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CHEMICAL KINETICS

"The branch of chemistry in which mechanism of the chemical reactions is studied by measuring the rate of reaction is called chemical kinetics."

In chemical kinetics, too fast or too slow reactions are not studied. In between these two extreme reactions, there are a number of reactions whose rate can be measured under reaction condition and only these reactions are studied in chemical kinetics.

Q. Which of the following reactions cannot be studied in chemical kinetics ?

(a) Photosynthesis (b) Rusting of iron
(c) Ionic reactions (b) All

- Photosynthesis, Photography and Ionic reactions are too fast reactions and therefore, the rate of these reactions cannot be measured under reaction conditions. Hence, these reactions are not studied in chemical kinetics.
- Rusting of iron, Formation of fossil fuels inside earth crust etc. are too slow reactions and therefore, the rate of these reactions cannot be measured under reaction conditions. Hence, these reactions are not studied in chemical kinetics.

Rate of the Reaction

"The rate of change of concentration of any reactants or any products with time is called the rate of the reactions."

Mathematically,

$$\text{Rate of reaction} = \frac{\textbf{Change in conc. of any reactants or products}}{\textbf{Time Interval}}$$

Let, change of conc. of any reactant or product in time interval Δt is Δx, then-

$$\text{Rate of reaction} = \frac{\Delta \mathbf{x}}{\Delta \boldsymbol{t}}$$

However, the rate of the reactions depends upon the conc. of reactants, which changes instantaneously with time. Hence, rate of the reaction also changes instantaneously with time. Thus, this expression gives only average rate of the reaction. In order to get instantaneous rate of reaction, let the change in conc. of a reactant or product in an infinitesimally small time Interval dt is dx, then,

$$\text{Instantaneous rate of reaction} = \frac{\mathbf{dx}}{\boldsymbol{dt}}$$

Instantaneous rate of reaction is considered to be actual rate of the reaction.

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Mode of Expressing the Rate of Reactions

The rate of a chemical reaction can be expressed either by rate of disappearance of any reactants or by rate of appearance of any products. Thus,

Rate of reaction = rate of disappearance of any reactants
= rate of appearance of any products

Let us consider following general reaction-

$$A + B \rightarrow C + D$$

Here, Instantaneous rate of reaction,

$\frac{dx}{dt}$ = rate of disappearance of reactant A
= rate of disappearance of reactant B
= rate of appearance of product C
= rate of appearance of product D

or $\frac{dx}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = +\frac{d[D]}{dt}$

Here, - sign indicates that, the conc. of reactants is decreasing with time while, + sign indicates that, the conc. of products is increasing with time.

For example, for following general reaction-

$$PCl_5 \rightarrow PCl_3 + Cl_2$$

Here, instantaneous rate of reaction,

$$\frac{dx}{dt} = -\frac{d[PCl_5]}{dt} = +\frac{d[PCl_3]}{dt} = +\frac{d[Cl_2]}{dt}$$

For the reactions of different stoichiometry, the rate of decrease of conc. of different reactants and the rate of increase of conc. of different products are different. Here, in order to get uniform rate of reaction, the rate of change of conc. of different reactants and products are divided by their respective number of moles in balanced chemical equation.

For example, for following reaction-

$$H_2 + I_2 \rightarrow 2HI$$

Here, rate of formation of HI is twice of the rate of utilization of H_2 and I_2.

Hence, Instantaneous rate of reaction, $\frac{dx}{dt} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = +\frac{1}{2}.\frac{d[HI]}{dt}$

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Similarly, for following reaction-

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Here, instantaneous rate of reaction , $\frac{dx}{dt} = -\frac{d[N_2]}{dt} = -\frac{1}{3}.\frac{d[H_2]}{dt}$

$$= +\frac{1}{2}.\frac{d[NH_3]}{dt}$$

Ques. Give rate expression of following reactions-

(i) $2SO_2 + O_2 \rightarrow 2SO_3$

(ii) $N_2 + O_2 \rightarrow 2NO$

Ques. Consider the reaction- $N_2 + 3H_2 \rightarrow 2NH_3$

Which of the following relation is incorrect-

(a) $-\frac{d[N_2]}{dt} = -\frac{1}{3}.\frac{d[H_2]}{dt}$ (b) $-\frac{3.d[N_2]}{dt} = -\frac{d[H_2]}{dt}$

(c) $-\frac{d[N_2]}{dt} = +\frac{1}{2}.\frac{d[NH_3]}{dt}$ (d) $-\frac{d[N_2]}{dt} = -\frac{1}{2}.\frac{d[H_2]}{dt}$

Molecularity of the Reactions

According to collision theory, chemical reaction occurs only when reactant molecules collide with each other. Here, "the minimum number of reactant molecules which collide simultaneously, in a single step elementary reaction to lead the reaction is called the molecularity of the reaction."

Depending upon molecularity being 1,2 or 3, the chemical reactions are designated as monomolecular, bimolecular and trimolecular reactions respectively. For example,

$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	Monomolecular
$H_2 + I_2 \rightarrow 2HI$	Bimolecular
$2NO_2 + O_2 \rightarrow 2NO_3$	Trimolecular

Molecularity of the chemical reactions cannot be fractional or zero. Also, it never exceeds 3. It is because, the simultaneous collisions of more than three reactant molecules is rare.

Molecularity is a theoretical concept, which is related with the mechanism of the reactions. It can easily be determined by observing balanced chemical reaction.

- If a chemical reaction involves more than three molecules, then it is considered to occur in multi-steps and the molecularity of each step is 1, 2 or 3 but, it is never more than 3.

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Order of the Reactions

By experimental measurement of the rate of the chemical reactions, it has been found that all the reactants represented in a balanced chemical reaction do not decide the rate of the reaction. In fact, the rate of the chemical reactions is decided only by those reactants whose concentration changes measurably during the reaction. Only these reactants decide the order of the reaction. By definition,

"The sum of the powers of the molar concentrations of different reactants represented in experimental rate expression of a chemical reaction is called the **order of the reaction**."

Let us consider following general reaction-

$$aA + bB \rightarrow \text{Products}$$

Let, the experimental rate expression of this reaction is as under-

$$\frac{dx}{dt} = k\,[A]^m[B]^n$$

Then, order of the reaction = (m+n)

This reaction is of m^{th} order with respect to reactant A and is of n^{th} order with respect to reactant B. The overall order of the reaction is (m+n).

Here, m and n are experimental numbers and are decided only by experiment. They have no relation with a and b i.e. stoichiometric coefficient of the reactants in balanced chemical reaction. They may or not may be equal to a and b.

For example, for the reaction-

$$2N_2O \rightarrow 2N_2 + O_2$$

Here, experimental rate,

$$\frac{dx}{dt} = k\,[N_2O]$$

$\therefore$ The order of the reaction = 1

Similarly, for the reaction-

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Here, experimental rate,

$$\frac{dx}{dt} = k\,[N_2O_5]$$

$\therefore$ The order of the reaction = 1

For the reaction-

$$H_2 + I_2 \rightarrow 2HI$$

Here, experimental rate,

$$\frac{dx}{dt} = k\,[H_2]\,[I_2]$$

$\therefore$ The order of the reaction = 1 + 1 = 2

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For the reaction-

$$2NO + O_2 \rightarrow 2NO_2$$

Here, experimental rate,

$$\frac{dx}{dt} = k\,[NO]^2[O_2]$$

∴ The order of the reaction = 2 + 1 = 3

The order of the reaction can also be fractional or zero and even negative. For example, for the reaction-

$$H_2 + Br_2 \rightarrow 2HBr$$

Here, experimental rate,

$$\frac{dx}{dt} = k[H_2]\,[Br_2]^{1/2}$$

∴ The order of the reaction = 1 + 1/2 = 3/2

Similarly, for the reaction-

$$CH_3CHO \rightarrow CH_4 + CO$$

Here, experimental rate,

$$\frac{dx}{dt} = k[CH_3CHO]^{3/2}$$

∴ The order of the reaction = 3/2

For, photosynthesis of HCl –

$$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$$

Here, experimental rate,

$$\frac{dx}{dt} = k[H_2]^0[Cl_2]^0$$

∴ The order of the reaction = 0

Here, rate of the reaction is independent of the molar conc. of both the reactants and therefore does not change with the change of the molar conc. of the reactants.

Similarly, decomposition of ammonia at the surface of Pt, Pd or Au is also a zero order reaction-

$$2NH_3 \rightarrow 2N_2 + 3H_2$$

Here, experimental rate,

$$\frac{dx}{dt} = k[NH_3]^0$$

∴ The order of the reaction = 0

Unlike molecularity, the order of the reactions can exceed 3. It is related to the kinetics of the reactions.

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Pseudo-Unimolecular Reactions

or

Pseudo-First Order Reactions

There are a number of reactions which have their molecularity 2, but they follow first order kinetics. These reactions are called Pseudo-unimolecular or Pseudo-first order reactions.

For example, for inversion of cane sugar -

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_{16} + C_6H_{12}O_{16}$$

Experimental rate,

$$\frac{dx}{dt} = k[C_{12}H_{22}O_{11}]\,[H_2O]^0$$

$\therefore$ The order of the reaction = 1 + 0 = 1

Here, the molecularity of the reaction is 2 but order is 1. Hence this reaction is Pseudo-unimolecular or Pseudo-first order reaction. In fact, in this reaction water is present in large excess and therefore, its conc. remains almost constant during the reaction. Thus, it does not decide the rate of the reaction.

Similarly, for acid hydrolysis of esters-

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

Experimental rate,

$$\frac{dx}{dt} = k[CH_3COOC_2H_5]\,[H_2O]^0$$

$\therefore$ The order of the reaction = 1 + 0 = 1

Here also, the molecularity of the reaction is also 2 but order is 1. Hence this reaction is also a Pseudo-unimolecular or Pseudo-first order reaction. In fact, also in this reaction, water is present in large excess and therefore, its conc. remains almost constant during the reaction. Thus, it does not decide the rate of the reaction.

*If a reactant is present in large excess then the rate of reaction becomes independent of the conc. of this reactant i.e. it is of zero order with respect to this reactant.

First Order Reaction

"Such reactions whose rate depends upon only one power of the molar conc. of the reactants are called first order reactions."

For example, for the reaction-

$$2N_2O \rightarrow 2N_2 + O_2$$

Here, Experimental rate,

$$\frac{dx}{dt} = k[N_2O]$$

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∴ The order of the reaction = 1

Similarly, for the reaction-

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Here, Experimental rate,

$$\frac{dx}{dt} = k[N_2O_5]$$

∴ The order of the reaction = 1

Second Order Reaction

"Such reactions whose rate depends upon two power of the molar conc. of the reactants are called second order reactions."

For example, for the reaction-

$$H_2 + I_2 \rightarrow 2HI$$

Here, Experimental rate,

$$\frac{dx}{dt} = k[H_2][I_2]$$

∴ The order of the reaction = 1 + 1 = 2

Third Order Reaction

"Such reactions whose rate depends upon three power of the molar conc. of the reactants are called third order reactions."

For example, for the reaction-

$$2NO + O_2 \rightarrow 2NO_2$$

Here, Experimental rate,

$$\frac{dx}{dt} = k[NO]^2[O_2]$$

∴ The order of the reaction = 2 + 1 = 3

Zero Order Reaction

"Such reactions whose rate is independent of the molar conc. of the reactants are called zero order reactions."

For example, photosynthesis of HCl –

$$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$$

Here, Experimental rate,

$$\frac{dx}{dt} = k[H_2]^0[Cl_2]^0$$

∴ The order of the reaction = 0

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Here, rate of the reaction is independent of the molar conc. of both the reactants and therefore, it does not change with the change of the molar conc. of the reactants.

Similarly, decomposition of ammonia at the surface of Pt, Pd or Au is also a zero order reaction-

$$2NH_3 \rightarrow 2N_2 + 3H_2$$

Here, Experimental rate,

$$\frac{dx}{dt} = k\,[NH_3]^0$$

$\therefore$ The order of the reaction = 0

Specific Rate Constant of the Reaction

Let us consider following general reaction-

$$aA + bB \rightarrow \text{Products}$$

Let, the experimental rate expression of this reaction is as under-

$$\frac{dx}{dt} = k\,[A]^m[B]^n$$

Where, k is a proportionality constant called specific rate constant of the reaction.

If , $[A] = [B] = 1$mole/litre

Then, $\frac{dx}{dt} = k$

Thus, "the rate of the reaction when the molar conc. of all the reactants is unity is called the specific rate constant of the reaction."

The specific rate constant of the reaction is the characteristic of the reaction at a given temperature. It also depends upon the nature of the reactants, but it is independent of the conc. of the reactants.

Unit of Specific Rate Constant for n^{th} order Reaction - $[Mol\ L^{-1}]^{1-n}Sec^{-1}$

For example, for I^{st} order reactions –

$$\text{Unit of } k = [Mol\ L^{-1}]^{1-1}Sec^{-1}$$
$$= [Mol\ L^{-1}]^0Sec^{-1}$$
$$= Sec^{-1}$$

For II^{nd} order reactions

$$\text{Unit of } k = [Mol\ L^{-1}]^{1-2}Sec^{-1}$$
$$= [Mol\ L^{-1}]^{-1}Sec^{-1}$$
$$= [Mol^{-1}\ L]Sec^{-1}$$

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For IIIrd order reactions

Unit of k = $[Mol\ L^{-1}]^{1-3}Sec^{-1}$

= $[Mol\ L^{-1}]\ Sec^{-1}$

= $[Mol^{-2}\ L^{2}]Sec^{-1}$

Rate Expression OR Rate Law

"The expression which gives actual relationship between the molar conc. of the reactants and the rate of the reaction is called rate expression or rate law of the reaction."

Let us consider following general reaction-

$$aA + bB \rightarrow \text{Products}$$

Let, the rate of this reaction is proportional to mth power of the molar conc. of reactant A and nth power of the molar conc. of reactant B. Then,

Experimental rate expression or rate law of this reaction will be as under-

$$\frac{dx}{dt} = k\,[A]^m[B]^n$$

Where, k is a proportionality constant called specific rate constant of the reaction.

Here, m and n are experimental numbers and are decided by experiment. They have no relation with a and b i.e. stoichiometric coefficient of the reactants in balanced chemical equatio. They may or not may be equal to a and b.

Equation of Zero Order Kinetics

Such reactions whose rate is independent of the molar conc. of the reactants are called zero order reactions.

Let us consider following reaction of zero order –

$$A \rightarrow \text{Products}$$

Let initial conc. of reactant A is a mole/litre and its conc. at time t is (a-x) mole/litre, then rate of reaction at time t,

$$\frac{dx}{dt} \propto (a-x)^0$$

or

$$\frac{dx}{dt} = k_0(a-x)^0$$

Where k_0 = rate constant for zero order reaction

or

$$\frac{dx}{dt} = k_0$$

or

$$dx = k_0 dt \qquad \text{---------- (1)}$$

On integrating eq. 1, we get-

$$\int dx = k_0 \int dt$$

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or $\mathbf{x = k_0 t + I}$ ---------- (2)

Where I = integration constant

Here, **if** $\mathbf{t = 0}$, **then,** $\mathbf{x = 0}$

$\therefore$ $\mathbf{I = 0}$

Therefore, from eq. (2), we get-

$$\mathbf{x = k_0 t}$$

or $$\mathbf{k_0 = \frac{x}{t}}$$

This is the integral equation of specific rate constant for reactions following zero order kinetics.

From this equation it is clear that, if x is plotted against t then a straight line having slope equal to k_0 and intercept equal to zero will obtained.

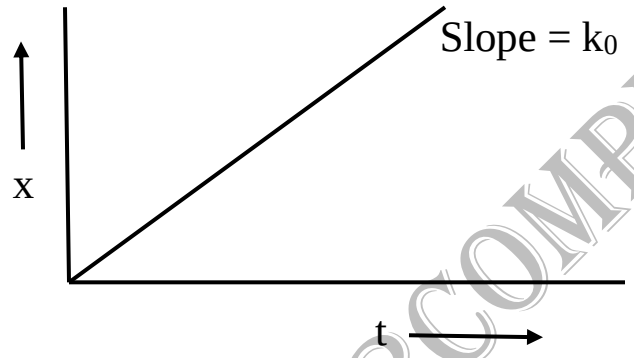


Fig.- Plot of x against t for zero order reactions

- If $\frac{dx}{dt}$ is plotted against t, then a straight line parallel to t axis is obtained. It shows that-

$$\frac{dx}{dt} = k_0$$

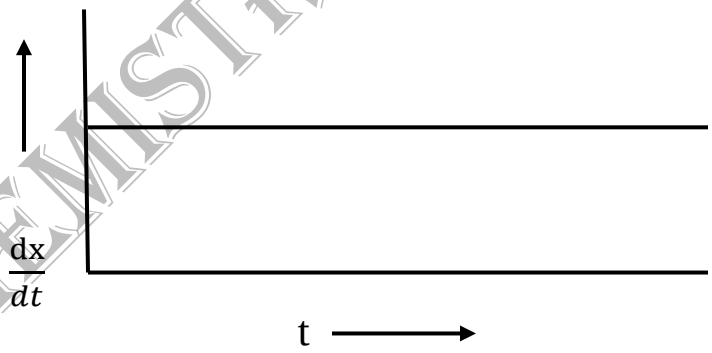


Fig.- Plot of $\frac{dx}{dt}$ against time t for zero order reactions

- If the conc. of product at time t_1 is x_1 and that at time t_2 is x_2 then-

$$k_0 = \frac{(x_1 - x_2)}{(t_1 - t_2)}$$

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Alternative derivation

Let us consider following reaction of zero order –

$$A \rightarrow \text{Products}$$

Let initial conc. of reactant A is $[A]_0$ and that at time t is $[A]_t$, then rate of reaction at time t -

$$-\frac{d[A]}{dt} \quad \alpha \quad [A]_t^0$$

or

$$-\frac{d[A]}{dt} = k_0[A]_t^0$$

Where k_0 = rate constant for zero order reactions

Here, $\because \quad -\frac{d[A]}{dt} = k_0$

$$\therefore \quad d[A] = -k_0 dt \qquad \text{---------- (1)}$$

On integrating eq. 1, we get-

$$\int d[A] = -k_0 \int dt$$

$$\therefore \quad [A]_t = -k_0 t + I \qquad \text{----------} \quad (2)$$

Where, I = integration constant

Here, If $t = 0$, then $[A]_t = [A]_0$

$$\therefore \quad I = [A]_0$$

Thus, from eq. (2), we get-

$$[A]_t = -k_0 t + [A]_0$$

This is also the integral equation of reactions following zero order kinetics. This equation is in the form of straight line equation (y = mx + c). From this equation it is clear that, if $[A]_t$ is plotted against t, then a straight line having a negative slope equal to $-k_0$ and intercept equal to $[A]_0$ will obtained.

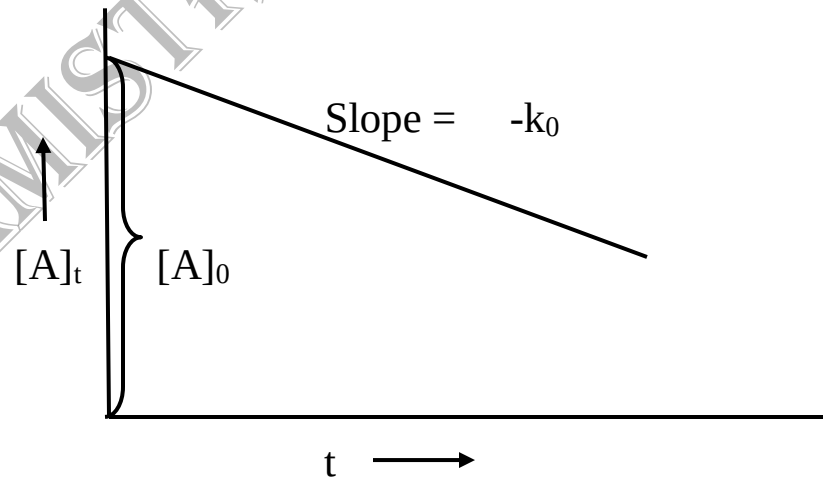


Fig.- Plot of conc. of reactant against time for zero order reactions

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On simplifying the above equation further, we get-

$$\mathbf{k} = \frac{[\mathbf{A}]_0 - [\mathbf{A}]_t}{t}$$

Equation of First Order Kinetics

Such reactions whose rate depends upon only upon one power of the molar conc. of the reactants are called first order reactions.

Let us consider following reaction of first order –

$$A \rightarrow \text{Products}$$

Let initial conc. of reactant A is a mole/litre and its conc. at time t is (a-x) mole/litre, then rate of reaction at time t,

$$-\frac{dx}{dt} \quad \alpha \quad (a-x)$$

$$\text{or} \quad -\frac{dx}{dt} = k(a-x)$$

Where, k = rate constant for first order reactions

$$\text{or} \quad -\frac{dx}{(a-x)} = kdt \quad \text{----------} \quad (1)$$

On integrating eq. 1, we get-

$$\int -\frac{dx}{(a-x)} = k \int dt$$

$$\text{or} \quad -\ln(a-x) = kt + I \quad \text{----------} \quad (2)$$

Where, I = integration constant

Here, If $t = 0$, then $x = 0$

$$\therefore \quad I = -\ln a$$

Thus, from eq. (2), we get-

$$-\ln(a-x) = kt - \ln a$$

$$\text{or} \quad kt = \ln a - \ln(a-x)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{a-x} \quad \text{----------} \quad (3)$$

Changing the base of logarithm from e to 10, we get-

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{----------} \quad (4)$$

This is the integrated equation of specific rate constant for reactions following first order kinetics.

Rearranging eq. (4), we get-

$$\log(a-x) = \frac{-kt}{2.303} + \log a$$

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This equation is in the form of straight line equation (y = mx + c). From this equation, it is clear that, if log (a-x) is plotted against t, then a straight line having negative slope equal to $\frac{-k}{2.303}$ and intercept equal to **log a** will obtained.

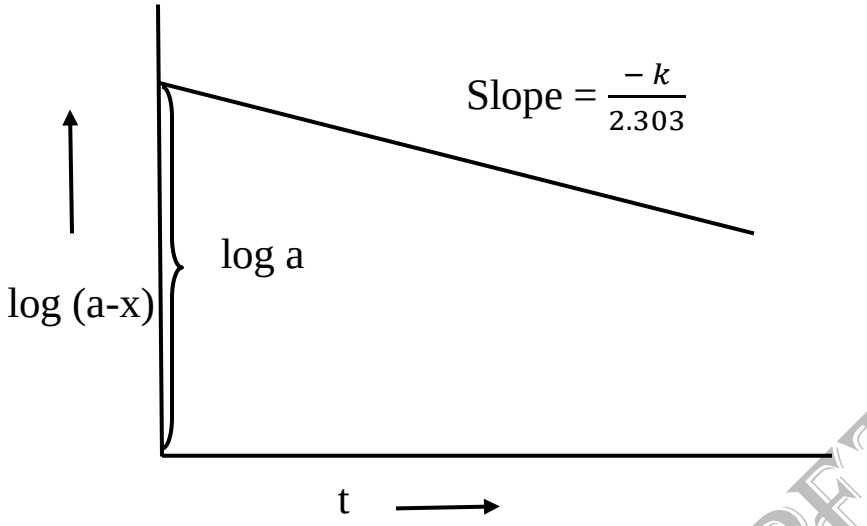


Fig.- Plot of log (a-x) against t for first order reactions

From the above equation-

$$\log \frac{a}{a-x} = \frac{kt}{2.303}$$

Thus, if log $\frac{a}{a-x}$ is plotted against t, then a straight line having a positive slope equal to $\frac{k}{2.303}$ and intercept equal to zero will obtained.

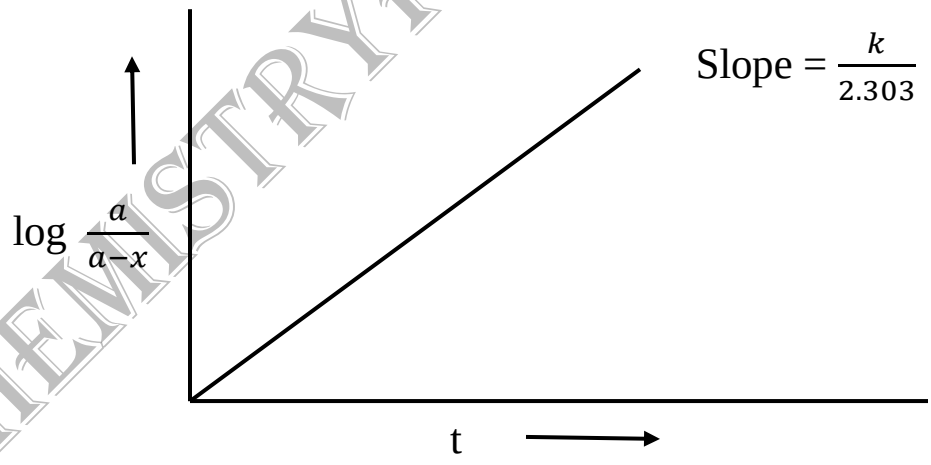


Fig.- Plot of log a/(a-x) against t for first order reactions

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Characteristics of First Order Reaction

(1) Unit of Rate Constant - From equation of First Order Kinetics-

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

Therefore, Unit of $k = \frac{1}{time} \ln \frac{Conc.}{Conc.}$

$= \text{Time}^{-1}$

e.g sec^{-1}, min^{-1}, $hour^{-1}$, $year^{-1}$ etc.

(2) Half Life Period- "The time taken in completion of one-half of a chemical reaction is called half life period ($t_{1/2}$) of the reaction."

From equation of First Order Kinetics-

$$\mathbf{k = \frac{2.303}{t} \log \frac{a}{a-x}}$$

Here, If $t = t_{1/2}$, then $x = \frac{a}{2}$

$$\therefore \quad \mathbf{k = \frac{2.303}{t_{1/2}} \log \frac{a}{a-\frac{a}{2}}}$$

$$\text{or} \quad \mathbf{k = \frac{2.303}{t_{1/2}} \log 2}$$

$$\mathbf{or} \quad \mathbf{t_{1/2} = \frac{2.303 \times 0.3010}{k}}$$

$$\mathbf{or} \quad \mathbf{t_{1/2} = \frac{0.693}{k}}$$

This is the expression of half life period for first order reactions.

Since, this expression does not involve conc. term a, the half life period of these reactions is independent of the initial conc. of the reactants.

Thus, for first order reactions, the time taken in completion of a definite proportion of the reaction is always constant and is independent of the initial conc. of the reactants.

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Difference between Molecularity and Order of the Reactions

S.NO.	Molecularity	Order of the Reactions
1.	It is the minimum number of reactants molecules which collide simultaneously to lead a chemical reaction.	It is the sum of the powers of the molar concentrations of different reactants represented in experimental rate expression of a chemical reaction.
2.	Molecularity of the chemical reactions cannot be fractional or zero .	The order of the reaction can be fractional or zero and even negative.
3.	Molecularity of the chemical reactions never exceeds 3.	Order of the chemical reactions can exceeds 3.
4.	Molecularity of the chemical reactions can easily be determined by observing balanced chemical reactions.	It cannot be determined by observing balanced chemical reactions but is always determined by experiment.
5.	It is a theoretical concept which is related with the mechanism of the reactions.	It is an experimental concept which is related with the kinetics of the reactions.

Activation Energy

According to collision theory, a chemical reaction occurs only when reactant molecules collide with each others. However, after collision there may or not may occur the chemical reaction. In fact, out of millions of collisions, only one or two collisions are there which lead the chemical reaction and are called **effective collisions**. On the other hand, most of the collisions remain ineffective in carrying out the reaction and are called **ineffective collisions**.

Whether a collision will be effective or not is decided by following two factors-

(1) Energy factor

(2) Orientation factor

(1)Energy factor

Only those collisions are effective in carrying out the reaction in which the colliding molecules possess an energy equal to or greater than a minimum amount of energy called **threshold energy**. This energy is required to break the old bonds present in colliding molecules.

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In ordinary condition, most of the molecules have energy lesser than threshold energy and this energy is called **average energy** of the molecules. Thus, these molecules require some additional energy, other than their average energy to take part in chemical reaction. This energy activates the molecule to take part in chemical reaction and is called **activation energy** for the molecules.

Thus, " the minimum energy, other than average energy required by reactant molecules to take part in chemical reaction and is called **activation energy** for the molecules."

Mathematically, activation energy is equal to the difference of threshold energy and average energy. i.e.

Activation energy = Threshold energy – Average energy

This relation amongst Activation energy, Threshold energy and Average energy is represented in following graph-

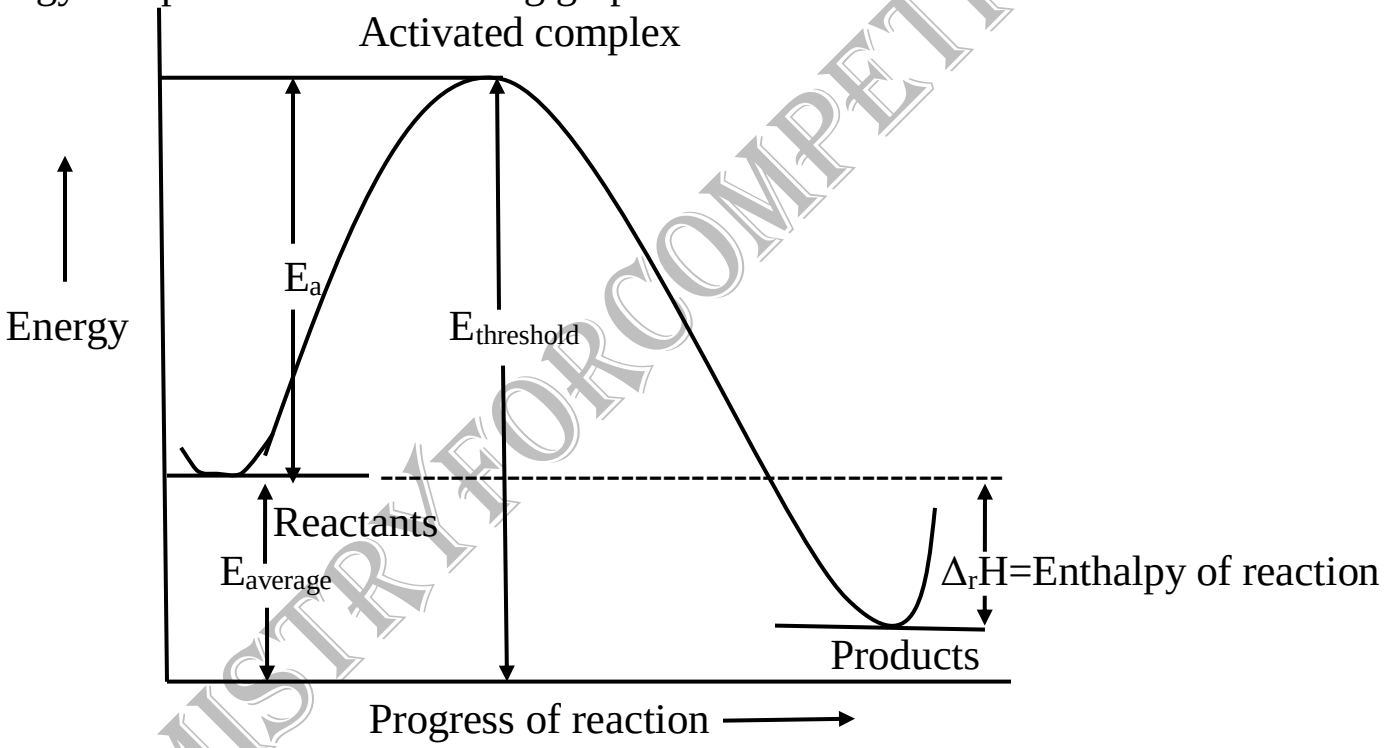


Fig – Reaction Profile

It is clear that, there is an energy barrier between reactants and products and during a chemical reaction reactants never convert directly into products. In fact, before taking part in reaction reactant molecules absorb energy equal to activation energy to reach at the peak of energy barrier and then convert into products by releasing energy. Here, if energy released is lesser than activation energy then the reaction is endothermic but if it is greater than activation energy then the reaction is exothermic in nature.

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The value of activation energy also gives idea about the velocity of the reaction. If the value of activation energy is low then it becomes easily available to most of the molecules and therefore they get participated in chemical reaction. Thus the rate of the reaction is high. Such reactions are called fast reactions. On the other hand, if the value of activation energy is high then it does not become easily available to most of the molecules and therefore they do not participated in chemical reaction. Thus the rate of the reaction is low. Such reactions are called slow reactions.

Role of Catalyst

A positive catalyst provides an alternative path of lower activation energy. Thus, this energy it becomes easily available to most of the molecules and therefore their collisions become effective and they get participated in chemical reaction. Thus the rate of the reaction gets increased.

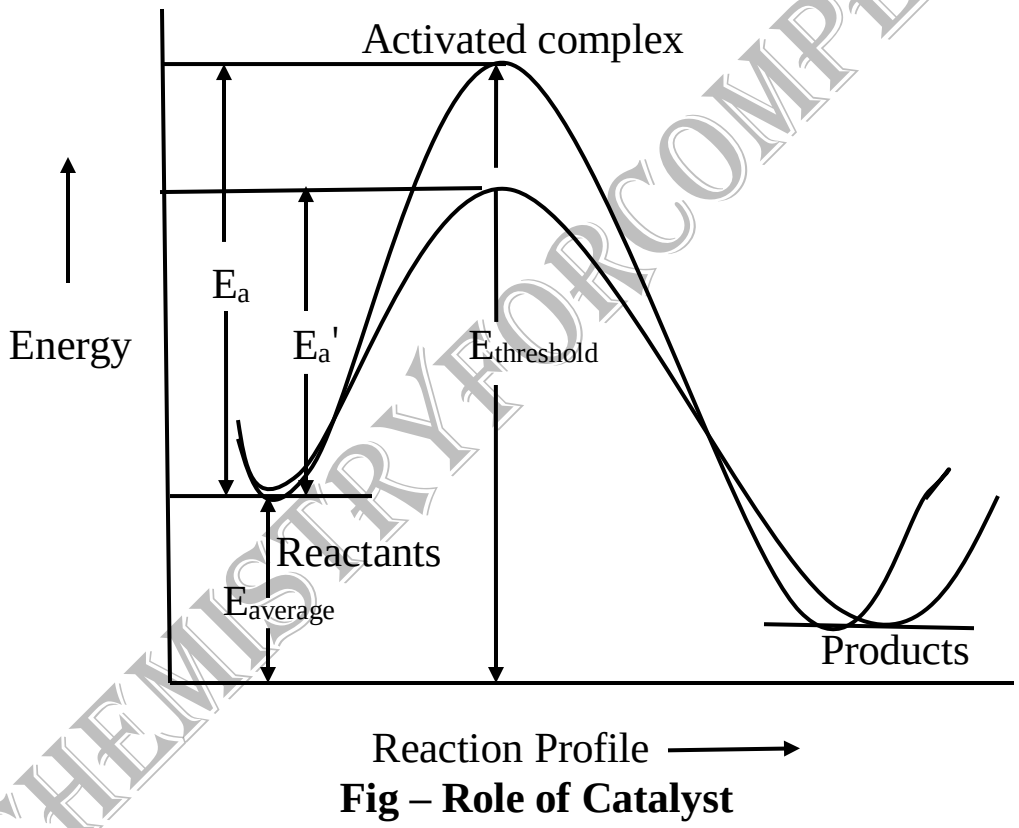


Fig – Role of Catalyst

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Effect of Temperature on the Rate of the Reactions (Arrhenius Equation)-

On experimental basis Arrhenius gave following empirical relationship between the rate constant k, activation energy E_a and absolute temperature T-

$$k = A\, e^{-Ea/RT} \quad \text{----------} \quad (1)$$

Where, A = Frequency factor

R = Gas constant

Taking logarithm of eq. (1), we get-

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

Changing the base of logarithms from base e to 10, we get-

$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

or

$$\log k = \log A - \frac{E_a}{2.303\, RT} \quad \text{--------} \quad (2)$$

This equation is in the form of straight line equation, y = mx + c, Hence, if log k is plotted against 1/T, then a straight line having a negative slope equal to $-\frac{E_a}{2.303\, R}$ and intercept equal to log A will obtained.

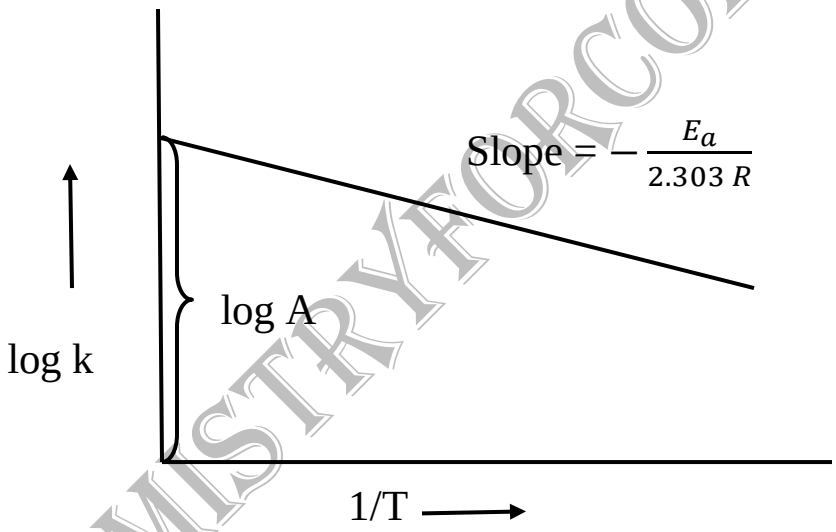


Fig.- Plot of log k against 1/T for the reactions

If rate constant for the reaction at temperature T_1 is k_1 and that at temperature T_2 is k_2, then from equation (2),

$$\log k_1 = \log A - \frac{E_a}{2.303\, RT_1}$$

and

$$\log k_2 = \log A - \frac{E_a}{2.303\, RT_2}$$

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Hence, $\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

or, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_2 \,.\, T_1}\right)$ ---------- (3)

This equation is called Arrhenius equation and gives the effect of temperature on the rate of the chemical reactions.

Temperature Coefficient

Effect of temperature on the rate of the chemical reactions is expressed in terms of temperature coefficient. By definition,

"The ratio of the rate constants of a chemical reaction at two different temperatures differing by 10^0 is called temperature coefficient of the reaction."
Mathematically,

$$\text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

It has been found that, for most of the molecular reactions, the rate of the reaction becomes twice or thrice of the initial for each 10^0 rise of temperature. Hence, temperature coefficient of most of the molecular reactions lies between 2 and 3. Thus,

$$\text{Temperature coefficient} \approx 2 - 3$$

Collision Theory of Reactions

This theory was for the first time proposed by Trautz and Lewis to explain the rate of the molecular reactions. It provides more mechanistic view of the rate of the reactions. However, this theory is applicable only for those reactions which involve either atoms or simple molecules as reactants.

According to this theory, chemical reaction occurs only when reactant molecules collide with each others. However, only those collisions are effective in carrying out the reaction in which the colliding molecules possess an energy equal to or greater than a minimum amount of energy called **threshold energy** and the **orientation of colliding molecules is proper**.

For example, in SN^2 mechanism of hydrolysis of haloalkanes, the attack of nucleophile (OH^-) should always be rear to the leaving group (X^-), otherwise the colliding molecules get bounced back without any reaction.

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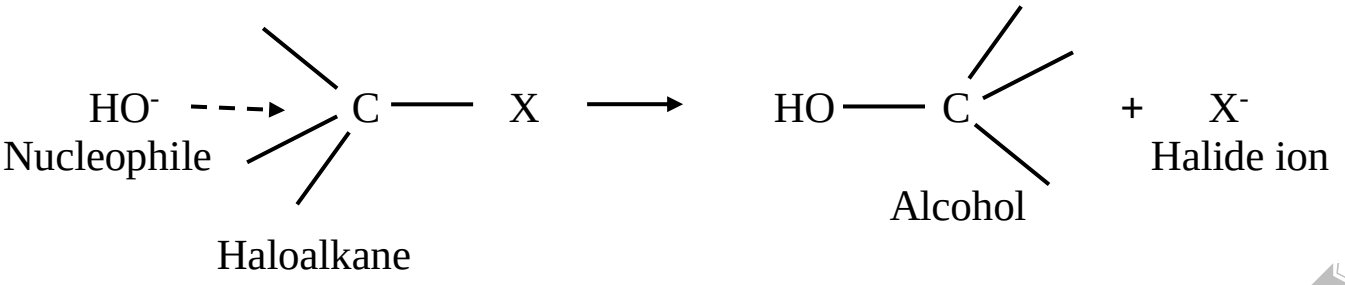


Fig.- Back side (Rear) attack of nucleophile (Proper Orientation)

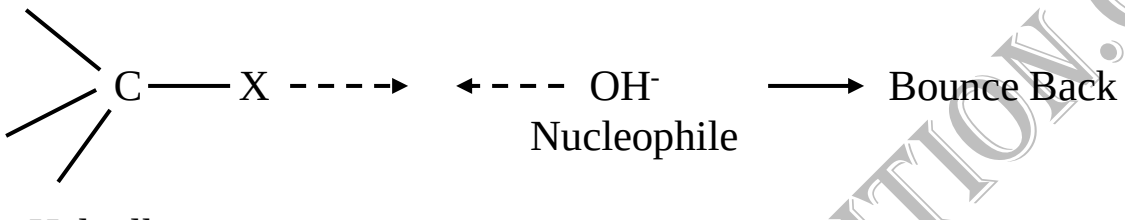


Fig.- Front attack of nucleophile (Improper orientation)

Let us consider following bimolecular elementary reaction –

$$A + B \rightarrow AB$$

Following Collision Theory,

$$\text{Rate} = Z_{AB}\, e^{-Ea/RT} \qquad \text{-------} \quad (1)$$

Where, Z_{AB} = Collision frequency (No. of collisions per sec. per unit volume of reaction mixture)

$e^{-Ea/RT}$ = The fraction of molecules having kinetic energy equal to or greater than E_a (activation energy), where $E_a >> RT$.

This equation holds good only for the reactions involving atoms or simple molecules as reactants, but shows deviation if reactants are complex molecules.

If orientation factor is taken into consideration, equation (1) takes following form-

$$\text{Rate} = P.Z_{AB}\, e^{-Ea/RT} \qquad \text{-------} \quad (2)$$

Where, P = probability factor or steric factor

This equation gives more satisfactory result for the rate of the reactions involving complex molecules.

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Competition Corner

(1) From Arrhenius equation-

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

Here, the value of k increases with increase of temperature.

If $T \to \infty$ then, $k = A$

(2) $\frac{k}{A} = e^{-Ea/RT}$ = Boltzman factor

= The fraction of molecules having their kinetic energy equal to or greater than E_a (activation energy), where $E_a >> RT$.

(3) $\because \quad k = A\, e^{-Ea/RT}$

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

or $\frac{d}{dT}(\ln k) = \frac{d}{dT}(\ln A) + \frac{d}{dT}(-\frac{E_a}{RT})$

or $\frac{d}{dT}(\ln k) = 0 - \frac{E_a}{R} \cdot \frac{d}{dT}(T^{-1})$

or $\frac{d}{dT}(\ln k) = \frac{E_a}{R}(T^{-2})$

or $\frac{d}{dT}(\ln k) = \frac{E_a}{RT^2}$

This is differential form of Arrhenius equation.

(4)Temperature Co-efficient- "The ratio of the specific rate constants of a chemical reaction at two different temperatures differing by 10^0 is called temperature co-efficient of the reaction."

Mathematically,

$$\text{Temperature co-efficient, } \mu = \frac{k_{t+10^0}}{k_t{}^0}$$

Experimentally it has been found that, for each 10^0 rise of temperature, the rate of most of the molecular reactions becomes twice or thrice of the initial rate of the reaction. Thus, temperature co-efficient of most of the molecular reactions lies between 2 to 3.

$$\text{Temperature co-efficient, } \mu = \frac{k_{t+10^0}}{k_t{}^0} \approx 2-3$$

Let, temperature co-efficient of a reaction is η and temperature of the reaction is increased from T_1 to T_2, so that, the rate of the reaction changes from r_1 to r_2. Then,

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{\Delta T/10}$$

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or $\frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^n$ Where, $n = \frac{T_2 - T_1}{10}$

(5) Relation between half life period of a n^{th} order reaction and initial conc. of reactant- For a n^{th} order reaction, half life period-

$$t_{\frac{1}{2}} \alpha \frac{1}{(a_0)^{n-1}}$$ where, a_0 = Initial conc. of reactant

If n = 0, then $t_{\frac{1}{2}} \alpha \frac{1}{(a_0)^{0-1}}$

$\alpha \frac{1}{(a_0)^{-1}}$

$\alpha \ a_0$

If n = 1, then $t_{\frac{1}{2}} \alpha \frac{1}{(a_0)^{1-1}}$

$\alpha \frac{1}{(a_0)^0}$ (Independent of a_0)

If n = 2, then $t_{\frac{1}{2}} \alpha \frac{1}{(a_0)^{2-1}}$

$\alpha \frac{1}{a_0}$

If n = 3, then $t_{\frac{1}{2}} \alpha \frac{1}{(a_0)^{3-1}}$

$\alpha \frac{1}{(a_0)^2}$

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