Temperature Dependence of the Rate of a Reaction

While cooking, if we keep the gas on low temperature, the food cooks slowly. But when we increase the temperature to its maximum, the food cooks quickly. Therefore, temperature increases the rate of a reaction. This dependence of rate on temperature can be explained by Arrhenius equation. Let's learn about and deduce this equation.

Temperature and Rate – the Relationship

By now, we know that temperature influences the rate of a reaction. As the temperature increases, the rate of a reaction increases. For example, the time taken to melt a metal will be much higher at a lower temperature but it will decrease as soon as we increase the temperature. It has been found that the rate constant is nearly *doubled* for a chemical reaction with a rise in temperature by 10°.



We can explain the dependence of the rate of a chemical reaction on temperature by Arrhenius equation.

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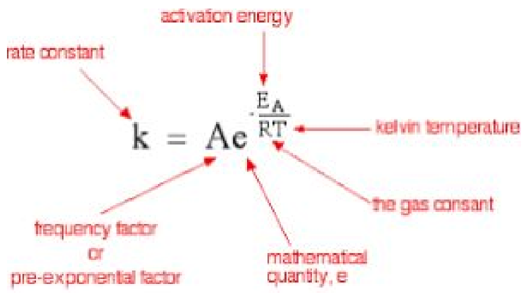
Arrhenius Equation

The equation was first proposed by Dutch chemist, J.H. Van’t Hoff but Swedish chemist, Arrhenius provided its physical justification and interpretation. The Arrhenius equation is based on the Collision theory. It is not an equation that is born out of pure math that we can derive. It is an empirical equation that fits experimental data in most of the situations. The Arrhenius equation looks like this,

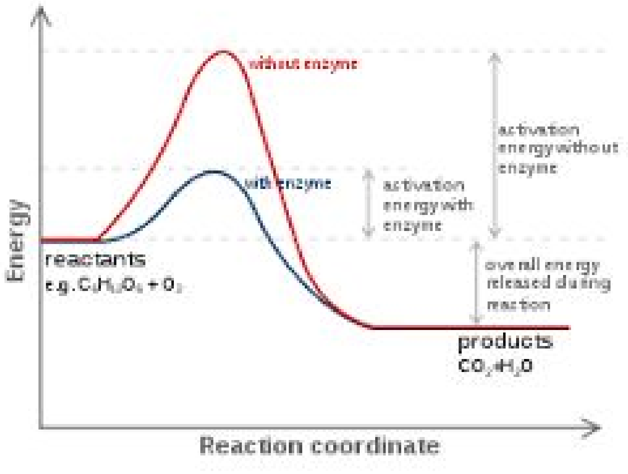
$$k = \mathrm{A}\ e^{-E_a/RT} \ldots\ldots\ldots\ldots\ldots\text{(I)}$$



(Source: chemguide.co.uk)

where A is the Arrhenius factor or the frequency factor. It is also known as the pre-exponential factor. This constant is specific to a particular reaction. R is the gas constant and E_a is the activation energy which we measure in joules/mole.

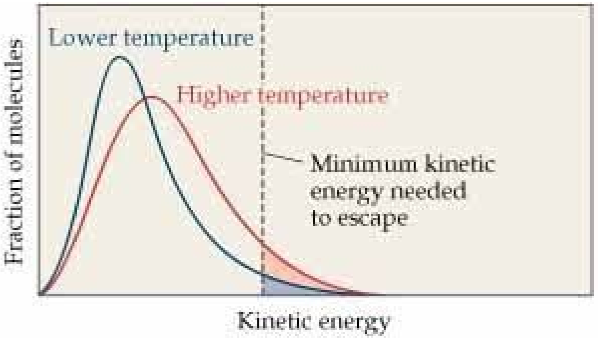
According to the Arrhenius equation, a reaction can only take place when a molecule of one substance collides with the molecule of another to form an unstable intermediate. This intermediate exists for a very short time and then breaks up to form two molecules of the product. The energy required to form this intermediate is known as activation energy (E_a).



(Source: en.wikipedia.org)

In a graph of potential energy vs reaction coordinate, the reaction coordinate represents the profile of energy change when reactants change into products. Some of the energy releases when the complex decomposes to form products. Therefore, the final enthalpy of the reactions depends only on the nature of the reactants and products.

Obviously, all the molecules do not have the same energy. The distribution of kinetic energy can be described by plotting the fraction of molecules with given kinetic energy vs kinetic energy. The peak of the curve in the graph corresponds to the most probable kinetic energy. When the temperature increases, the maximum of the curve moves to the higher energy value. Therefore, the curve broadens.



(Source: wps.prenhall.com)

Increasing the temperature increases the fraction of molecules, which collide with energies greater than the activation energy E_a.

Temperature dependence of Rate of Reaction in Arrhenius Equation

In Arrhenius equation, the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules colliding with activation energies more than E_a. Taking natural logarithms of both sides of the equation I, we get,

$$\ln k = -E_a/RT + \ln A \text{ …………..(II)}$$

Therefore, from the Arrhenius equation, we can find that increasing the temperature or decreasing the activation energy will result in an increase in the rate of the reaction and an exponential increase in the rate constant. In a graph of activation energy vs rate of reaction, slope $= -E_a/R$ and intercept $= \ln A$.

At temperature T_1, equation II will be

$\ln k_1 = -E_a/RT_1 + \ln A$ …………………(III)

At temperature T_2 , equation II will be

$\ln k_2 = -E_a/RT_2 + \ln A$ …………………(IV) (k_1 and k_2 are the rate constants at temperature T_1 and T_2)

Subtracting equation III from equation IV, we get

$\ln k_2 - \ln k_1 = E_a/RT_1 - E_a/RT_2$

$\therefore \ln k_2 / k_1 = (E_a /R)[1/T_1 - 1/T_2]$

$\therefore \log k_2 / k_1 = (E_a /2.303R)[(T_2 - T_1)/T_1T_2]$

A Solved Question for You

Q: Why does the rate of a reaction increase when the temperature increases?

Solution: When the temperature increases, the fraction of molecules that have kinetic energies more than the activation energy of the reaction increases. Therefore, the total activation energy of the reaction decreases. Thus, the rate of the reaction increases.