

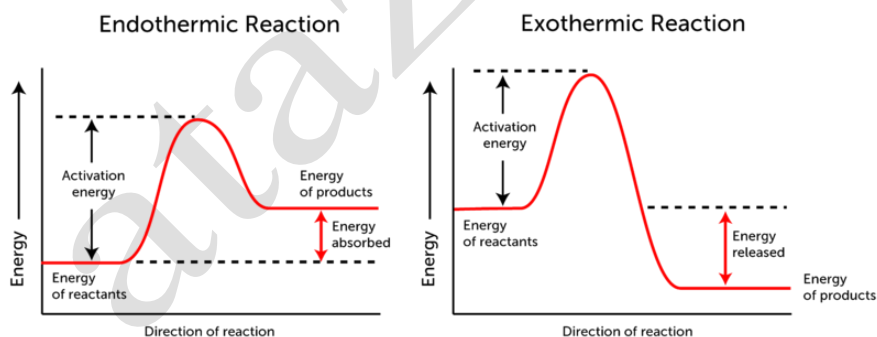
### Reason for considering slowest step as rate determining step

Imagine you have a cycle factory and there are various parts for assembling. If paddle of cycle takes 10 hrs for completion and rest all the parts takes less than 1 hr then in one day one can assemble only two cycle (assuming factory runs for 20 hrs) because in 20 hrs only paddle for two cycle are produced. Similarly until the slowest step of reaction is completed products cannot be formed. Hence, slowest step is considered as Rate Determining step.

### Difference between Order and Molecularity

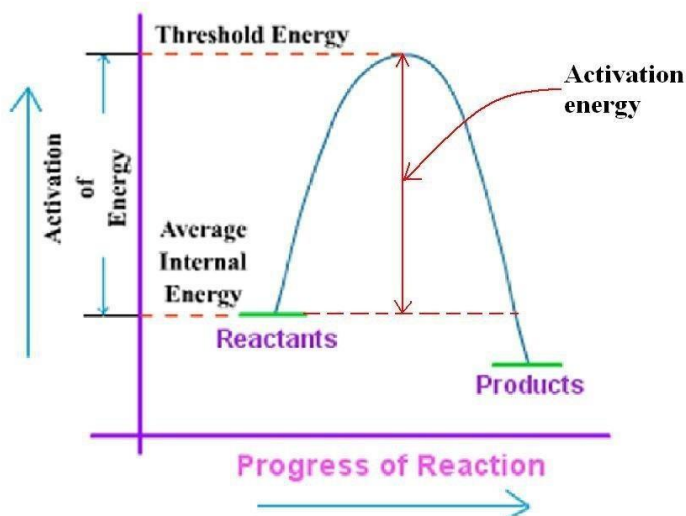
Molecularity	Order
It is the number of reacting species undergoing simultaneous collision	It is the sum of the powers of the concentration terms in the rate law expression
It is a theoretical concept	It is experimentally determined
It has integral values only	It can have fractional values also
It cannot be zero	It can be zero
It provides no information on reaction mechanism	The slowest step in the reaction can be judged by the order of the reaction and this gives further information about the mechanism

### Activation Energy



Energy given to the reactant to reach the threshold value of energy is called as activation energy.

## Threshold Energy



It is the minimum amount of energy at which reaction takes place.

### Average kinetic energy of a reaction

As the temperature of a system increases, the reaction rate increases. Temperature ( $T$ ) is a measure of the average kinetic energy of the particles of a substance. At higher  $T$ , the fraction of molecules with energies greater than the activation energy ( $E_a$ ) increase.

### Effect of temperature on rate constant

Temperature is considered a major factor that affects the rate of a chemical reaction. It is considered a source of energy in order to have a chemical reaction occur. Arrhenius, a Swedish chemist, believed that the reactants in a chemical reaction needed to gain a small amount of energy in order to become products. He called this type of energy the activation energy. The amount of energy used in the reaction is known to be greater than the activation energy in the reaction. Arrhenius came up with an equation that demonstrated that rate constants of different kinds of chemical reactions varied with temperature. This equation indicates a rate constant that has a proportional relationship with temperature.

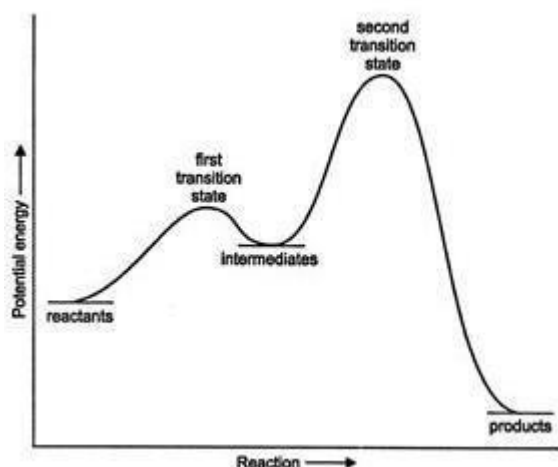
### Most probable kinetic energy

Kinetic energy of maximum fraction of molecule is known as most probable kinetic energy. It is important to note that with increase of temperature, peak shifts forward but downward. This means that with increase of temperature, (i) most probable kinetic energy increases. (ii) the fractions of molecules possessing most probable kinetic energy decreases.

### Effect of catalyst on rate of reaction

A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change. A catalyst provides an alternate path to a reaction which has relatively less activation energy. As we already know that lower activation energy means Higher rate constant (from Arrhenius equation), hence, higher rate of reaction.

### Intermediate complex formation theory



A reaction intermediate or an intermediate is a molecular entity that is formed from the reactants (or preceding intermediates) and reacts further to give the directly observed products of a chemical reaction. Most chemical reactions are stepwise, that is they take more than one elementary step to complete. An intermediate is the reaction product of each of these steps, except for the last one, which forms the final product. Reactive intermediates are usually short lived and are very seldom isolated. Also, owing to the short lifetime, they do not remain in the product mixture.

### **Adsorption theory of catalysts**

Adsorption theory: According to this theory, reactants are adsorbed on the surface of the catalyst and form a film. Due to high concentration of the reactants on the film, reaction proceeds at a faster rate.

Modern adsorption theory: According to this theory, reactants are adsorbed at the active centers i.e. free valencies etc. on the solid surface and form activated complex which under strain forms new molecules and leaves the surface. This explains, why the finely divided catalyst has greater activity.

### **Describe different methods for increasing the catalytic activity of the catalyst**

There are following methods to increase activity of the catalyst :

1. Treatment by hydrogen enhance catalytic activity.
2. Treatment by high temperature.

### **Characteristics of a catalyst and a catalysed reaction**

The catalyst remains unchanged (in mass and chemical composition ) in the reaction (Activity of catalyst). A small quantity of the catalyst is required. e.g. One mole of colloid Pt catalysis. The catalyst does not change the equilibrium constant. But the equilibrium approaches earlier.  
Characteristic of catalytic reaction : Catalysis reactions are catalyst dependent.

### **Collision theory of chemical reactions**

The collision theory explains that gas-phase chemical reactions occur when molecules collide with sufficient kinetic energy. The collision theory is based on the kinetic theory of gases; therefore only dealing with gas-phase chemical reactions are dealt with.

### **Collision Frequency**

According to Collision theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

### Orientation and energy factor affecting the number of effective collision

When the chemical reaction occurs, the reactant molecules collide with each other with sufficient energy and correct orientation due to which desired products form. If the orientation is not proper, products do not form. The energy of activation of reactant molecules should be same to achieve activation state.

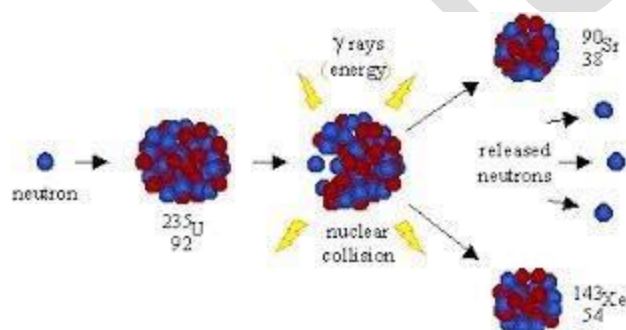
### Limitations of collision theory

Collision theory does not provide any prediction of steric factor. Calculated value for rate constant is usually too high for measured value. Measured activation energies are lower than the energies of bond.

### Transition state theory

Transition state theory (TST) explains the reaction rates of elementary chemical reactions. The theory assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated transition state complexes. TST is used primarily to understand qualitatively how chemical reactions take place.

### Nuclear Chemistry

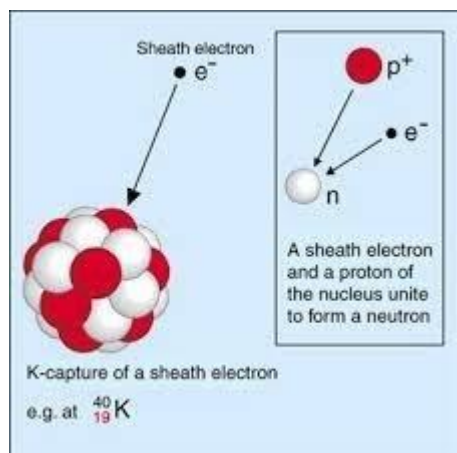


It is the chemistry of radioactive elements such as the Actinides, Radium and Radon together with the chemistry associated with equipment (such as nuclear) which are designed to perform nuclear processes.

### Radioisotopes

The radioisotope is the isotopic element which has an unstable nucleus and emits radiation during its decay when it converts into its stable form.

## K capture



In some nuclides, the nucleus may capture an electron from K shell. The vacancy created during this can be filled by electron from higher levels giving rise to characteristic X-rays. This process is known as K-electron capture. An example of K capture is

### Activity and specific activity

It is a activity per quantity of a radio nucleotide and is a physical property of that radionuclide. Activity is a quantity related to radioactivity. The SI unit of activity is the Becquerel (Bq), equal to one reciprocal second.

### Average life period of radio-active elements

Average life period of the radioactive elements is expected to be somewhat longer than the half-life. If in a given radioactive element, half of its elements have decayed after one half life, some well-defined average life expectancy can be assumed which is the mean life of the atoms.

### Nuclear chemistry

Nuclear chemistry is the subfield of chemistry dealing with radioactivity, nuclear processes and nuclear properties. It includes the study of the production and use of radioactive sources for a range of processes.

### Chemical Kinetics

The study of rates of reactions, mechanism of the reaction and factors affecting the rate of reaction is named as Chemical Kinetics.

### Unit of rate of reaction

Rate of reaction generally has the units as moles per liter per sec.

### Reactions on the basis of rates

On the basis of rate of reaction chemical reaction can be classified as fast reactions (ionic reactions) and very very slow reactions (ex. rusting of iron). Fast reactions are generally completed in a matter of second while very very slow reactions might take years to complete.

### Difference in rates of the reaction

1. A reaction involves the breaking and making of bonds. Since different bonds require different amounts of energy for breaking and different amounts of energies are evolved when different kinds of new bonds are formed, the rates of different reactions are different.
2. Another reason is due to activation energy.

### Significance of positive and negative sign in the rate of a reaction

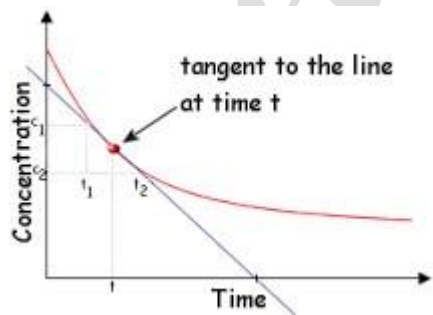
The positive sign shows that rate of formation of product where as the negative sign shows that rate of disappearance of reactant in rate of reaction.

### Calculate rate of a reaction reaction

Average rate = change in concentration of a species/change in time.

Instantaneous rate = The rate of reaction at instant rate.

### Rate of reaction from concentration versus graph



A tangent is drawn to the curve at the time  $t_1$ , at which the rate of reaction is to be determined. The negative slope of the tangent to the reactant concentration versus time is the instantaneous

rate of consumption of the reactant at time  $t_1$ . The positive slope of the tangent to the curve of product concentration versus time is the instantaneous rate of formation of the product.

### **Significance of positive and negative slopes in rates of reaction**

The negative slopes indicate reactant concentration, i.e. consumption of reactant.

The positive slopes indicate rate of formation of product.

### **Law of mass action**

The law of mass action is a mathematical model that explains and predicts behaviours of solution in dynamic equilibrium. It states that the rate of a chemical reaction is directly proportional to the product of the masses of the reactants.

Necessarily, this implies that for a chemical reaction mixture that is in equilibrium, the ratio between the concentration of reactants and products is constant.

### **Active masses**

The concentration of a reacting substance expressed usually in moles per liter the concentration of the portion of a dissolved electrolyte that is dissociated into ions and is capable of carrying the electric current.

### **Rate Law**

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 same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

### **Characteristics of Rate Constant**

Rate constant is a constant and does not depend on concentration of reactants. However, it depend on temperature of reaction. One can predict the order of reaction by units of rate constant.



### Differentiate between rate law and law of mass action

Rate law applies to speed of reaction. Law of mass action applies to extent of reaction. The rate law is concerned with the velocity or rate of a reaction. The law of mass action is concerned with the position of equilibrium in a reversible reaction i.e. at equilibrium both forward and back reactions are taking place at equal rates. The law of mass action says nothing about this rate but only tells us what the reactant and product concentrations will be at equilibrium.

### Application of Rate Law

Rate Law of a reaction can be predicted only from experimental data. Once rate law is derived then one can predict order of the reaction. Also we can predict rate of disappearance of some reactant with the help of rate law.

### Order of a reaction

$$r = k[A]^x[B]^y.$$

The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

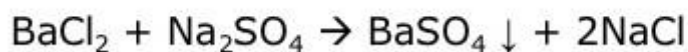
For example: (see figure) order of reaction will be  $x+y$ .

### Application of Order of reaction

If, order of reaction is known we can predict rate of reaction if concentration of reactant is changed. Also if order is known one can predict the mechanism of the reaction.

### Elementary Reaction

Barium chloride gives a white precipitate of barium sulphate and sodium chloride.



An "elementary reaction" is a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step and with a single transition state. In an elementary reaction stoichiometry coefficients of reactants are order with respect to that particular reactant. Example ionic exchange reaction which occur almost instantly.

## Complex reactions

Complex reaction mechanisms can consist of a number of electron transfer steps, with some chemical steps preceding or succeeding the electron transfer steps or taking place in between them. Most organic electrochemical reactions are complex, involving large numbers of electrons in the overall reaction. In these kinds of reaction order of reaction is determined by observing the slowest step or rate determining step.

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