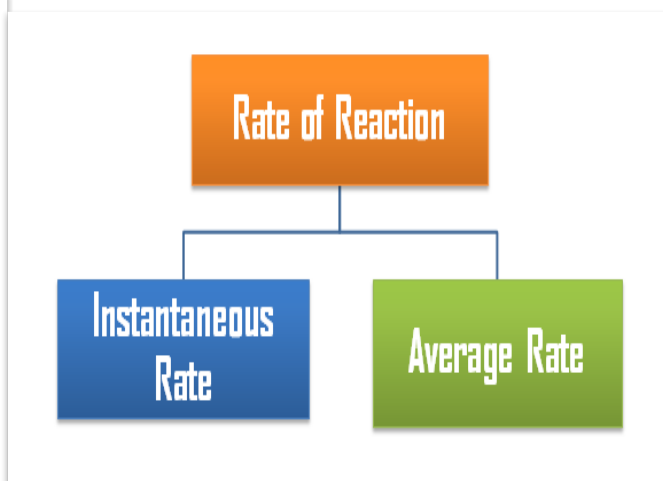
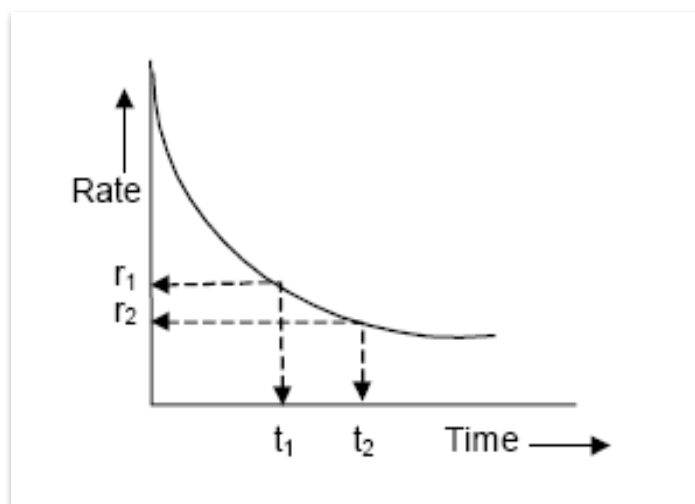


Chemical Kinetics

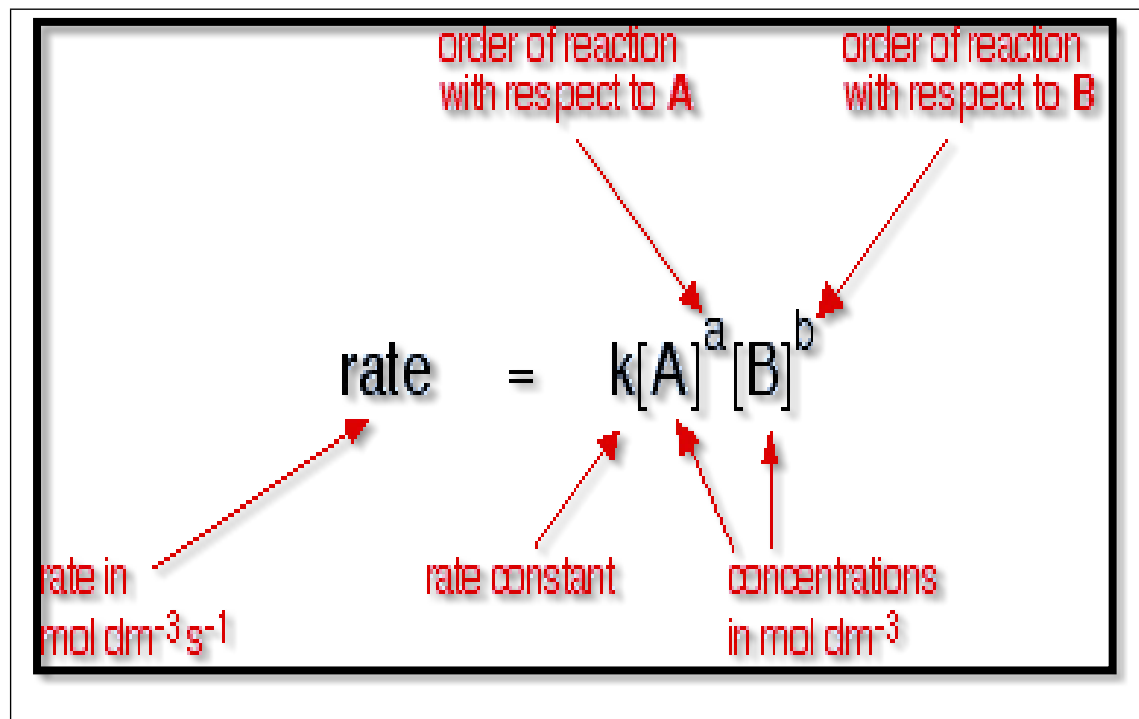
Rate of Reaction

- Rate of change of extent of reaction is the rate of reaction.
- Rate of reaction is positive for product and negative for reactant.
- For reaction $aA \rightarrow bB$
Rate = $1/b(\Delta[B]/\Delta t) = -1/a(\Delta[A]/\Delta t)$
- It goes on decreasing as the reaction progress due to decrease in the concentration(s) of the reactant(s).



- Unit of rate of reaction : $\text{mol L}^{-1} \text{s}^{-1}$
- The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.
- In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentrations of the reactants decreases, i.e., products are produced.
- The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.

Order of Reaction



For reaction $aA + bB + \dots \rightarrow cC + \dots$

$R \propto [A]^m[B]^n$ or $R = k[A]^m[B]^n \dots$

Where m and n may or may not be equal to a & b .

m is order of reaction with respect to A and n is the order of reaction with respect to B.
 $m + n + \dots$ is the overall order of the reaction.

Elementary Reaction:

- It is the reaction which completes in a single step.
- A reaction may involve more than one elementary reactions or steps also.
- Overall rate of reaction depends on the slowest elementary step and thus it is known as rate determining step.

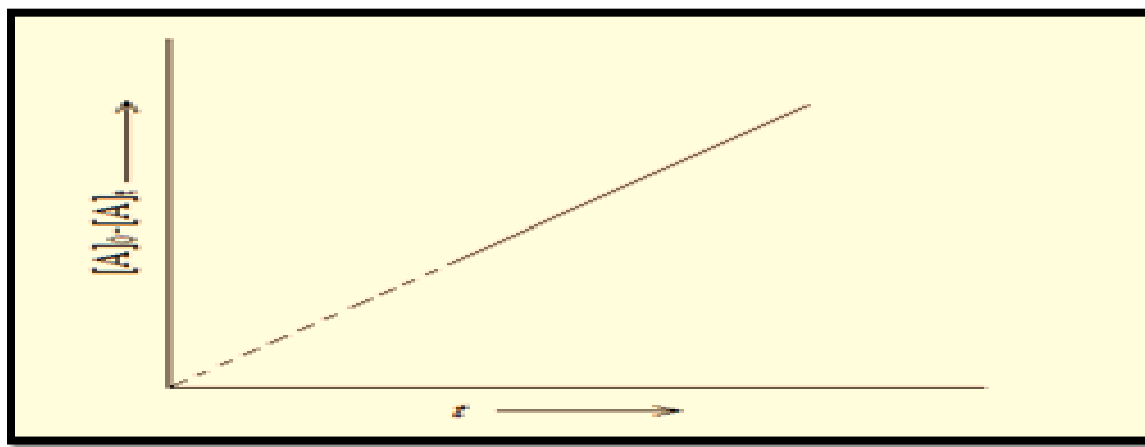
Molecularity of Reaction:

- Number of molecules taking part in an elementary step is known as its molecularity.
- Order of an elementary reaction is always equal to its molecularity.
- Elementary reactions with molecularity greater than three are not known because collisions in which more than three particles come together simultaneously are rare.

Chemical Reaction	Molecularity
$\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2$	Unimolecular
$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	Bimolecular
$2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$	Trimolecular

$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	Bimolecular
$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	Trimolecular
$2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{FeCl}_2$	Trimolecular

**Differential and Integrated Rate Laws:
Zero Order Reactions:**



For Reaction: $\text{A} \rightarrow \text{Product}$

$$[\text{A}]_0 - [\text{A}]_t = k_0 t$$

Where,

$[\text{A}]_0$ = Initial concentration of A

$[\text{A}]_t$ = Concentration of A at time t.

k_0 = Rate constant for zero order reaction.

Half Life:

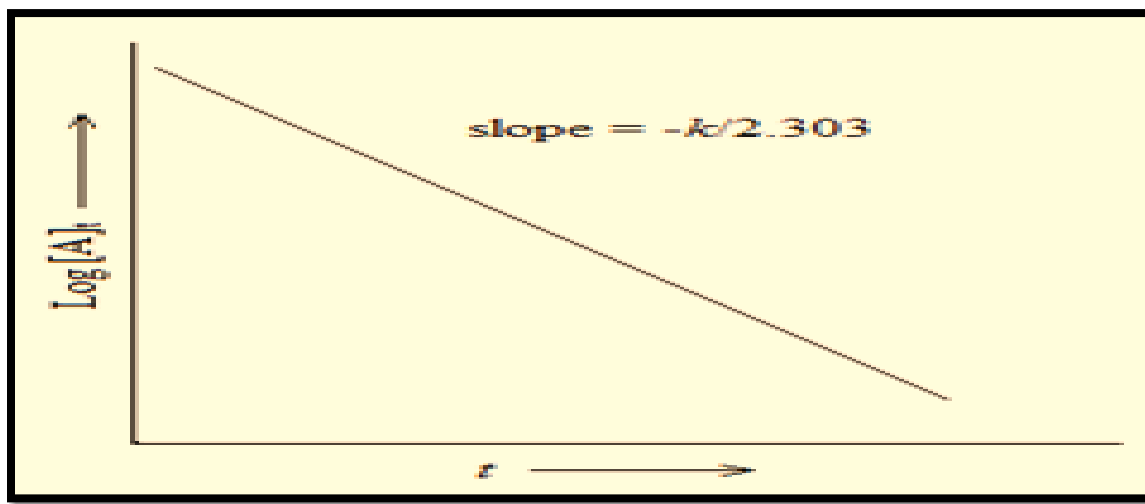
$$t_{1/2} = [\text{A}]_0 / 2k$$

Unit of rate constant = $\text{mol dm}^{-3}\text{s}^{-1}$

Examples:

- Enzyme catalyzed reactions are zero order with respect to substrate concentration.
- Decomposition of gases on the surface of metallic catalysts like decomposition of HI on gold surface.

First Order Reactions:



A → Product

$$\frac{\Delta [A]}{[A]} = -k_1 \Delta t$$

$$\text{or } k_1 = \frac{2.303}{t} \log \left(\frac{[A]_0}{[A]_t} \right)$$

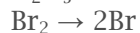
Half Life:

$$t_{1/2} = 0.693/k_1$$

Half life is independent of the initial concentration of the reactant for a first order reaction.

Units of $k_1 = \text{s}^{-1}$

Examples:

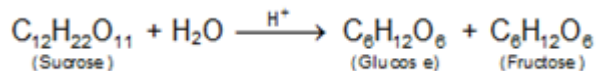


Pseudo First Order Reactions:

These are the reactions in which more than one species is involved in the rate determining step but still the order of reaction is one.

Examples:

- Acid hydrolysis of ester: $\text{CH}_3\text{COOEt} + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{EtOH}$
- Inversion of cane sugar:



- Decomposition of benzenediazonium halides $\text{C}_6\text{H}_5\text{N}=\text{NCl} + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$

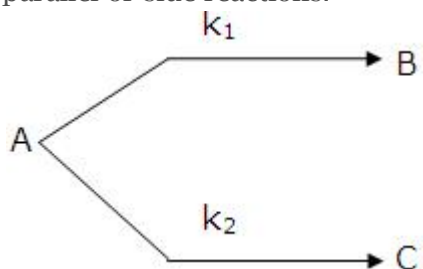
Half - Life of a nth Order Reaction:

$$kt_{1/2} = (2^{n-1}-1)/(n-1)[A_0]^{n-1}$$

Where, n = order of reaction $\neq 1$

Parallel Reactions:

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



If we assume that both of them are first order, we get.

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

k_1 = fractional yield of B $\times k_{av}$

k_2 = fractional yield of C $\times k_{av}$

If $k_1 > k_2$ then

A \rightarrow B main and

A \rightarrow C is side reaction

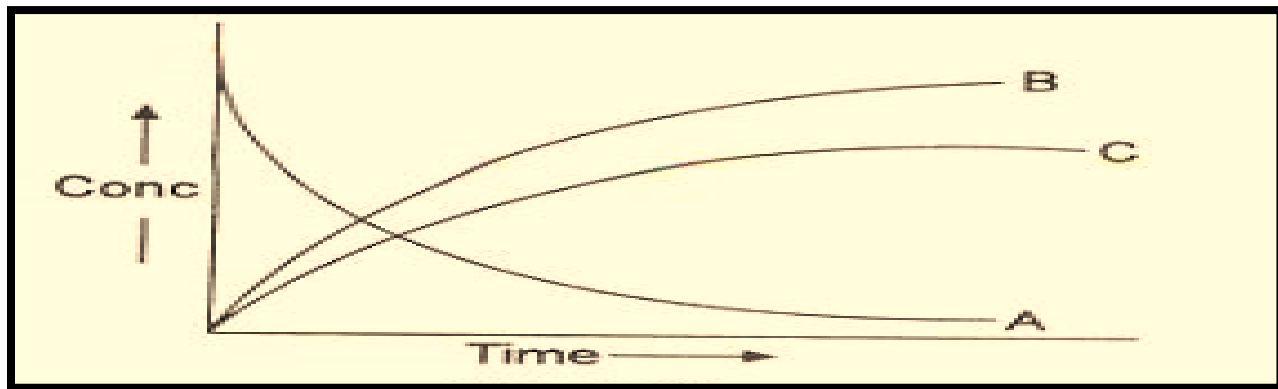
Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

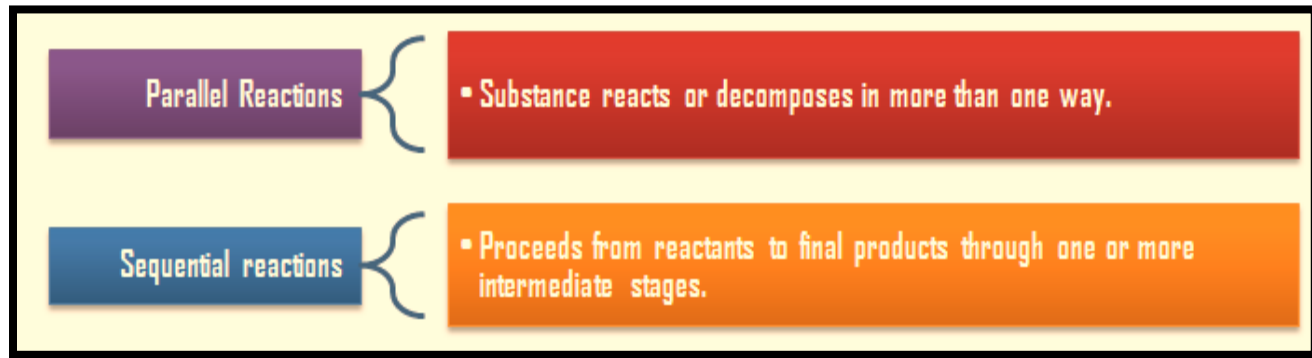
$$\frac{x}{y} = \frac{k_1}{k_2}$$

i.e

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2 .

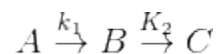




Sequential Reactions:-

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$A \rightarrow B \rightarrow C$ and so on



$$-\frac{d[A]}{dt} = k_1[A] \dots\dots(i)$$

$$\frac{d[B]}{dt} = k_1[A] - K_2[B] \dots\dots(ii)$$

$$\frac{d[C]}{dt} = k_2[B] \dots\dots(iii)$$

Integrating equation (i), we get

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C] = \frac{[A]_0}{k_2 - k_1} [k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t})]$$

$$t_{\max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

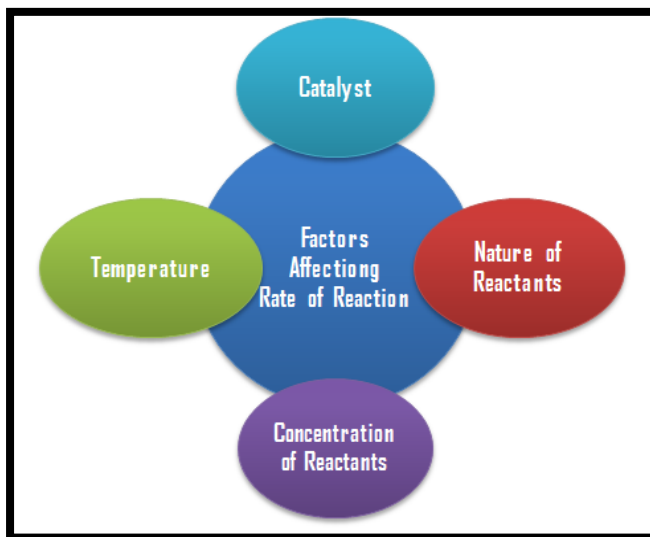
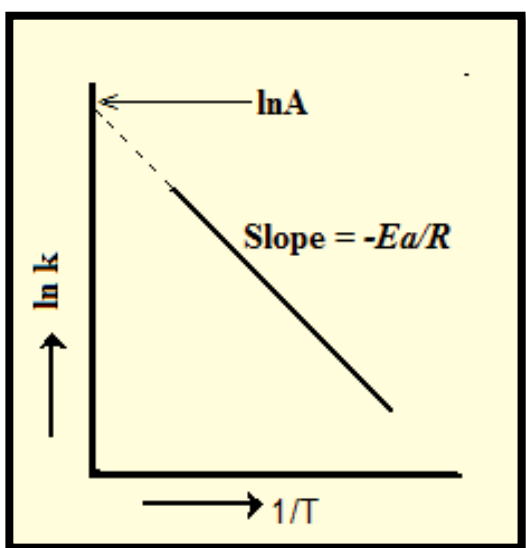
$$B_{\max} = [A]_0 \left[\frac{k_2}{k_1} \right]^{k_2/k_1 - k_2}$$

Arrhenius Equation:

$$k = A \exp(-E_a/RT)$$

Where, k = Rate constant

A = pre-exponential factor
 E_a = Activation energy



Temperature Coefficient:

The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10°C.

μ = Temperature coefficient = $k_{(t+10)}/k_t$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2 ; then the ratio of rate constants or rate may be calculated as

$$\frac{k_{T_2}}{k_{T_1}} = \mu^{\frac{T_2 - T_1}{10}} = \mu^{\frac{\Delta T}{10}}$$

$$\log \frac{k_{T_2}}{k_{T_1}} = \mu^{\frac{T_2 - T_1}{10}} = \Delta T \log \mu$$

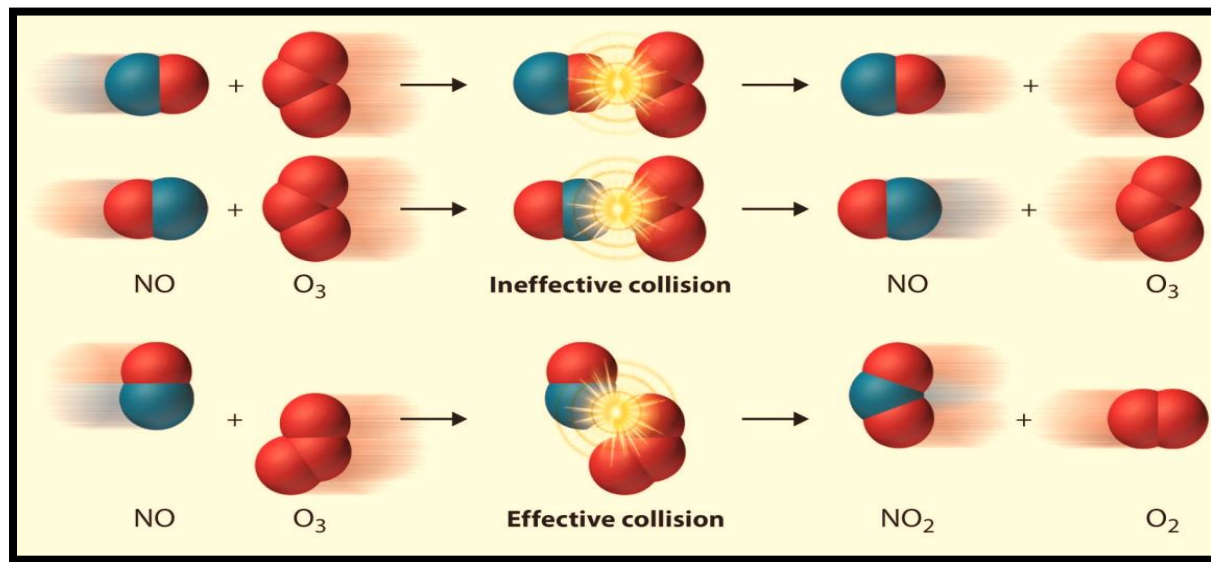
$$\frac{k_{T_2}}{k_{T_1}} = \text{antilog} \left[\frac{\Delta T}{10} \log \mu \right]$$

Its value lies generally between 2 and 3.

Collision Theory of Reaction Rate:-

- A chemical reaction takes place due to collision among reactant molecules.
- The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z).
- The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.
- Every collision does not bring a chemical change.
- The collisions that actually produce the products are effective collisions.

- The effective collisions which bring chemical change are few in comparison to the form a product are ineffective elastic collisions, i.e., molecules just collide and
- disperse in different directions with different velocities.
- For a collision to be effective, the following two barriers are to be cleared.
 1. Energy Barrier
 2. Orientation Barrier



Radioactivity:-

All radioactive decay follow 1st order kinetics

For radioactive decay $A \rightarrow B$

$$-\frac{dN_A}{dt} = \lambda N_A$$

Where, λ = decay constant of reaction

N_A = number of nuclei of the radioactive substance at the time when rate is calculated.

Arrhenius equation is not valid for radioactive decay.

Integrated Rate Law: $N_t = N_0 e^{-\lambda t}$

Half Life: $t_{1/2} = 0.693/\lambda$

Average life time: Life time of a single isolated nucleus, $t_{av} = 1/\lambda$

Activity: Rate of decay

$$A = \frac{dN_A}{dt}, \text{ Also, } A_t = A_0 e^{-\lambda t}$$

Specific Activity: activity per unit mass of the sample.

$$\text{Specific activity} = \frac{\left(\lambda \times \frac{w}{M} \times Av \right)}{w} = \frac{\lambda \times Av}{M}$$

Units: dps or Becquerre