Chemical Kinetics

Chemical kinetics is the science about rates and mechanisms of chemical reactions.

Tasks of chemical kinetics:

1. The establishment of factors affecting rates of chemical reactions.

2. The establishment of mechanism of chemical reactions.

Basic Concepts of Chemical Kinetics. Simple and Complex Reactions

Simple reactions have one step and their stoichiometric equations exactly express the real process.

For example: $NO_2 + NO_2 = N_2O_4$

Complex reactions have several steps and their stoichiometric equations don′t express the real process which consists from several steps.

For example: $H_2O_2 + 2HI = I_2 + 2H_2O$

The first step $H_2O_2 + HI = HOI + H_2O$

The second step $\underline{HOI + HI = I_2 + H_2O}$

$$H_2O_2 + 2HI = I_2 + 2H_2O$$

Most reactions are complex. The mechanism of every chemical reaction is determined by the sum of steps. Every individual step of mechanism of chemical reaction is called a simple reaction.

Homogeneous and heterogeneous reactions.

ü Homogeneous reaction refers to reaction occurring amongst species present in the same phase, or in liquid and gaseous solutions.

$$N_2 + O_2 \xrightarrow{t} 2NO$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

ü When different phases occur, for example between two immiscible liquids or a solid and a liquid, the reaction is referred to as heterogeneous. The reaction can occur only at the surface of contact of the two phases.

For example: $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$.

Rates of Reactions

Chemical reactions proceed at different rates. The reaction of neutralization between aqueous acids and bases occurs almost instantaneously, while the rusting of iron is slow.

The rates of chemical processes in vivo differ greatly. The time of the total renewal of bone tissue is 4-7 years, the time of a half proteins renewal –

70 days, chemical reactions responsible for neural activity run instantly.

The rate of chemical reaction is a basic concept in chemical kinetics.

The average rate of a reaction can be measured by the change of molar concentration of one of the reactants or products per unit time.

$$V = \pm\frac{\Delta C}{\Delta t}$$

" + " DC of products;

" – " DC of reactants.

ΔC is the change of concentration in mole /liter;

Δt is the change of time in sec., min., hour;

$$[V] = [\frac{mol}{liter \cdot sec.}] or [\frac{mol}{liter \cdot min}]$$

The average rate of chemical reaction is the rate in the period of time Δt (from t_0 till t).

In practice the instantaneous rate (R) is used.

The instantaneous rate is the rate (R) at the given moment of time.

The smaller the period of time Δt the nearer the average rate (V) to the instantaneous rate (R).

$$R = \lim_{t \to t_0} \overline{V} = \lim_{t \to t_0} \left(\frac{\Delta C}{\Delta t}\right)$$

The instantaneous rate is the limit of the average rate $\frac{\Delta C}{\Delta t}$ as t tends towards t_0.

$$R = \pm \frac{dC}{dt}.$$

The derivative from concentration (C) to time (t) characterizes the instantaneous rate (real rate) of chemical reaction.

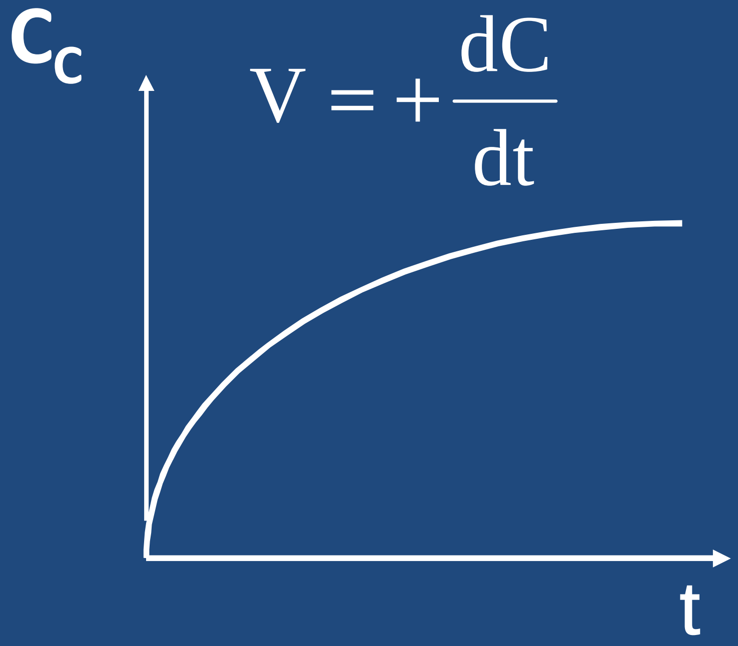
Measurement of rate of a chemical reaction.

Rate of reaction is always to be determined experimentally and cannot be predicted theoretically.

1. Direct methods.

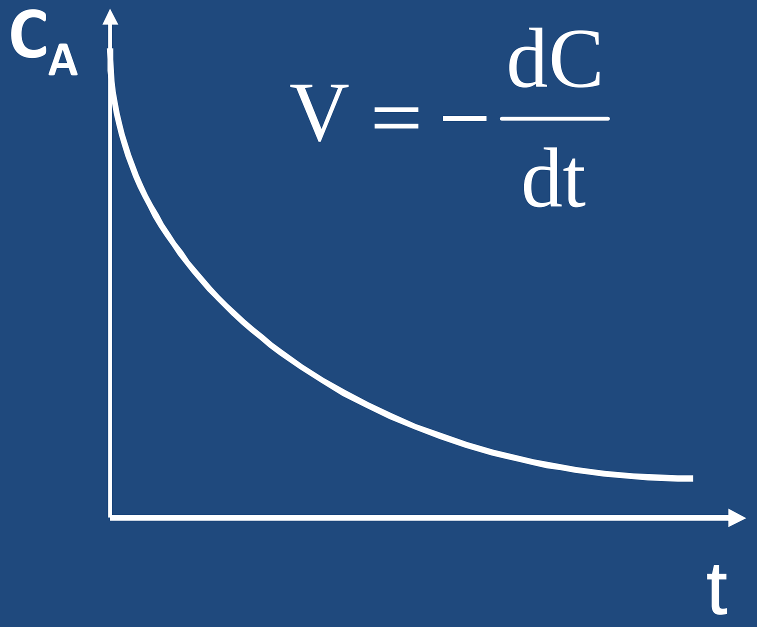
The concentration of reactants or products is determined depending on time. By plotting C against t a graph of the type shown in the figures is obtained. This graphs are called a Rate Curve.

$$A + B \rightarrow C$$



$$V = +\frac{dC}{dt}$$

The concentration increases



$$V = -\frac{dC}{dt}$$

The concentration decreases

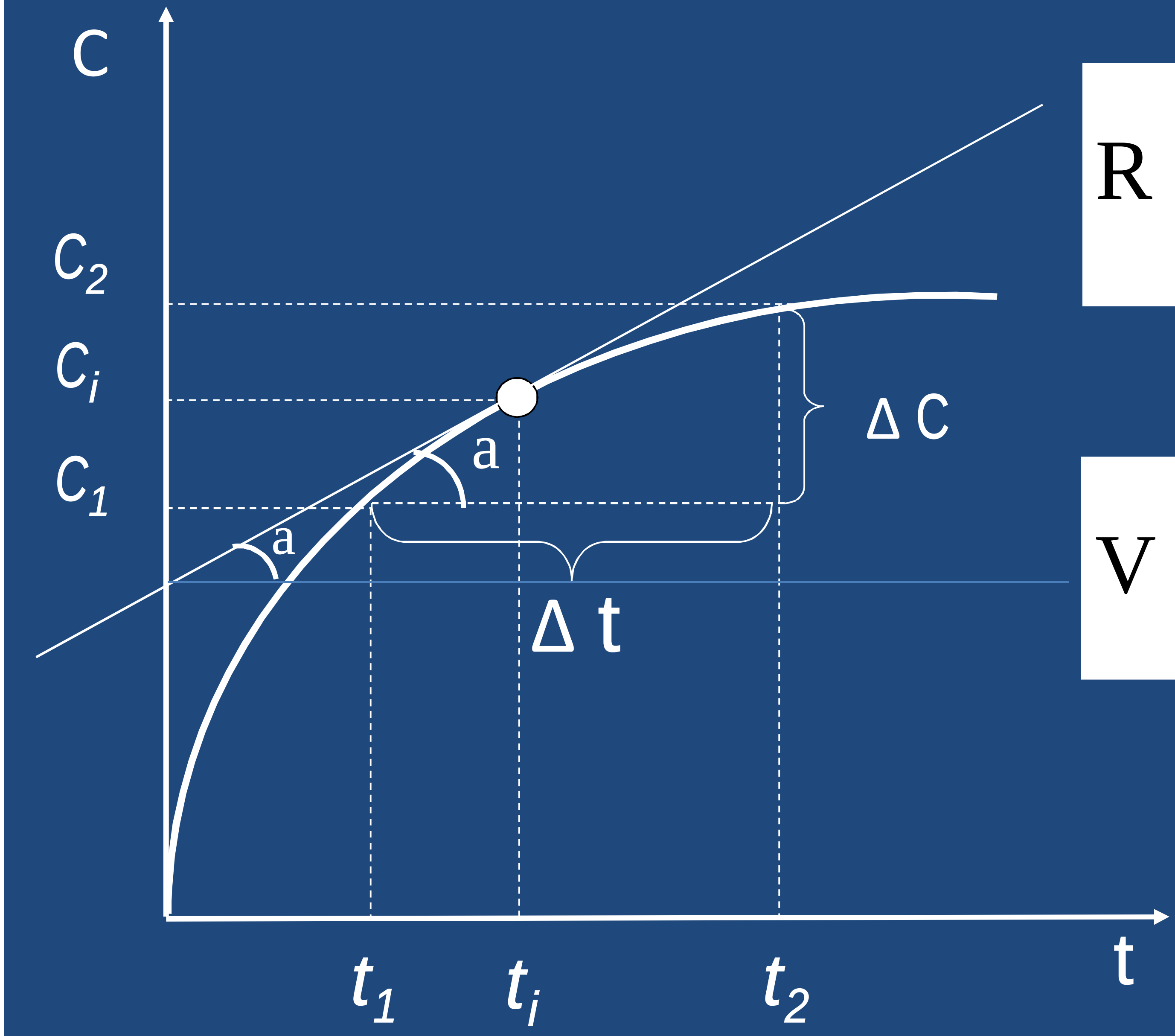
Knowing the Rate Curve for any substance it is easy to calculate the rate of decomposition or formation of the substance by measuring slope of Rate Curve.

The slope of the Rate Curve characterizes the real rate at the given moment, i.e. the tangent a of slope numerically equals the real rate.

Mathematically:

tangent of a approximately equals the ratio of ΔC to Δt and equals the average rate: tga » $\frac{\Delta C}{\Delta t}$ » V,

or in differential form: tga = $\frac{dC}{dt}$ = R.



$$R = \frac{dC_i}{dt_i} = tg\alpha$$

$$V = \frac{\Delta C}{\Delta t} \approx tg\,\alpha$$

If Δ t is less, then V is nearer to R.

2. Indirect methods.

During a chemical reaction the properties of the reaction mixture are apt to change with time. The rate of the reaction is determined by measuring a changing property, such as intensity of colour, pH (negative common logarithm of H^+ concentrations), conductivity et al.

Factors Influencing the Rate of a Reaction

1. Nature of reactants

$$H_2 + F_2 \rightarrow 2HF$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$H_2 + Br_2 \rightarrow 2HBr$$

2. Effect of temperature

3. Effect of concentration

E.g. a very dilute aqueous hydrochloric acid solution reacts with zinc more slowly than a more concentrated solution of the acid. However, the quantitative influence of the concentration and how the reaction rate changes can be found only by experiment.

4. Effect of pressure (gaseous systems)

5. The form of vessel

6. Catalysts

The effect of concentration on the reaction rate.

It is expressed by basic postulate of chemical kinetics:

The instantaneous rate of a chemical reaction at a constant temperature is directly proportional to the product of the concentrations of the reactants to powers is expressed with small numbers.

For the balanced reaction $A + B \rightleftarrows C + D$,
the kinetic equation is:

$$R = \pm \frac{dC}{dt} = k[A]^m[B]^n, \quad R \approx V,$$

where R(V) is the rate; k is the rate constant; [A] and [B] are the concentrations of the reactants A and B;
m, n are small numbers.

Concentrations of solids are assumed to be 1 (constant) and they can be left out of kinetic equation.

Physical sense of k:

k is a such rate of the reaction when concentration of the reactants equal 1 mol/L, i.e.

$$\frac{dC}{dt} = k \text{ at } [A] = [B] = 1 \text{ mol/L.}$$

Sometimes k is called the specific rate.

Chemical sense of k:

the rate constant of the chemical reaction is quantitative measure of reaction ability of molecules.

The more k the more rate of the reaction.

The rate constant doesn’t depend on the reactants concentration, but depends on temperature.

m is the order with respect to reactant A,

n   is the order with respect to reactant B.

The sum (m + n) is called the common (total) order of the reaction.

The order of the reaction is the formal magnitude and depends upon the concentration, the temperature, the catalyst. The order of the reaction can be positive, negative, whole or fractional numbers, zero.

The order of the reaction is determined by experimentally and it is not necessarily related to the equation written for the reaction. The order of the reaction cannot be predicted before.

How can we find the reaction order?

Experiment:

It is balanced reaction: $A + B \rightleftarrows C + D$

$$R = k[A]^m[B]^n$$

Take the substance A in excess and its concentration remains constant. Then we study the rate of the reaction to reactant B, changing its concentration.

[B] ® R Then the order of the reaction
2[B] ® 4R with respect to reactant B is n,
3[B] ® 9R $n = 2$

If we take the substance B in excess its concentration remains constant. Then we study the rate of the reaction to reactant A, changing its concentration.

[A] ® R Then the order of the reaction
2[A] ® 2R with respect to reactant A is m,
3[A] ® 3R $m = 1$

Classification of the Reactions in Order

1. Zero order reactions

Here the rate doesn’t depend on the concentration. The rate is constant.

Kinetic equation is: $R = \pm \frac{dC}{dt} = k_0$,

where C is concentration in mol/liter, t is time in seconds; k_0 is the rate constant.

$[k_0] = [C][t^{-1}] = [mol \cdot liter^{-1} \cdot sec^{-1}]$.

2. First order reactions.

Here the rate depends on the concentration.

Kinetic equation is: $R = \pm \frac{dC}{dt} = k_1C^1$,

where k_1 is the rate constant.

$[k_1] = [sec^{-1}]$.

3. Second order reactions.

Kinetic equation is: $R = \pm \frac{dC}{dt} = k_2C^2$

or $R = k_2C_1C_2$, where k_2 is the rate constant.

$[k_2] = [\text{ liter} \times \text{mol}^{-1} \cdot \text{sec}^{-1}]$

The units of rates of different order reactions are equal and therefore we can compare them.

The reaction rate constants have different units and we cannot compare them. It may be compared the rate constants of chemical reactions if orders of reactions are equal.

Half – Life of a Reaction

The time in which half of the reactant is consumed is called the half-life of a reaction. It is the time in which the concentration of a reactant is reduced to one half of its initial concentration and is written as $t_{1/2}$.

1) For the first order reaction the half-life is: $t_{1/2} = \frac{0,693}{k_1}$

This equation shows that half-life for a first order reaction is independent of the initial concentration.

2) For a second order reaction the half-life is: $t_{1/2} = \frac{1}{k_2 C_0}$

This equation shows that half-life for a second order reaction depends on the initial concentration of the reactant (indirectly proportional).

The more $t_{1/2}$ the more substance is in the organism.

This concept is important for toxicology and pharmacology.

The Law of mass action

It is formulated by Guldberg and Waage (1867).

The Law of mass action is a particular case of base postulate of chemical kinetics and is only applied for simple reactions.

The Law of mass action states that for a homogeneous system at constant temperature

the rate of simple reaction is directly proportional to the active masses of reactants in powers are corresponding to the stoichiometric coefficients in chemical equation.

$$aA + bB \rightleftarrows cC + dD$$

$R_f = k_1 [A]^a[B]^b;$ $R_r = k_2 [C]^c[D]^d$

Molecularity

It is defined as the number of molecules colliding and leading to chemical transformations. Molecularity characterizes the simple reaction, i.e. elementary act of the reaction (individual steps by which a reaction proceeds).

Molecularity has a definite physical sense .

Classification of molecularity:

1. Unimolecular reactions are some molecular decompositions and intramolecular rearrangements:

$CH_3NH_2 \rightarrow HCN + 2H_2$; $CaCO_3 \rightarrow CaO + CO_2$.

2. Bimolecular reactions are those resulting from collision of two molecules of the same or different species:

$CO + Cl_2 \rightleftarrows COCl_2$; $I_2 + H_2 \rightleftarrows 2HI$

3. Trimolecular reactions are those which require a collision between three molecules: $2NO + H_2 = N_2O + H_2O$.

Practically no reactions of a higher molecularity are known.

Molecularity is always a whole number and never greater than three.

A molecularity of four is not known because collision of four particles in a single step is not favorable.

When the equation of the reaction indicates that a large number of molecules participate, this usually means that the process must proceed in a more complicated manner, namely through two or more consecutive stages of which each is due to collision between two, or, rarely, three molecules.

For example, $3H_2 + N_2 \rightleftarrows 2NH_3$.

It is a complex reaction.

For simple reactions the order of reaction and molecularity coincides.

For complex reactions the order of reaction and molecularity doesn't coincide more off.

$$H_2O_2 + 2HI \rightarrow I_2 + 2H_2O.$$

First step: $H_2O_2 + HI \rightarrow HOI + H_2O$ slow

Second step: $HIO + HI \rightarrow I_2 + H_2O$ fast

General rate of this reaction is determined by the slowest step, which is called the rate controlling or rate determining step.

The *seeming molecularity* of this reaction is three. This reaction is complex; the order of this reaction is two. It is known, if molecularity and the order don't coincide, it means:

1) the reaction is complex,

2) the rate of this reaction is limited by rate determining step.

The Effect of Temperature on the Reaction Rate

Besides the concentrations of the reactants, the reaction rate must be influenced by the temperature, since raising the temperature increases the velocity of motion of the molecules, thus increasing the number of collisions. This dependence between the temperature and the reaction rate was first analyzed by Vant-Hoff (1887).

Vant Hoff’s Rule: *each 10-degree rise in temperature approximately will speed up the reaction by 2-4 times.*

At temperature T the reaction rate is V_T at temperature T+10 the reaction rate is V_{T+10} then $V_{T+10}/ V_T = \boldsymbol{\gamma}$, where $\boldsymbol{\gamma}$ *is Vant Hoff’s coefficient*.

$$V_T=V_0\boldsymbol{\gamma}^{DT/10}.$$

The $\boldsymbol{\gamma}$ *shows how many times does the reaction rate increase for a rise in temperature of 10°C.*

Collision Theory

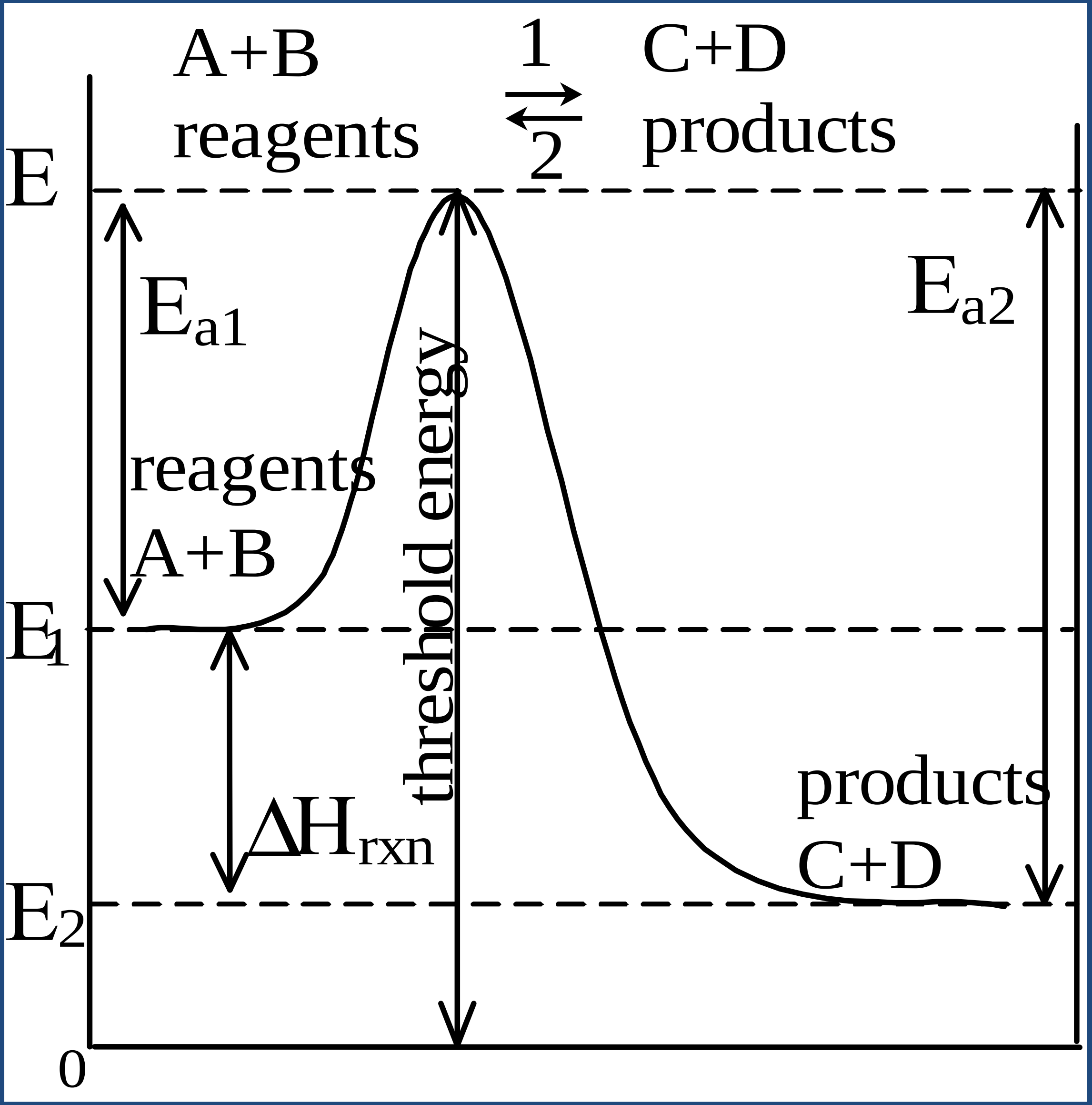
The collision theory gives more exact dependence between temperature and the rate of reaction.

This theory is connected with Arrhenius (1889).

The collision theory is built on a number of assumptions.

1. A chemical reaction takes place when collisions take place between the reacting particles: atoms, molecules or ions.
2. No each collision between reactants is effective; effective only those collisions which involve more than a certain amount of energy, result in the formation of products. Not all collisions between reactants can lead to a reaction

Energetic diagram



E_1 – the average energy which the reactants have before they can react in the forward direction.

E_2 – the average energy which the products have before they can react in the reverse direction.

E – the minimum energy which the reactants or products must have before they can react by collision.

It is called *threshold energy* (*energy barrier*).

E_a– the minimum energy, which needed to add to average energy of molecules to be collisions effective, is called the *activation energy.*

It is a part of threshold energy. If the activation energy is high the rate of the reaction is low. Conversely, a low activation energy means a high reaction rate.

Ea_1 – the activation energy of forward reaction (1).

Ea_2 – the activation energy of reverse reaction (2). $Ea_1 < Ea_2$

DH_{rxn} – is the heat effect of a reaction.

ΔH of forward reaction (1) is negative ($\Delta H < 0$). In other words this reaction is exothermic ($E_1 > E_2$).

ΔH of reverse reaction (2) is positive ($\Delta H > 0$), i.e. an endothermic reaction ($E_2 < E_1$) .

Normally, only a small fraction of the reacting molecules have enough kinetic energy to exceed the activation energy.

The higher the temperature the greater the kinetic energy of reacting molecules and the larger is a fraction of active molecules in a mixture.

Thus increase in temperature accelerates most chemical reactions.

According with Arrhenius

the fraction of active collisions from total numbers of collisions is denoted as **α**:

$$\boldsymbol{\alpha} = \boxed{\mathbf{e}^{-\,\mathbf{Ea/RT}}} = Z/Z_o,$$

where e is the base of natural logarithm;

Z_o is the total number of collisions;

Z is the number of active collisions;

E_a is the energy of activation [$J{\cdot}mol^{-1}$];

R is the molar gas constant equal to

8.314 J/mol K;

T is absolute temperature.

Arrhenius suggested the equation:

$$k=A\cdot\alpha, \quad k=A\times e^{-Ea/RT},$$

where k is rate constant;

A is the total numbers of double collisions per second in 1см^3 of reaction system, it is a preexponential factor;

$\alpha = e^{-Ea/RT}$ is exponential factor, it gives the fraction of collisions with energies greater or equal to activation energy.

As the rate constant k is a product of two multipliers A and $e^{-Ea/RT}$ the k is a measure of the number of activated molecules per unit volume or *it has a sense of the number of active collisions.*

Why does the reaction rate (R) increase with the increase of temperature (T) ?

1. If ↑T in 100^0 A↑ in 1,2 time;

2. a) E_a =100 kJ/mol, T= 300 K $\alpha = ?$

$$\alpha = e^{-\frac{E_a}{RT}} = 10^{-\frac{E_a}{2{,}3\cdot RT}} = 10^{-\frac{100\,000}{2{,}3\cdot 8{,}31\cdot 300}} = \boxed{10^{-17{,}44}}$$

b) E_a =100 kJ/mol, T= 400 K $\alpha = ?$

$$\alpha = e^{-\frac{E_a}{RT}} = 10^{-\frac{E_a}{2{,}3\cdot RT}} = 10^{-\frac{100\,000}{2{,}3\cdot 8{,}31\cdot 400}} = \boxed{10^{-13}}$$

α increases in 22 000 time !!!

Another example:

a) E_a =200 kJ/mol T= 300 K α =?

$$a = 10^{-\frac{200\,000}{2{,}3 \cdot 8{,}31 \cdot 300}} = \boxed{10^{-35}}$$

b) E_a =200 kJ/mol T= 400 K α =?

$$\alpha = 10^{-\frac{200\,000}{2{,}3 \cdot 8{,}31 \cdot 400}} = \boxed{10^{-26}}$$

Conclusion:

α increases in 1 000 000 000 time => **k**↑ => **R**↑

The following conclusions can be drawn from the Arrhenius equation

$$k=A\times e^{-Ea/RT}$$

1. Even a slight decrease in the activation energy increases the rate of reaction quite substantially.

2. The temperature generally affects the reaction rate to a greater extent when the activation energy of a reaction is higher.

3. Reactions with high activation energies proceed at low rates when the temperature is low, but the influence of the temperature on the rate of such reactions is usually more appreciable (the temperature coefficient γ is larger).

The Arrhenius equation shows that the rate constant of a reaction grows with a decreasing activation energy.

The collision theory is not free from limitations.

The collision theory only states that reaction can proceed after active collision from total number of collisions.

It doesn’t explain reaction’s mechanism.

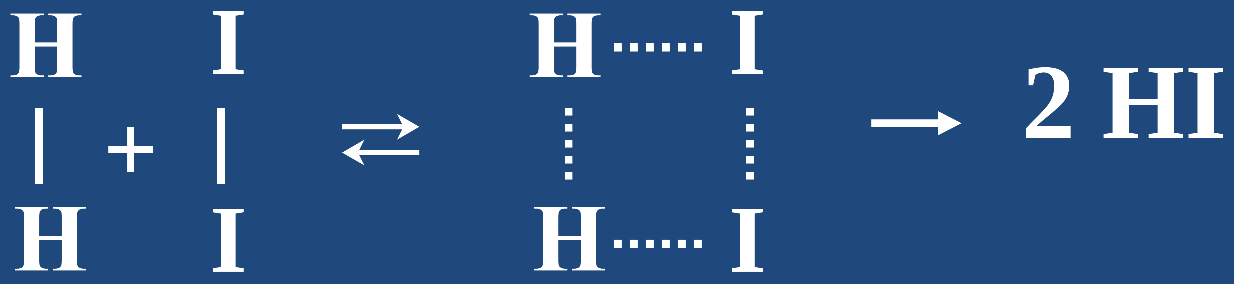
The Transition State Theory

1. As we have already chemical reactions involve the breaking and formation of bonds.

2. In the case of reactants H_2 and I_2 the activated complex would be H_2I_2. The activated complex may break down to form two molecules of HI or may reform the reactant molecules H_2 and I_2.

3. The activated complex can be detected experimentally or isolated. It is an unstable arrangement of atoms that has a transient existence in which the H–H and I–I bonds are weakened and partially broken while the H–I bonds are only partially formed.

The complex is said to be in the transition state.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H} \end{array} + \begin{array}{c} \mathrm{I} \\ | \\ \mathrm{I} \end{array} \rightleftarrows \begin{array}{ccc} \mathrm{H} & \cdots\cdots & \mathrm{I} \\ \vdots & & \vdots \\ \mathrm{H} & \cdots\cdots & \mathrm{I} \end{array} \longrightarrow 2\,\mathrm{HI}$$

activated complex,

it time of life is ≈ 10^{-12} seconds.

The Fundamental Tenets

The Transition State Theory

$$\mathrm{A+B \rightarrow C+D}$$

$$\mathrm{A+B \leftrightarrow X^{\neq} \rightarrow C+D}$$

activated complex (AC)

1. $K^{\neq}_{ch.eq.} = \dfrac{\left[X^{\neq}\right]}{[A]\cdot[B]}, \left[X^{\neq}\right] = K^{\neq}_{ch.eq.}\cdot[A]\cdot[B]$

2. $R = [X^{\neq}]\cdot p$

The disintegration frequency of AC

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{C} + \mathrm{D}$$

$$R = K^{\neq}_{ch.eq.} \cdot [A] \cdot [B] \cdot p$$

$$R = k_V \cdot [A] \cdot [B]$$

$$k_V \cdot \cancel{[A]} \cdot \cancel{[B]} = p \cdot K^{\neq}_{ch.eq.} \cancel{[A]} \cdot \cancel{[B]}$$

$$\boxed{k_V = p \cdot K^{\neq}_{ch.eq.}}$$

It is a basic equation of the Transition State Theory

$$\Delta G^{0\neq} = -RT\ln K^{\neq}{}_{ch.eq.},\; K^{\neq}_{ch.eq.} = e^{-\frac{\Delta G^{0\neq}}{RT}}$$

There are basic equations of:

$k_V = p\cdot e^{-\frac{\Delta G^{0\neq}}{RT}}$	The Transition State Theory
$k_V = A\cdot e^{-\frac{E_a}{RT}}$	The Collision Theory

These theories supplement each other.

R depends on E_a and $\Delta G^{o\neq}$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

$$k_V = p \cdot e^{-\frac{\Delta H^{\neq}}{RT}} \cdot e^{-\frac{\Delta S^{\neq}}{R}}$$

$$k_V = \underbrace{p \cdot e^{-\frac{\Delta S^{\neq}}{R}}}_{\text{Entropy factor (A)}} \cdot \underbrace{e^{-\frac{\Delta H^{\neq}}{RT}}}_{\text{Enthalpy factor } (\Delta H^{\neq} = E_a)}$$

E_a is the enthalpy of the activated complex formation.

It shows us mutual correlations between Thernodynamics and Kinetics!

Catalysis and Catalysts

Substances that are not consumed in a reaction, but affect its rate, are called *catalysts*.

The phenomenon of the change in the rate of a reaction under the action of such substances is known as *catalysis.*

Reactions proceeding under the action of catalysts are called *catalytic*.

The action of a catalyst in the majority of cases is explained by the fact that it lowers or increases the activation energy of a reaction. The catalyst is called *negative*, when it increases the activation energy; the catalyst is called *positive*, when it lowers the activation energy.

Activation energy of catalytical and noncatalytical chemical reactions

Reaction	E_a kJ/mol		Catalyst
	without a catalyst	with a catalyst	
$2H_2O_2$ ® $2H_2O + O_2$	750	55	I_2

In the presence of a catalyst a reaction proceed through other intermediate stages than without it, and these stages are more accessible from the energy viewpoint.

The catalyst doesn’t affect on the total number of collisions in practice but has effect on the activation energy.

Catalyst have no effect on chemical equilibrium since they equally accelerate or lower the direct or reverse reactions. Catalysts only accelerate or lower the establishment of equilibrium in the system. Catalysts have no effect on the equilibrium constant (K_c).

Depending on the physical state of the catalyst and reacting substances, homogeneous and heterogeneous catalysis are distinguished.

Examples of a *homogeneous catalysis* are:

a) $2CO + O_2 \xrightarrow{H_2O} 2CO_2$;

b) $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$;

c) the action of various enzymes in biological processes.

Examples of a *heterogeneous catalysis* are:

a) $N_2 + 3H_2 \overset{Pt}{\rightleftarrows} 2NH_3$; b) $2SO_2 + O_2 \overset{Fe}{\rightleftarrows} 2SO_3$.

Autocatalysis is a process when a product of a reaction acts as a catalyst:

$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + 10\ CO_2 + K_2SO_4 + 8\ H_2O$

Catalyst: Mn^{2+}

Enzymes

Catalysis plays a very great role in biological systems. Most chemical reactions proceeding in the digestive system, in the blood and cells of animals and man are catalytic reactions. The catalysts, which in this case are known as enzymes, are simple or complex proteins.

The human organism contains about 30000 various enzymes; each of them is an effective catalyst of the corresponding reaction.

Distinctive traits (properties) of enzymes:

1. *High catalityc (enzymatic) activity.*

$2H_2O_2 \xrightarrow{Fe^{2+}} 2H_2O + O_2$ $E_a = 42$ kJ/mol

$2H_2O_2 \xrightarrow{Catalase} 2H_2O + O_2$ $E_a = 7{,}1$ kJ/mol.

2. *High enzymatic specificity to substrate. High selectivity (one enzyme activates only one or two biochemical reactions).*

Enzymes exhibit specificity of action. In many instances, this property is the essential characteristic.

For example, amylase splits starch, but doesn’t split a saccharose although they are built of glucose residues.

3. *Enzymes act under mild conditions*: body temperature $25^0 – 40^0$C; normal pressure.

4. *Enzymatic reactions proceed without side reactions (side effects).*

5. *The rate of any enzymatic reaction depends on the enzyme and substrate concentrations.*

L.Michaelis and M. Menten have developed a general theory of enzymatic kinetics.

They proposed the following chemical reaction

$$E+S \underset{k_2}{\overset{k_1}{\leftrightarrows}} [ES] \xrightarrow{k_3} E+P,$$

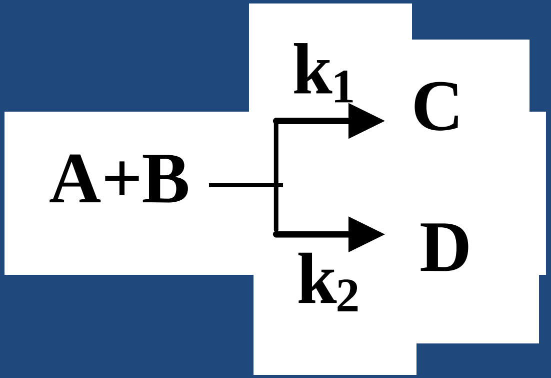
i.e *the enzyme* E *reacts with the substrate* S *to form an intermediate complex* [ES] *which further dissociates into a free enzyme and the reaction product* P.

Concept about Kinetics of Complex Reactions

Most reactions are complex. They are: *simultaneous, consecutive, conjugate, reversible* reactions.

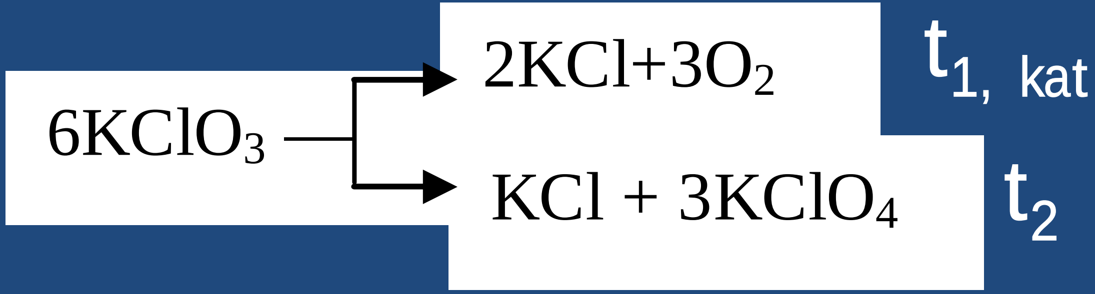
The theory of kinetics of complex reactions is based on the principle that each of simple reactions of the mechanism takes place independently and each obeys the kinetic equations of the simple reaction.

1. Simultaneous reactions are those of the type



$$A+B \xrightarrow{k_1} C$$
$$A+B \xrightarrow{k_2} D$$

In such reactions the initial substance or substances can react simultaneously in different directions. An example of parallel reactions is the decomposition of potassium chlorate, which at moderate temperatures may occur in two parallel directions:



$$6KClO_3 \xrightarrow{t_{1,\ kat}} 2KCl+3O_2$$
$$6KClO_3 \xrightarrow{t_2} KCl + 3KClO_4$$

$t_1 > t_2$

2.*Consecutive reactions* are those of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C,$$

where B is an intermediate in the formation of C, and k_1 and k_2 are the rate constants of the two stages of the reaction.

The number of stages may be more than two, and the stages may be not unimolecular.

Consecutive reactions are very wide spread. Among them is hydrolysis of ATP or starch.

$$\text{ATP} \xrightarrow{H_2O} \text{ADP} \xrightarrow{H_2O} \text{AMP}$$

We point out that if one of the stages proceeds at a considerably lower rate than all others the over-all rate of the reaction will be determined by the rate of this stage.

3. *Conjugated reactions* are defined as reactions of the type:

$$A+B \rightarrow \mathbf{M} \quad (a) \quad <= \quad A+C \rightarrow N \quad (b),$$

of which one, for example (a), takes place only together with the other, i.e. induced by the other (b).

The free energy released by hydrolysis of ATP is necessary for the synthesis of proteins and peptides in living organism.

$\Delta G<0$ hydrolysis of ATP – exergonic reaction;

$\Delta G>0$ formation of peptide bond – endergonic reaction.

4. *Reversible reactions proceed under given conditions both in the forward and reverse directions simultaneously*

$$A+B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C+D,$$

where k_1 is the rate constant of forward reaction;

k_2 is the rate constant of the reverse reaction.

The state of a system when the rates of the forward and reverse reactions are equal: $V_1 = V_2$; $k_1\,C(A)C(B) = k_2\,C(C)C(D)$ is called a state of chemical equilibrium.

It is readily seen that on reaching a state of chemical equilibrium the concentration of each component of the reaction will remain constant !!

Chemical equilibrium is dynamic, i.e. its setting in does not mean that the reaction has stopped.

Chemical equilibrium is characterized by a quantity known as the *chemical equilibrium constant*.

The chemical equilibrium constant *is the ratio of the rate constant of the forward and reverse reactions*:

$$\frac{k_1}{k_2} = \frac{C(C)C(D)}{C(A)C(B)} = K_c ,$$

where K_c is the *chemical equilibrium constant* expressed in terms of the *equilibrium concentrations* of the reactants and products.

The equilibrium constant depends on nature of the reactants and the temperature.

5. *Chain reactions*

Chain reactions proceed with the participation of *active centers* – atoms, ions or radicals (fragments of molecules) having unpaired electrons and displaying, as a result, a very high reactivity.

Example: $H_2+Br_2 = 2HBr$.

The chain reactions consist of some steps.

The first step – the initiation of the chain. Bromine molecules dissociate and this process can be expressed by the equation: $Br_2 \rightarrow Br^\bullet + Br^\bullet$.

The second step – the propagation of the chain

$Br^\bullet + H_2 \rightarrow HBr + H^\bullet$ $H^\bullet + Br_2 \rightarrow HBr + Br^\bullet$

$Br^\bullet + H_2 \rightarrow HBr + H^\bullet$ $H^\bullet + HBr \rightarrow H_2 + Br^\bullet$

The third step – the breaking of the chain (or the termination of the chain):

$Br^\bullet + Br^\bullet \rightarrow Br_2$.

6. *Photochemical Reactions* take place under the influence of light (visible light, ultra-violet) or more seldom, infrared rays.

The most important photochemical reaction is the photosynthesis taking place in plants. the reaction

$$6CO_2+6H_2O \rightarrow C_6H_{12}O_6+6O_2$$

Under the action of solar light chlorophyll converts the CO_2 of the air into complex molecules of organic substances. In this case the light energy transforms into the energy of chemical bonds. This process is endothermal, taking place with increase in the Gibbs free energy ($\Delta G>0$). It cannot occur in the absence of light.