SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادى

SOUTH VALLEY UNIVERSITY - FACULTY OF EDUCATION
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Chemical Kinetics

For 2nd chemistry student (faculty of science)

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Chemical
Kinetics

Kinetics

- Studying the rate of chemical reaction.
- Studying the factors effect on reaction rate
- Besides information about the speed at which reactions occur, kinetics also sheds light on the reaction mechanism (exactly *how* the reaction occurs).

Kinetics

- People are interested in measuring the speed of reactions due to:

1) Trying to find out how the reaction happen.
2) Controlling reaction by Knowing the factors that affect the speed of the reaction.
3) Get the largest output or products in lower time.

Kinetics

- Examples:
- 1-Reducing the speed of reactions that spoil the food

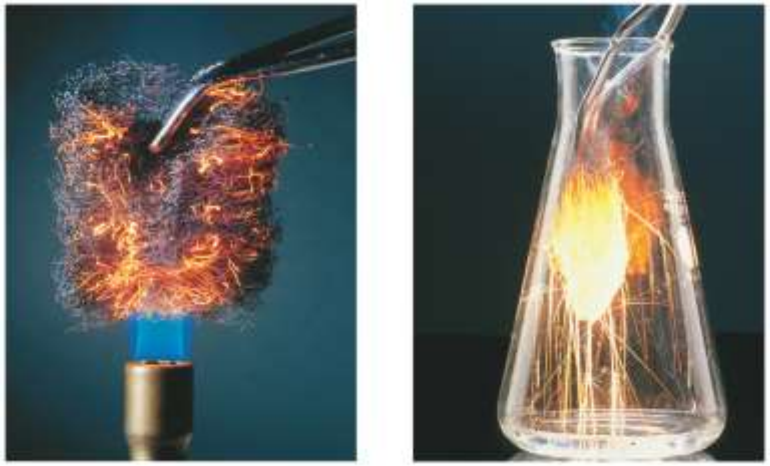
  2-Increase ammonia production by increasing the pressure of hydrogen and nitrogen
  3-Accelerate the reaction of zinc with hydrochloric acid by increasing the acid concentration.

  4- Preserving foods in a refrigerator ... to control the reactions that occur to foods and cause their decomposition and thus spoilage

  5- Also, keep the medicine at the temperature recommended by the manufacturer, so as not to cause unwanted reactions

Factors That Affect Reaction Rates

- **1-Concentration of Reactants**
    - As the concentration of reactants increases, the probability ofreactant molecules to collide increases.
- .



Factors That Affect Reaction Rates

- .
- **2-The nature of surface area of the reactants**
- play an important role in the speed of the reaction, for example the interaction of a powder of silver nitrate crystals with a powder of potassium iodide crystals is faster than the reaction of small pieces of each. Likewise, two solutions of each react faster than the two crushed ones.
- **Catalysts**

Factors That Affect Reaction Rates

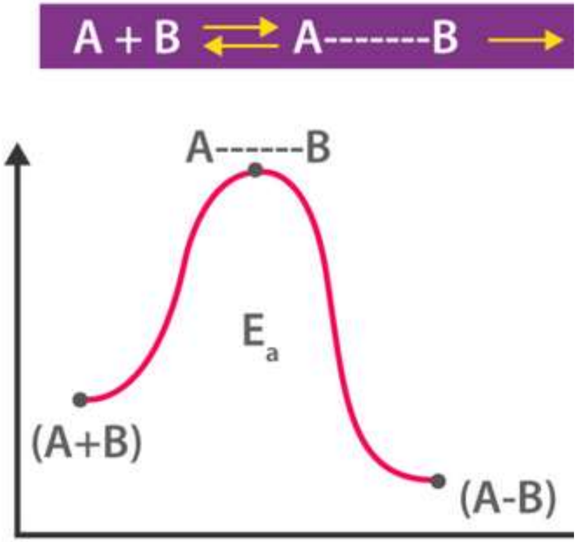
- .
- **3-Temperature**
    - At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.
- .

Factors That Affect Reaction Rates

- .
- **Activation energy**
  - Is the minimum energy required to cause a reaction to occur. The higher the activation energy, the slower the rate of the reaction.
  - In order for the reaction to take place, some or all of the chemical bonds in the reactants must be broken so that new bonds, those of the products, can form

Factors That Affect Reaction Rates

- .**Activation energy**
- By increasing the temperature, the number of collisions between reactant molecules per second (frequency of collision). Increases, thereby increasing the rate of the reaction an intermediate is formed which remains in equilibrium with the main reactant..



Factors That Affect Reaction Rates

- **Activation energy**

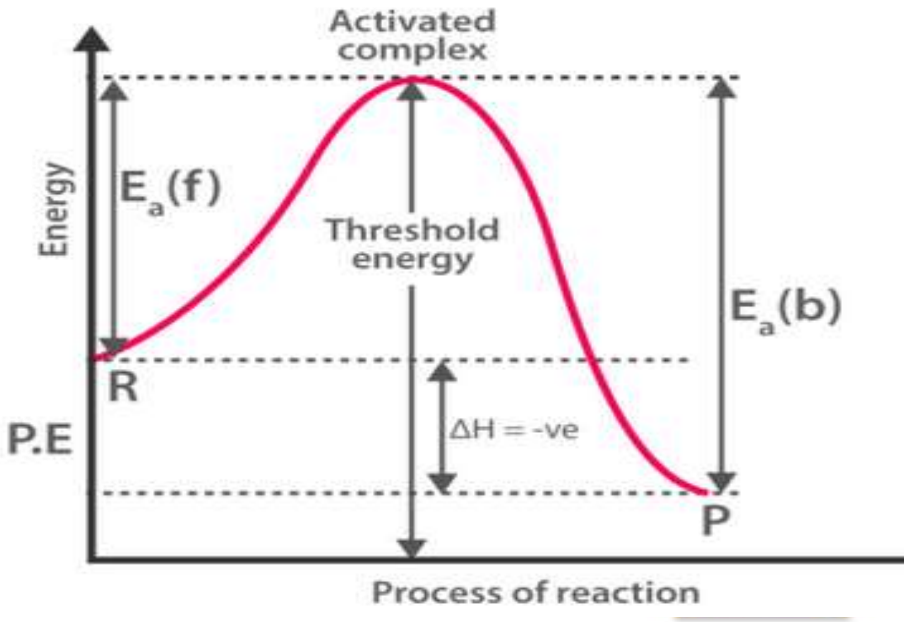
This unstable state called the **transition state.** The reactant molecules don’t stay there long, but quickly proceed to the next step of the chemical Reaction.

.Types of chemical reaction

A-Exothermic reaction

$$\Delta H = (E_a)_f - (E_a)_b$$

$$\Delta H = \text{-ve value}$$



Factors That Affect Reaction Rates

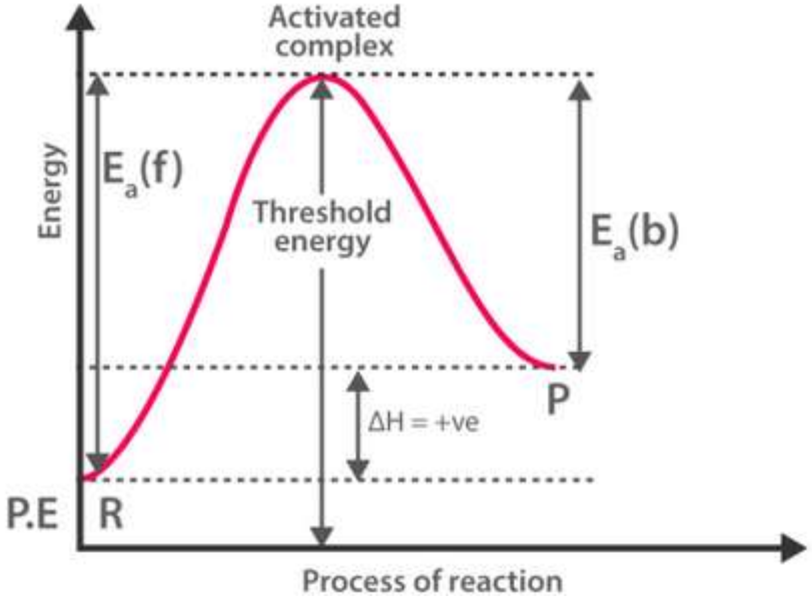
- **Activation energy**

.Types of chemical reaction

b-Endothermic reaction

$$\Delta H = (E_a)_b - (E_a)_f$$

$$\Delta H = +ve \text{ value}$$



Factors That Affect Reaction Rates

- **The Arrhenius Equation**

The Arrhenius equation is crucial for calculating the rates of chemical reactions and, importantly, the quantity of energy necessary to start them.

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

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction. R is the universal gas constant (units of energy per temperature increment per mole), T represents the absolute temperature (usually measured in kelvins), and E is the activation energy

Factors That Affect Reaction Rates

- **The Arrhenius Equation**

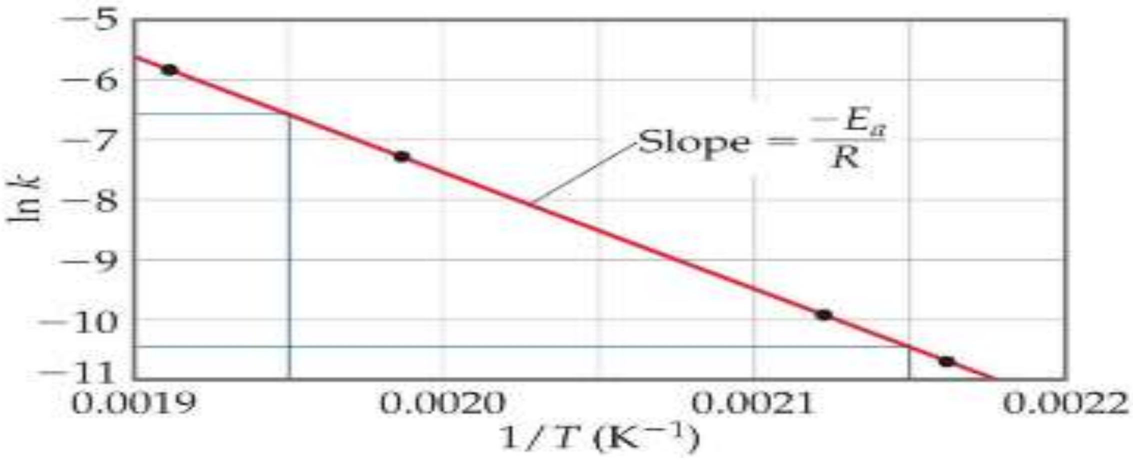
$$\begin{array}{ccccc} \ln k & = & -\dfrac{E_a}{RT} & + & \ln A \\ \updownarrow & & \updownarrow & & \updownarrow \\ y & = & mx & + & b \end{array}$$

many data points

$H_3C{-}N{\equiv}C{:} \longrightarrow H_3C{-}C{\equiv}N{:}$

Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

T (K)	1/T (K^{-1})	ln k
462.9	2.160×10^{-3}	−10.589
472.1	2.118×10^{-3}	−9.855
503.5	1.986×10^{-3}	−7.370
524.4	1.907×10^{-3}	−5.757



Factors That Affect Reaction Rates

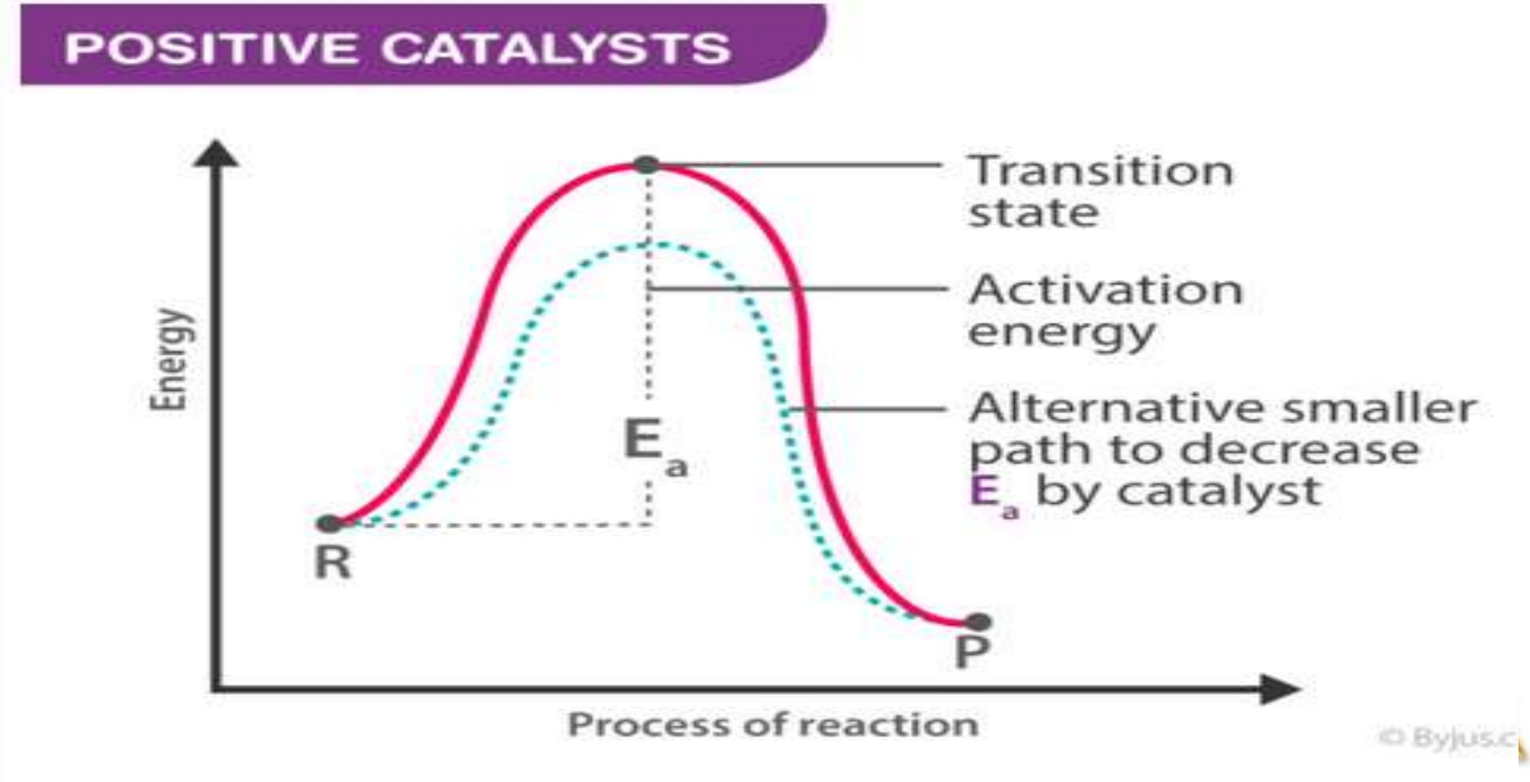
- .
- **4-Catalysts**
  - Catalyst agents are substances that increase the speed of chemical reactions without consuming during the reaction, by reducing the activation energy of the forward and reverse reactions together, that is done by finding an alternative way for the reaction to go easily where the activation energy required for the reaction is less than in the presence of the catalyst

Factors That Affect Reaction Rates

- .
- **4-Catalysts**

.Types of Catalysts

.Positive Catalysts

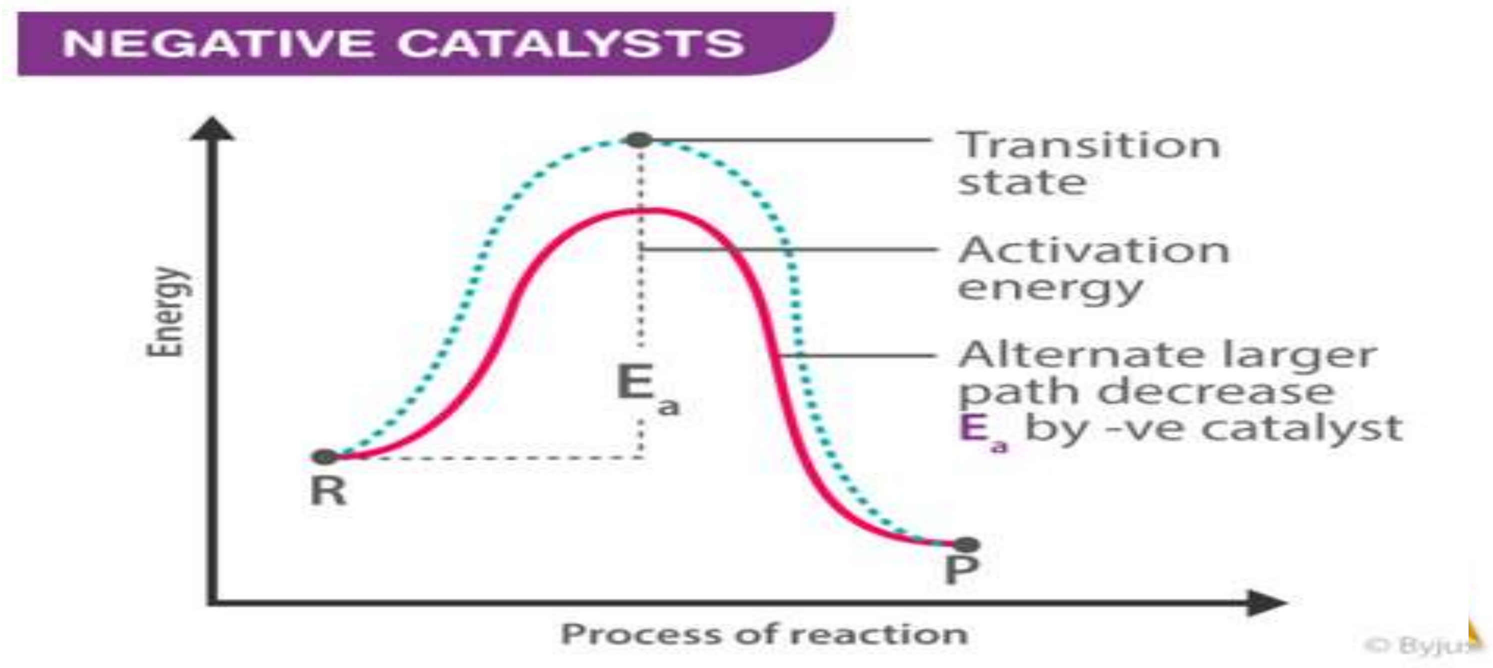


Factors That Affect Reaction Rates

- **4-Catalysts**

.Negative Catalysts

A catalyst that decreases or retards or helps in slowing down the rate of reaction is called negative catalysts. As Preservatives

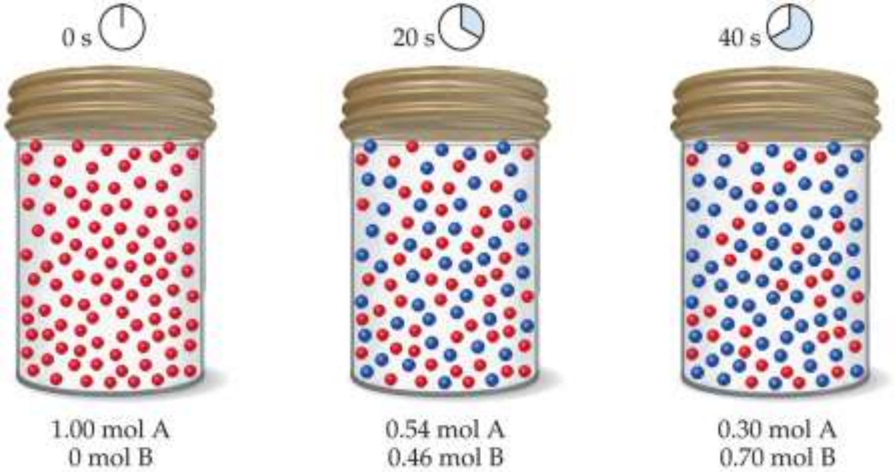


Factors That Affect Reaction Rates

- **5- Stirring**
  - Stirring the chemical reaction mixture increases the energy of motion of the reactants and thus increases the probability of collisions and thus increases the speed of the chemical reaction.

Reaction Rates

Rxn Movie



Rates of reactions can be determined by monitoring the change in concentration of either reactants or products as a function of time. **Δ[A] vs Δt**

Reaction Rates

- . (i) the rate of decrease in concentration of any one of the reactants, or(ii)the rate of increase in concentration of any one of the products.

  - A → B

- One mole of the reactant A produces one mole of the product B.
- If [A]1 and [B]1 are the concentrations of A and
- B respectively at time t1and [A]2 and [B]2 are their concentrations at time t2 then
- ,Δt=t2 – t1 Δ[A] = [A]2 – [A]1 Δ [B] = [B]2 – [B]1
- The square brackets in the above expressions are used to express molar concentration.

Reaction Rates

$$\text{Reactant} \rightarrow \text{Products}$$

$$A \rightarrow B$$

$$\text{Average rate} = \frac{\text{change in number of moles of B}}{\text{change in time}}$$

$$= \frac{\Delta(\text{moles of B})}{\Delta t} \qquad = \frac{\Delta[B]}{\Delta t}$$

Since reactants go away with time: $\text{Rate} = -\frac{\Delta[A]}{\Delta t}$

Since, Δ[A] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.

Reaction Rates

- It is clear that units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be at m s^{-1}
- **Types of reaction rate**
- The rate of reaction can be classified into average and instantaneous rate depending on the amount of time period
- **1-Average rate it is the rate of reaction through certain interval time.** The change in concentration divided by the change in time

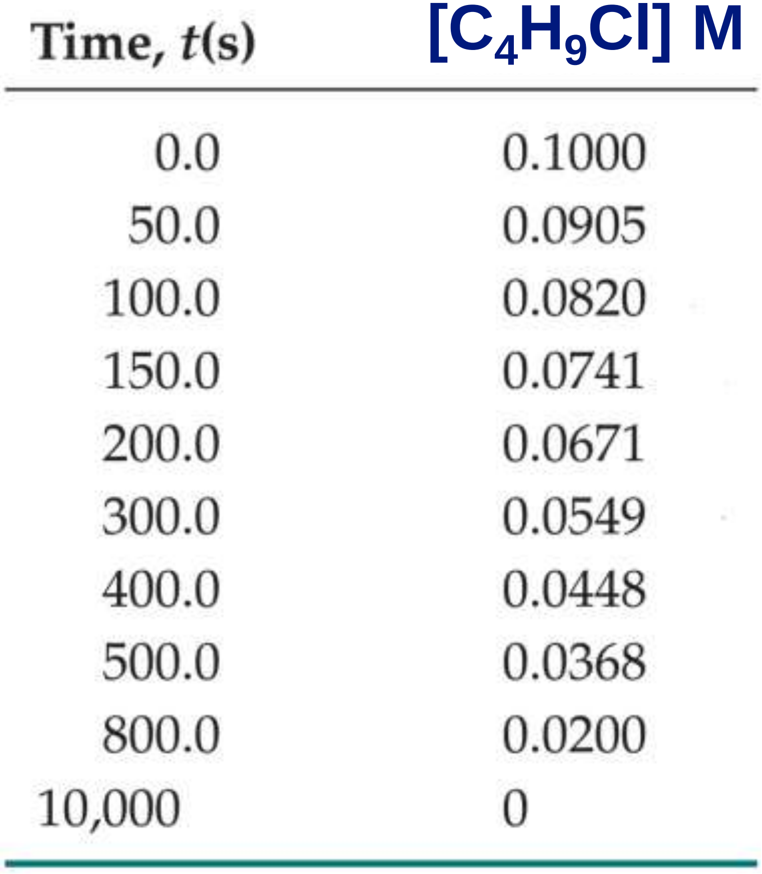
Reaction Rates

- **2- Instantaneous rate of reaction:. It is the** rate at a particular time
- -instantaneous rate obtained from the straight line tangent that touches the curve at a specific point slopes give instantaneous rates instantaneous rate also referred to as the real rate at a particular time

- **3- Initial rate of reaction it is a special case of Instantaneous rate and defined as the rate of reaction at time = Zero**
- **-** Obtained from the straight line tangent that touches the curve at a time= zero. And the slope give initial rate of reaction

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

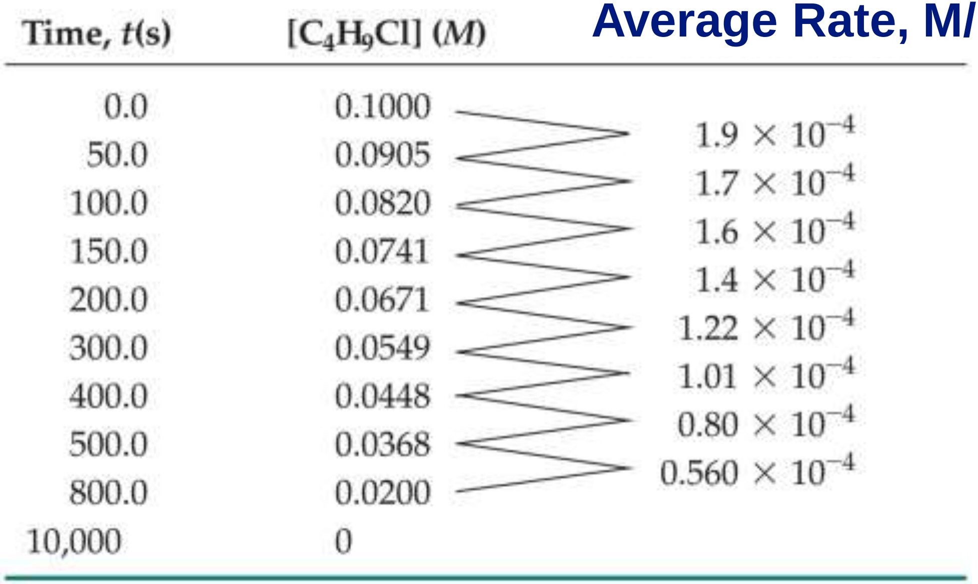


Time, *t*(s)	$[C_4H_9Cl]$ M
0.0	0.1000
50.0	0.0905
100.0	0.0820
150.0	0.0741
200.0	0.0671
300.0	0.0549
400.0	0.0448
500.0	0.0368
800.0	0.0200
10,000	0

In this reaction, the concentration of butyl chloride, $\mathbf{C_4H_9Cl}$, was measured at various times, **t**.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$



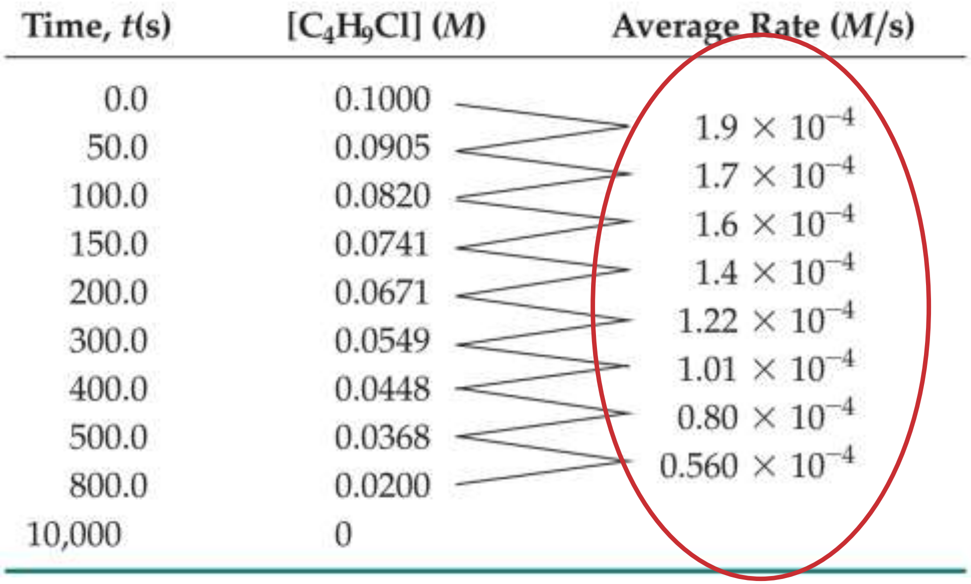
Time, t(s)	$[C_4H_9Cl]$ (M)	**Average Rate, M/s**
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

$$average\ rate = \frac{\Delta\left[C_4H_9\right]}{\Delta t}$$

$$average\ rate = \frac{\Delta\left[C_4H_9\right]}{\Delta t} = \frac{0.1000 - 0.0905\ M}{50.0 - 0.0\ s}$$

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$



Time, *t*(s)	$[C_4H_9Cl]$ (*M*)	Average Rate (*M*/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

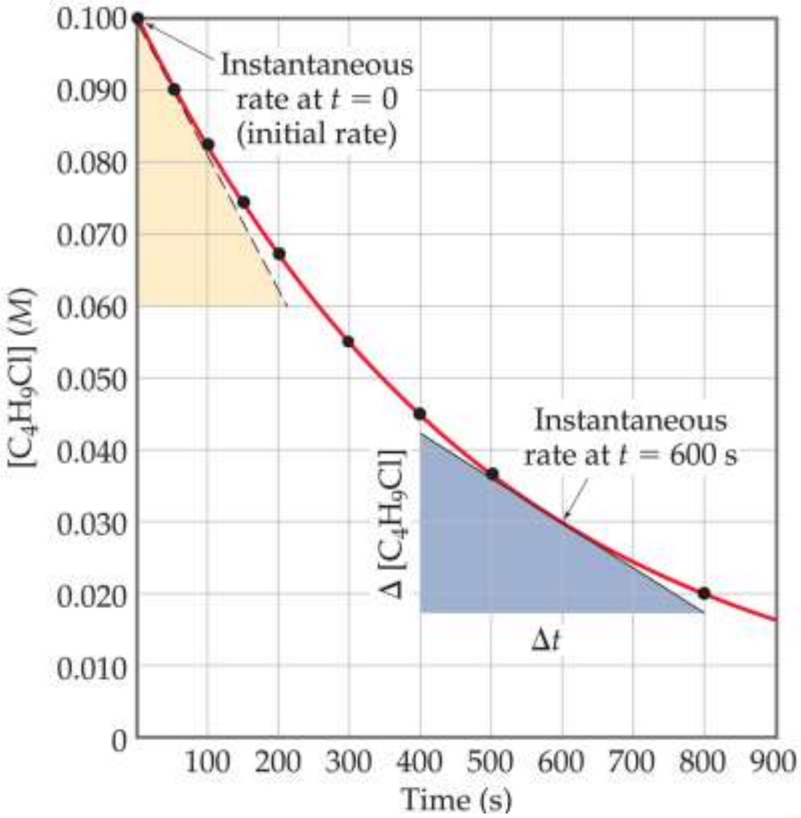
- Note that the average rate decreases as the reaction proceeds.
- This is because as the reaction goes forward, there are fewer collisions between reactant molecules.

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- A plot of concentration vs. time for this reaction yields a curve like this.
- The slope of a line tangent to the curve at any point is the instantaneous rate at that time.

$$\frac{\Delta[A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

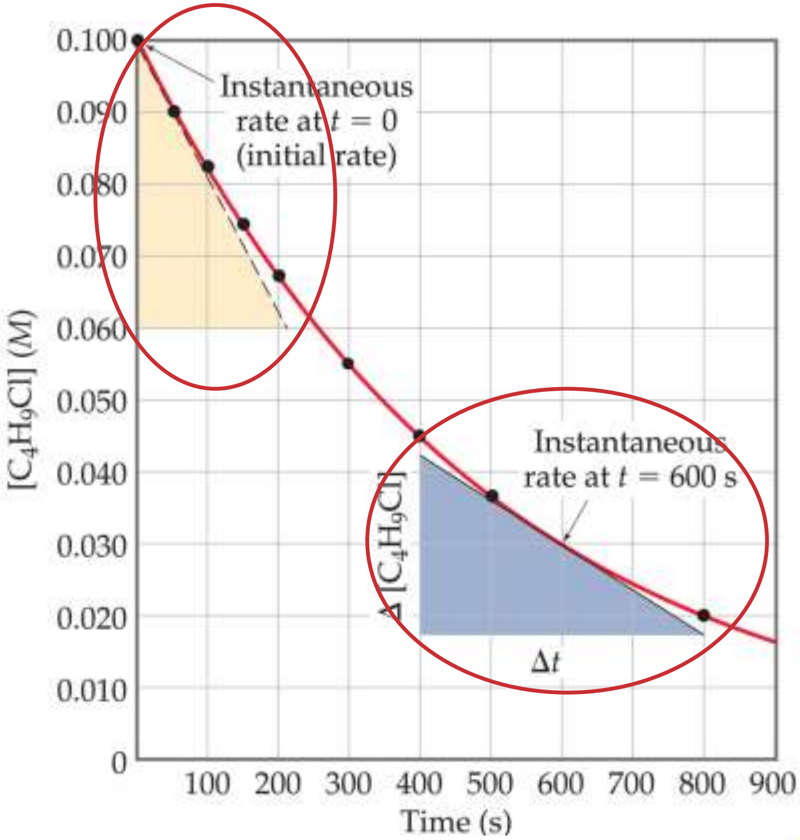


Chemical Kinetics

Reaction Rates

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- The reaction slows down with time because the concentration of the reactants decreases.

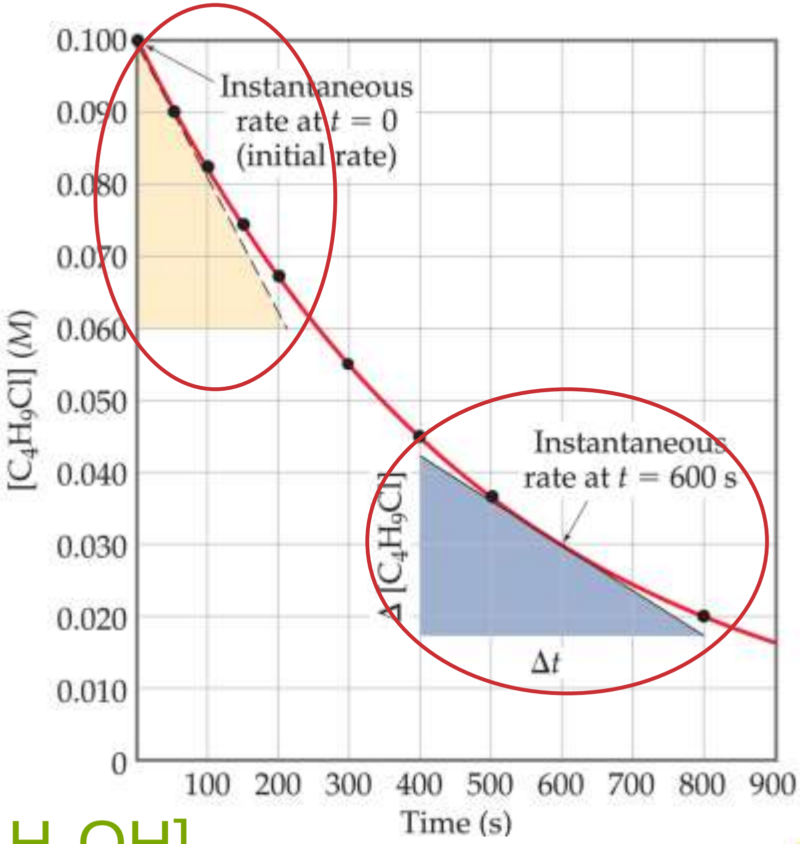


$$\frac{\Delta [A]}{\Delta t} \Rightarrow \frac{d[A]}{dt}$$

Reaction Rates and Stoichiometry

$C_4H_9Cl(aq) + H_2O(l) \rightleftharpoons C_4H_9OH(aq) + HCl(aq)$

- In this reaction, the ratio of C_4H_9Cl to C_4H_9OH is 1:1.
- Thus, the rate of *disappearance* of C_4H_9Cl is the same as the rate of *appearance* of C_4H_9OH



$$\text{Rate} = \frac{-\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Reaction Rates and Stoichiometry

- What if the ratio is *not* 1:1?

$$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

- The rate of disappearance of HI is twice that than
- the rate of appearance of H_2.

$$rate = -\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Reaction Rates and Stoichiometry

- To generalize, for the reaction

$$aA + bB \longrightarrow cC + dD$$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Reactants (decrease)

Products (increase)

Reaction Rates and Stoichiometry

(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction

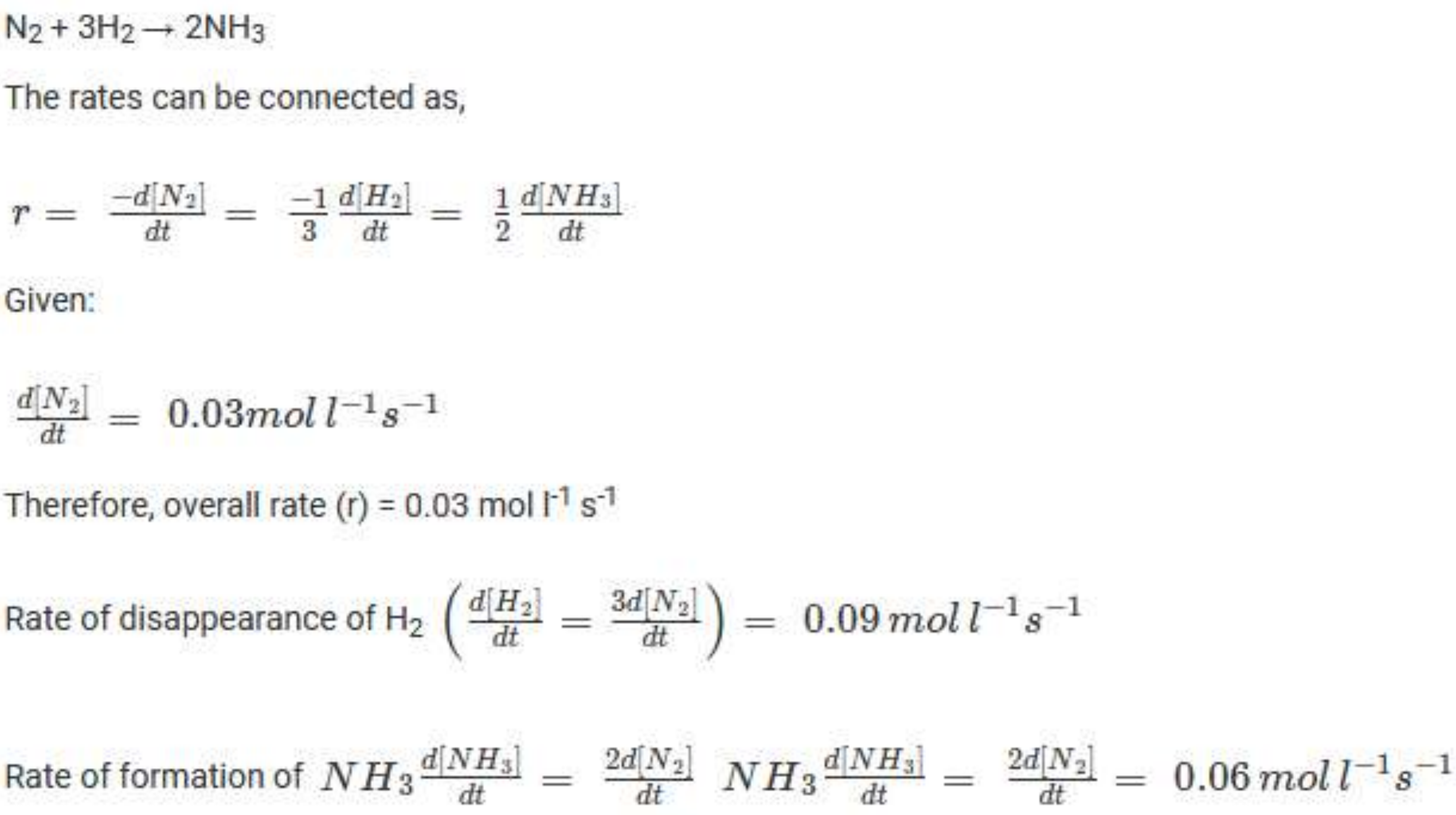
$$2\,O_3(g) \longrightarrow 3\,O_2(g)?$$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

(b) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]/\Delta t$?

$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}(6.0 \times 10^{-5}\,M/\text{s}) = 4.0 \times 10^{-5}\,M/\text{s}$$

Reaction Rates and Stoichiometry



$N_2 + 3H_2 \rightarrow 2NH_3$

The rates can be connected as,

$$r = \frac{-d[N_2]}{dt} = \frac{-1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

Given:

$$\frac{d[N_2]}{dt} = 0.03 mol\, l^{-1} s^{-1}$$

Therefore, overall rate (r) = 0.03 mol l^{-1} s^{-1}

Rate of disappearance of H_2 $\left(\frac{d[H_2]}{dt} = \frac{3d[N_2]}{dt}\right) = 0.09\, mol\, l^{-1} s^{-1}$

Rate of formation of $NH_3 \frac{d[NH_3]}{dt} = \frac{2d[N_2]}{dt}$ $NH_3 \frac{d[NH_3]}{dt} = \frac{2d[N_2]}{dt} = 0.06\, mol\, l^{-1} s^{-1}$

Concentration and Rate

Consider a general reaction

$aA + bB \rightarrow cC + dD$ where a, b, c and d are the stoichiometric coefficients of reactants and products. The rate expression for this reaction is

$\text{Rate} \propto [A]^x [B]^y$ (4.4)

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as $\text{Rate} = k [A]^x [B]^y$

k is a proportionality constant called rate constant.

rate law is the expression in which reaction rate is given in terms of molar concentration of reactants which 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

Order of reaction

The Order of reaction refers to the relationship between the rate of a chemical reaction and the concentration of the species taking part in it.

And defined as the sum of powers of the reactants concentration that affect on the rate of reaction must be raised

It indicates to what extent the concentration of a species affects the rate of a reaction, as well as which species has the greatest effect

Molecularity of an elementary reaction is

defined as the number of reactant molecules taking part in the reaction.

Note

- For gas phase reactions, rate law is expressed in terms of partial pressures, which are related to the molar concentrations.

- The rate law of the reaction is determined experimentally so it cannot be determined theoretically from the chemical equation of the reaction.

- In some cases, the rate law does not depend on the reaction stoichiometry.

- Exponents are usually positive whole numbers or zero

- The units of the rate constant depend on the order of reaction.

Note

Reaction order represents the number of species whose concentration directly affects the rate of reaction.

It can be obtained by adding all the exponents of the concentration terms in the rate expression.

The order of reaction does not depend on the stoichiometric coefficients corresponding to each species in the balanced reaction.

The reaction order of a chemical reaction is always defined with the help of reactant concentrations and not with product concentrations.

The value of the order of reaction can be in the form of an integer and It can even have a value of zero

Chemical Reaction	Molecularity
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Trimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2CO + O_2 \rightarrow 2CO_2$	Trimolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Trimolecular

Note:

- Molecularity is a theoretical concept.
- Molecularity cannot be zero, -ve, fractional, infinite and imaginary.
- Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

Concentration and Rate

The units of the rate constant

The rate constant is a proportionality factor in the rate law of chemical kinetics that relates the molar concentration of reactants to reaction rate. It is also known as the reaction rate constant or reaction rate coefficient and is indicated in an equation by the letter *k*

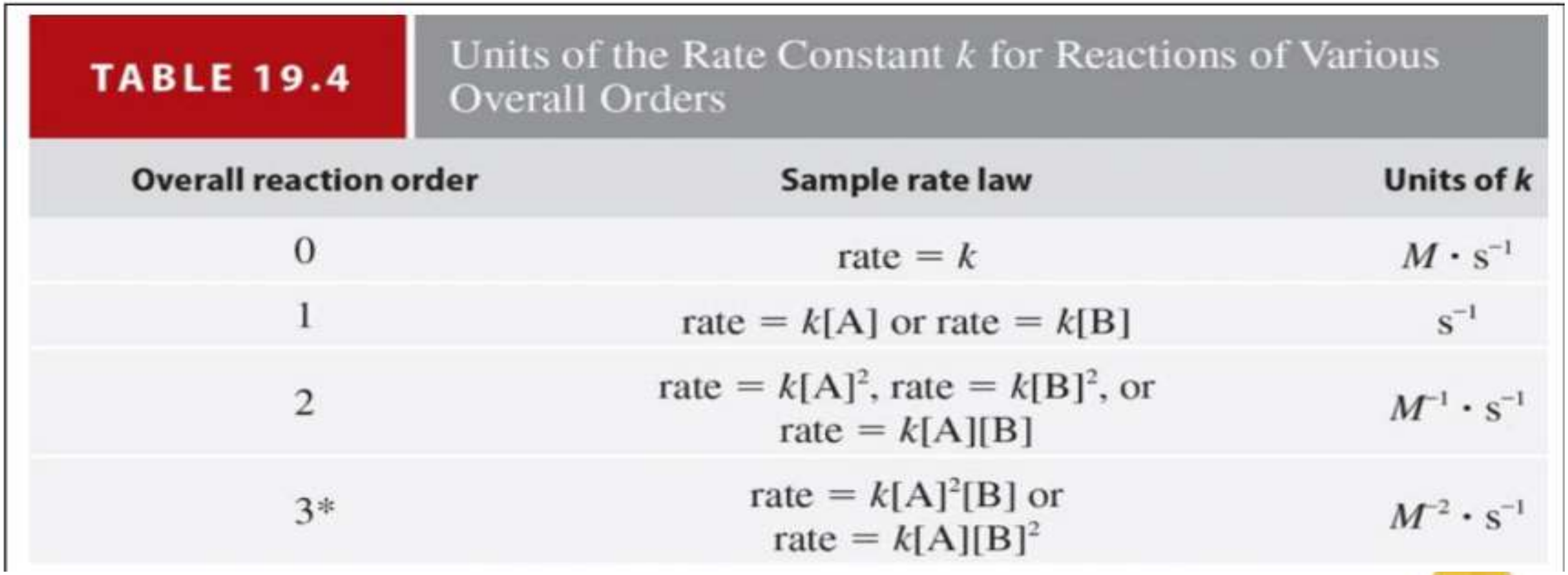


TABLE 19.4 Units of the Rate Constant *k* for Reactions of Various Overall Orders

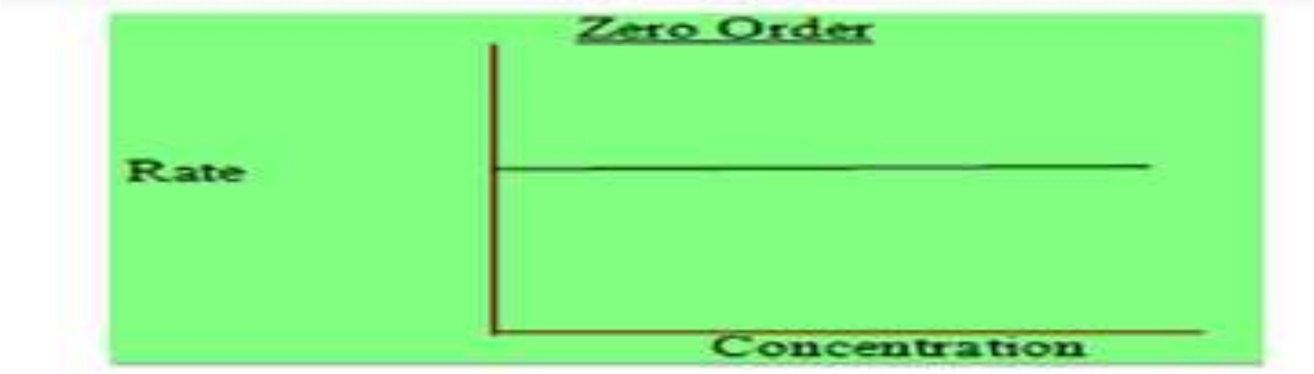
Overall reaction order	Sample rate law	Units of *k*
0	rate = k	$M \cdot s^{-1}$
1	rate = $k[A]$ or rate = $k[B]$	s^{-1}
2	rate = $k[A]^2$, rate = $k[B]^2$, or rate = $k[A][B]$	$M^{-1} \cdot s^{-1}$
3*	rate = $k[A]^2[B]$ or rate = $k[A][B]^2$	$M^{-2} \cdot s^{-1}$

Types of reaction order

ZERO ORDER REACTION

When the reaction rate is independent of concentration of the reacting substance, it depends on the zero power of the reactant and therefore is zero order reaction. In this type of reaction, the limiting factor is something other than concentration, for example, or absorption of light in certain photochemical reactions and catalytic reaction . The rate of decomposition can be described mathematically as:

$$dx/dt = K$$



zero-order reactions

Types of reaction order

ZERO ORDER REACTION

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \rightarrow P$$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]^0$$

As any quantity raised to power zero is unity

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

$$d[R] = -k\,dt$$

Integrating both sides

$$[R] = -k\,t + I \qquad (4.5)$$

where, I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (4.5)

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

$$[R]_0 = I$$

Substituting the value of I in the equation (4.5)

$$[R] = -kt + [R]_0 \qquad (4.6)$$

Types of reaction order

ZERO ORDER REACTION

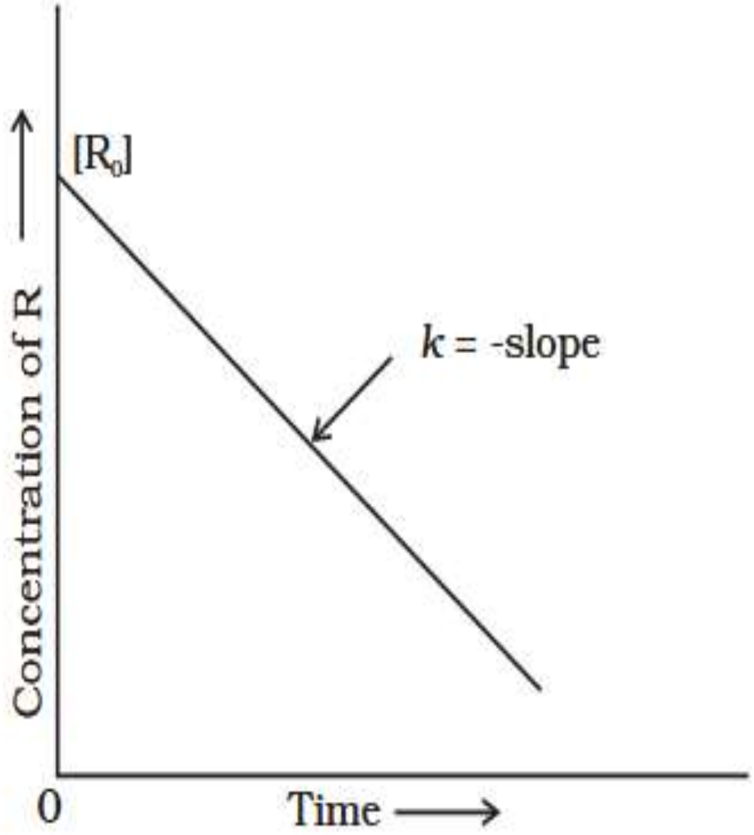
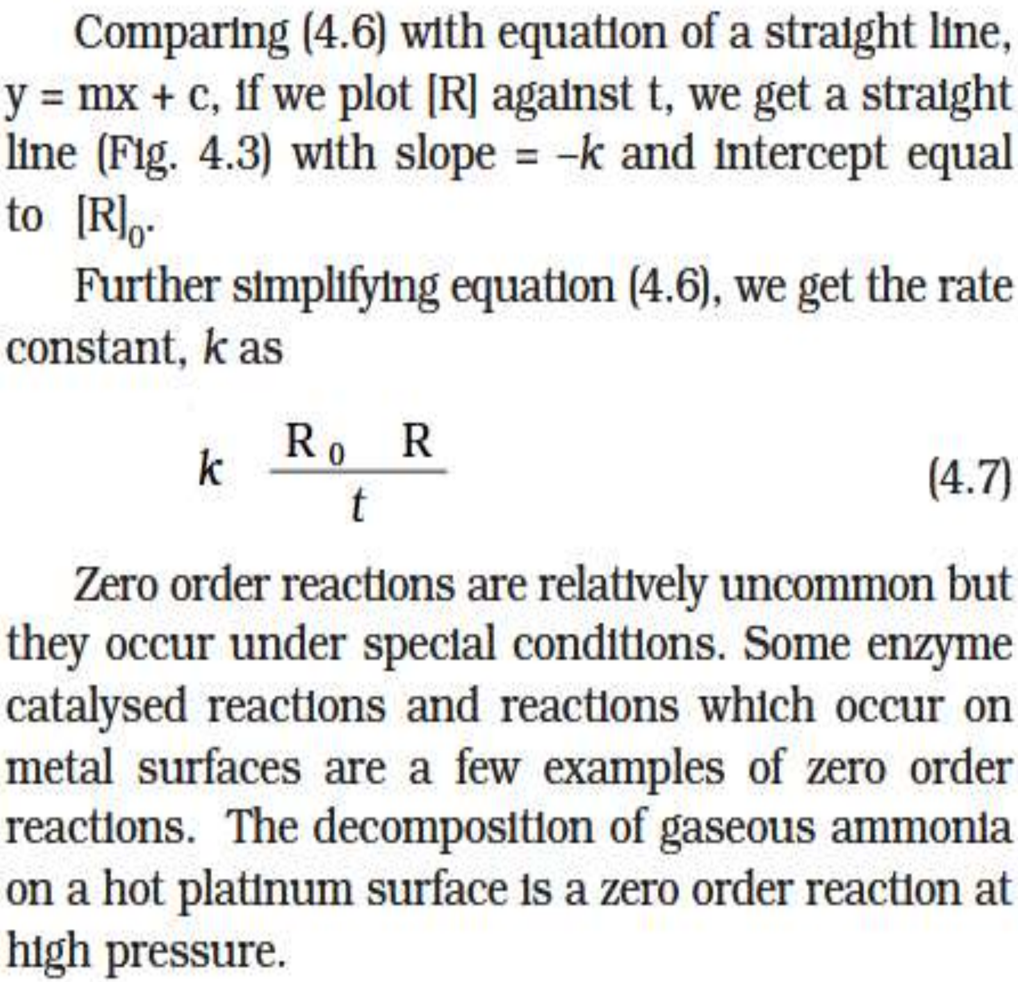


Fig. 4.3: *Variation in the concentration vs time plot for a zero order reaction*



Comparing (4.6) with equation of a straight line, y = mx + c, if we plot [R] against t, we get a straight line (Fig. 4.3) with slope = $-k$ and intercept equal to $[R]_0$.

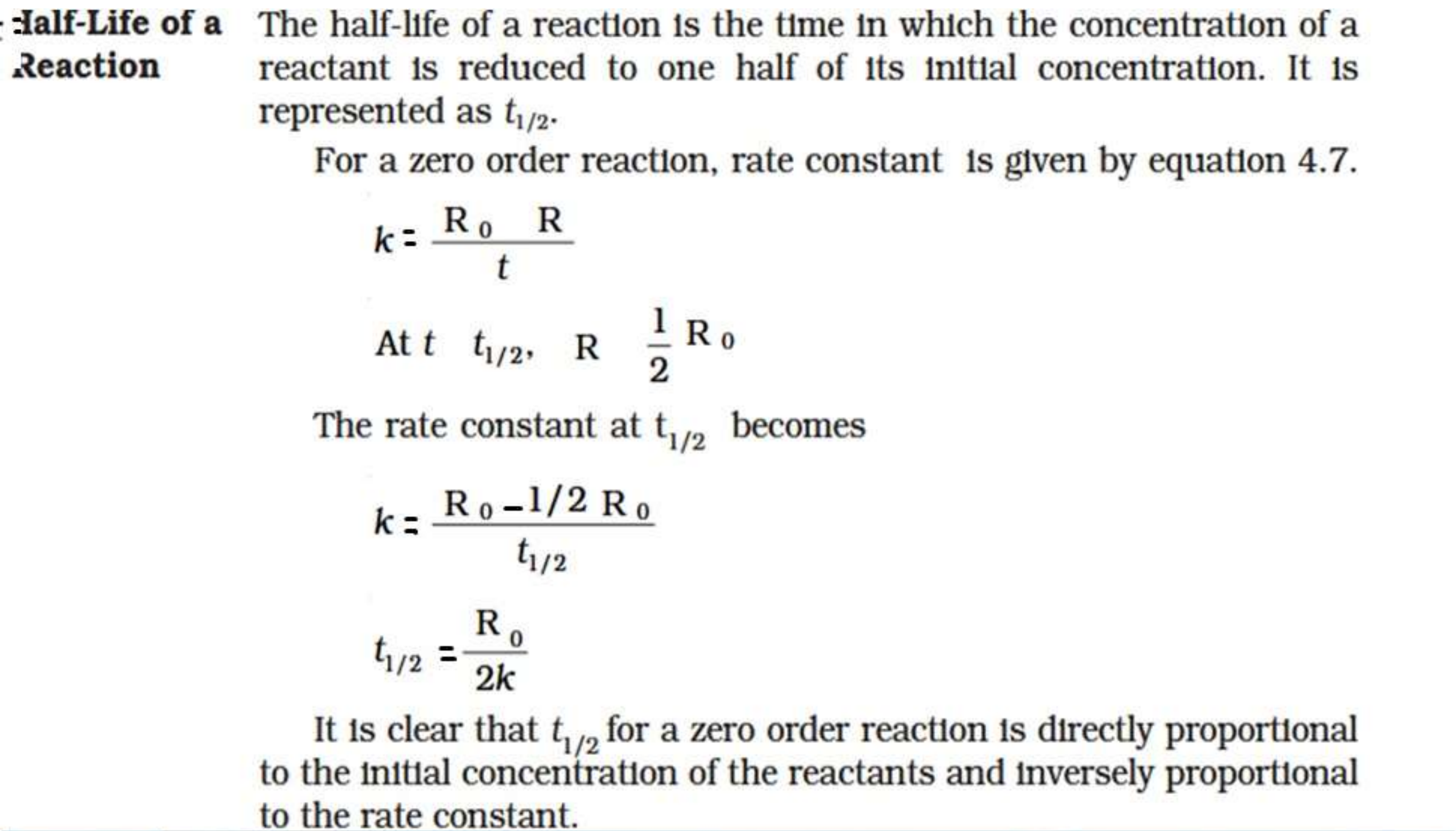
Further simplifying equation (4.6), we get the rate constant, k as

$$k \quad \frac{R_0 \quad R}{t} \qquad (4.7)$$

Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.

Types of reaction order

ZERO ORDER REACTION



Half-Life of a Reaction

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

For a zero order reaction, rate constant is given by equation 4.7.

$$k = \frac{R_0 \quad R}{t}$$

$$\text{At } t \quad t_{1/2}, \quad R \quad \frac{1}{2} R_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{R_0 - 1/2\, R_0}{t_{1/2}}$$

$$t_{1/2} = \frac{R_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

Types of reaction order

ZERO ORDER REACTION

It is a constant quantity that does not change with time

It does not depend on the concentration of the reactants

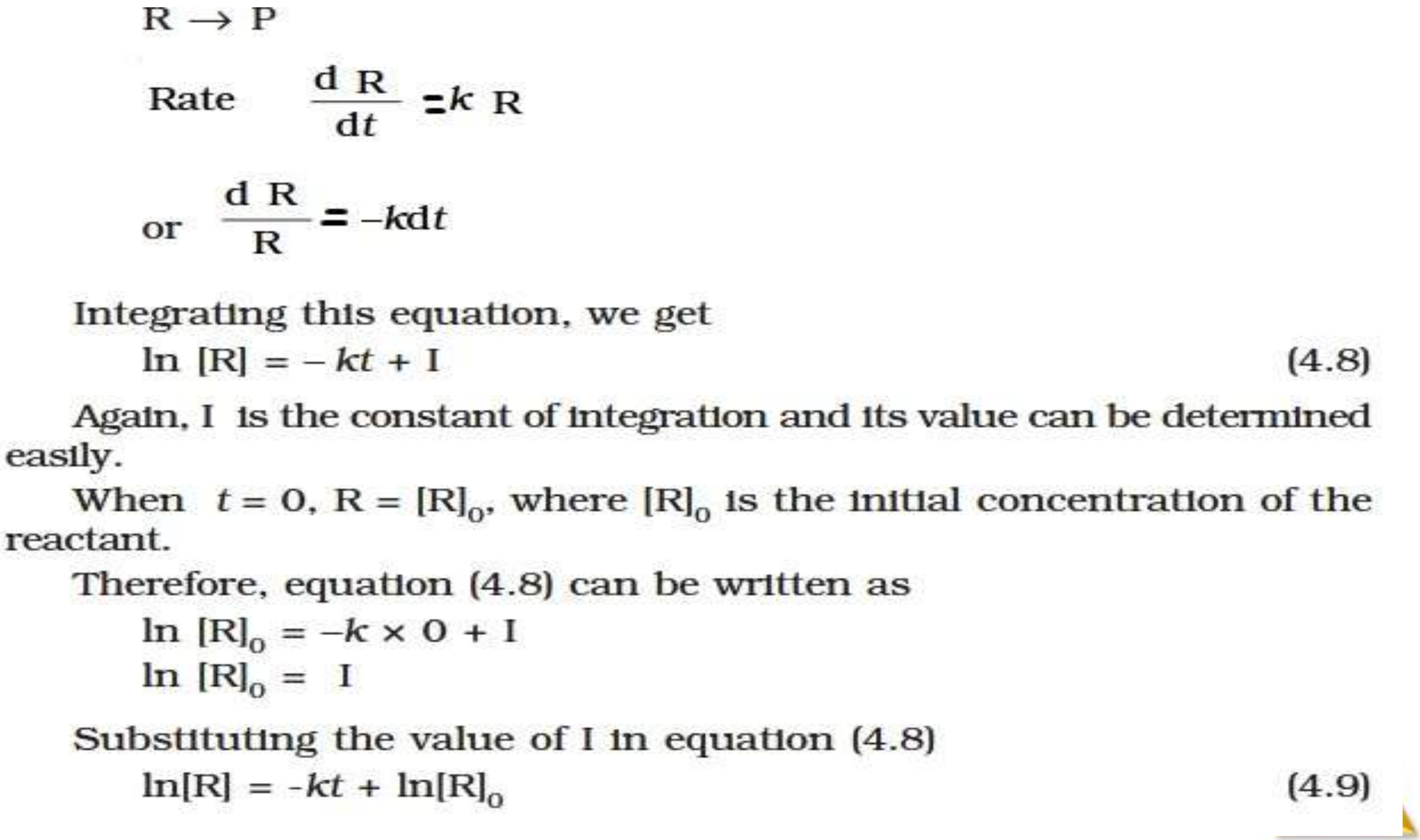
The reaction order is not equal to the molecularity

It consider uncommon reaction

Types of reaction order

First ORDER REACTION

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant



$$R \rightarrow P$$

Rate $$\frac{d\ R}{dt} = k\ R$$

or $$\frac{d\ R}{R} = -k\,dt$$

Integrating this equation, we get

$$\ln [R] = -kt + I \qquad (4.8)$$

Again, I is the constant of integration and its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (4.8) can be written as

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

$$\ln [R]_0 = I$$

Substituting the value of I in equation (4.8)

$$\ln[R] = -kt + \ln[R]_0 \qquad (4.9)$$

Types of reaction order

First ORDER REACTION

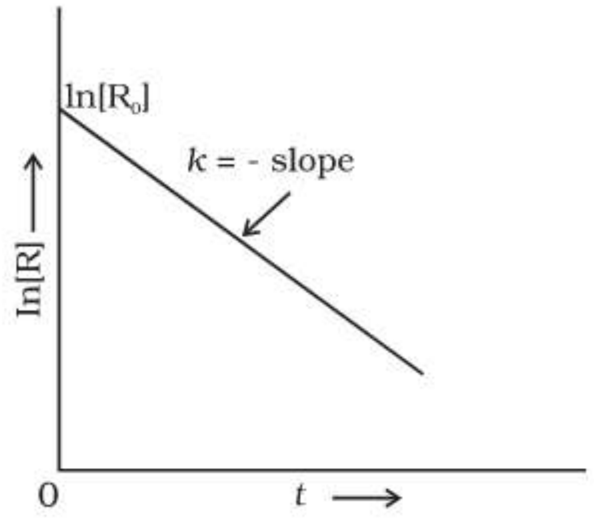


Fig. 4.4: *A plot between ln[R] and t for a first order reaction*

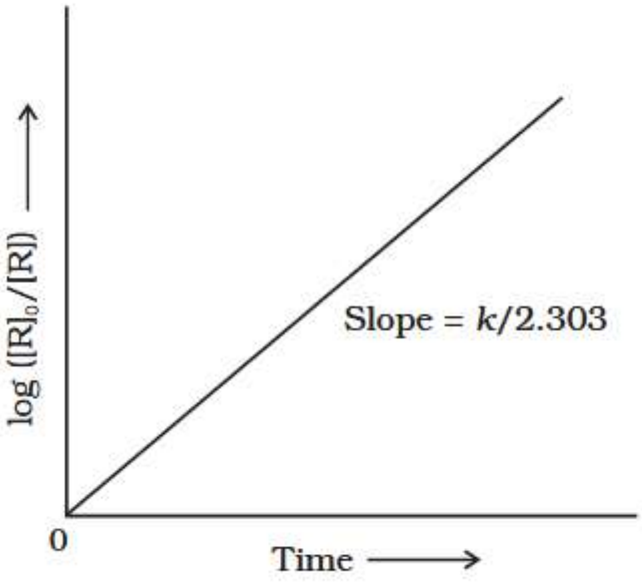


Fig. 4.5: *Plot of log $[R]_0/[R]$ vs time for a first order reaction*

Types of reaction order

First ORDER REACTION

$$k \quad \frac{2.303}{t}\log\frac{R_0}{R}$$

$$\text{at} \quad t_{1/2} \quad R \quad \frac{R_0}{2}$$

So, the above equation becomes

$$k \quad \frac{2.303}{t_{1/2}}\log\frac{R_0}{R/2}$$

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

$$t_{1/2} \quad \frac{2.303}{k} \quad 0.301$$

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

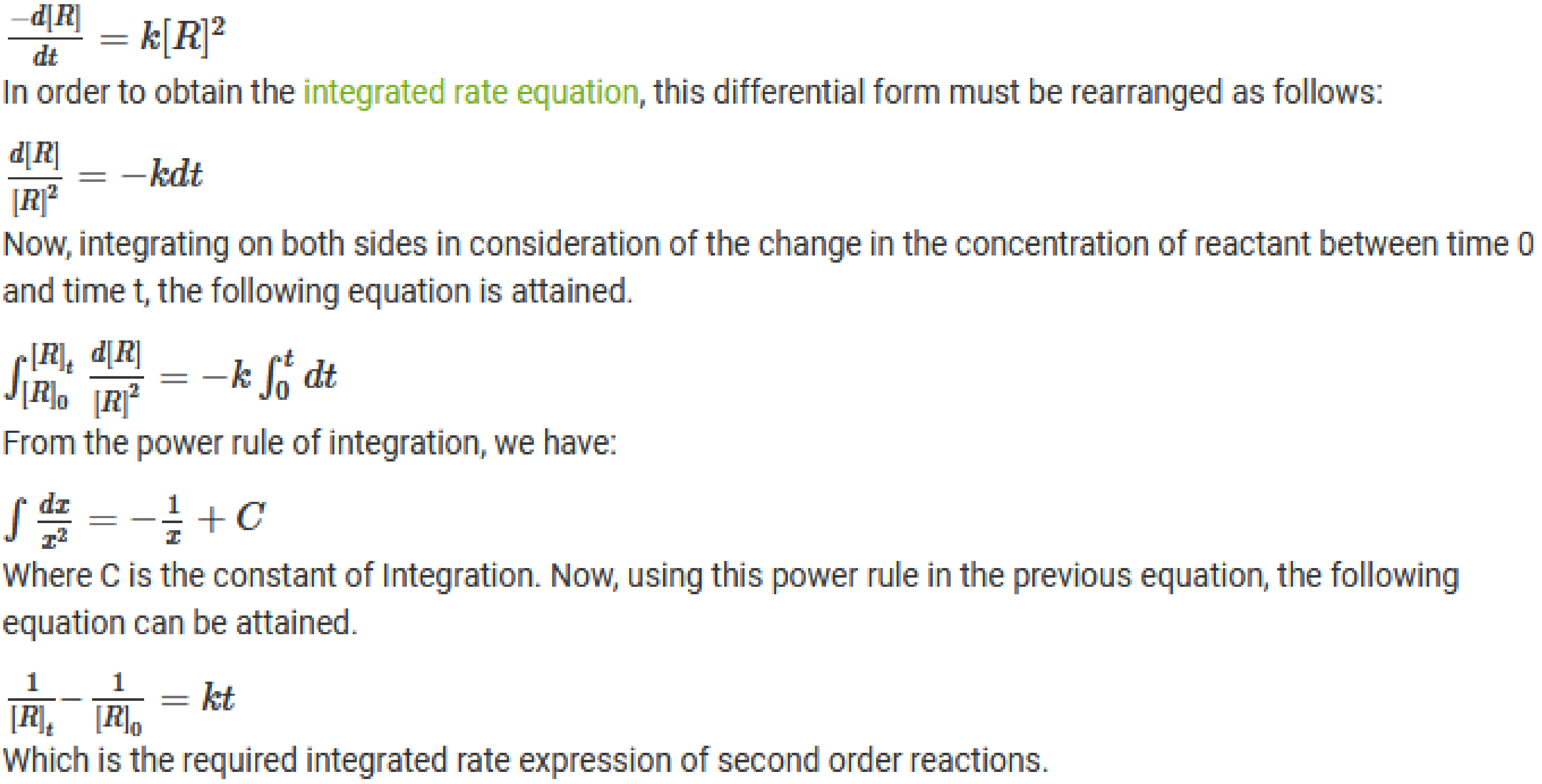
It can be seen that for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species. The half-life of a first order equation is readily calculated from the rate constant and vice versa.

For zero order reaction $t_{1/2} \propto [R]_0$. For first order reaction $t_{1/2}$ is independent of $[R]_0$

Types of reaction order

Second ORDER REACTION

The second order reactions are chemical reactions which depend on either the concentrations of two first-order reactants or the concentration of one-second order reactant.



$$\frac{-d[R]}{dt} = k[R]^2$$

In order to obtain the integrated rate equation, this differential form must be rearranged as follows:

$$\frac{d[R]}{[R]^2} = -kdt$$

Now, integrating on both sides in consideration of the change in the concentration of reactant between time 0 and time t, the following equation is attained.

$$\int_{[R]_0}^{[R]_t} \frac{d[R]}{[R]^2} = -k \int_0^t dt$$

From the power rule of integration, we have:

$$\int \frac{dx}{x^2} = -\frac{1}{x} + C$$

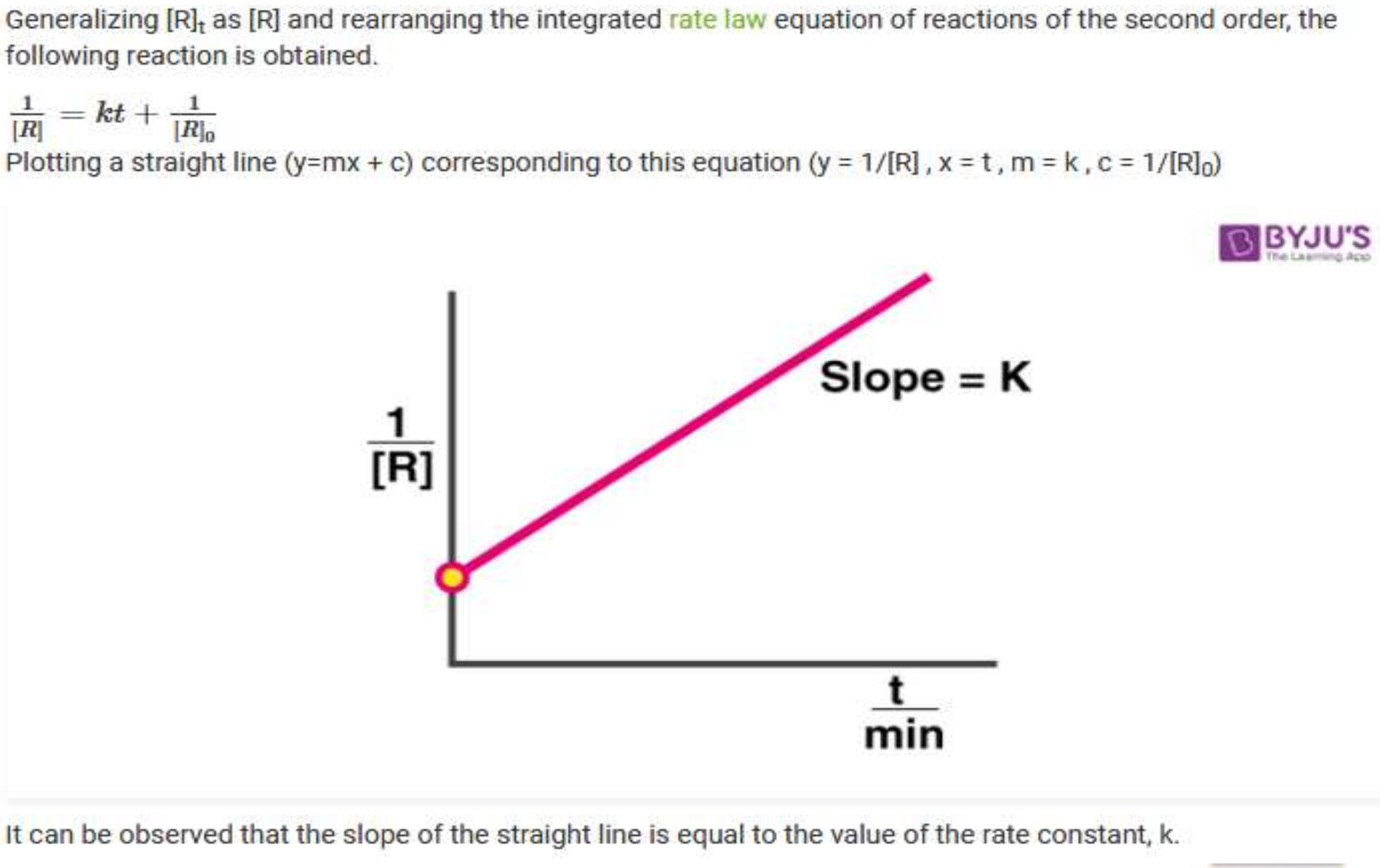
Where C is the constant of Integration. Now, using this power rule in the previous equation, the following equation can be attained.

$$\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$$

Which is the required integrated rate expression of second order reactions.

Types of reaction order

Second ORDER REACTION



Generalizing $[R]_t$ as [R] and rearranging the integrated rate law equation of reactions of the second order, the following reaction is obtained.

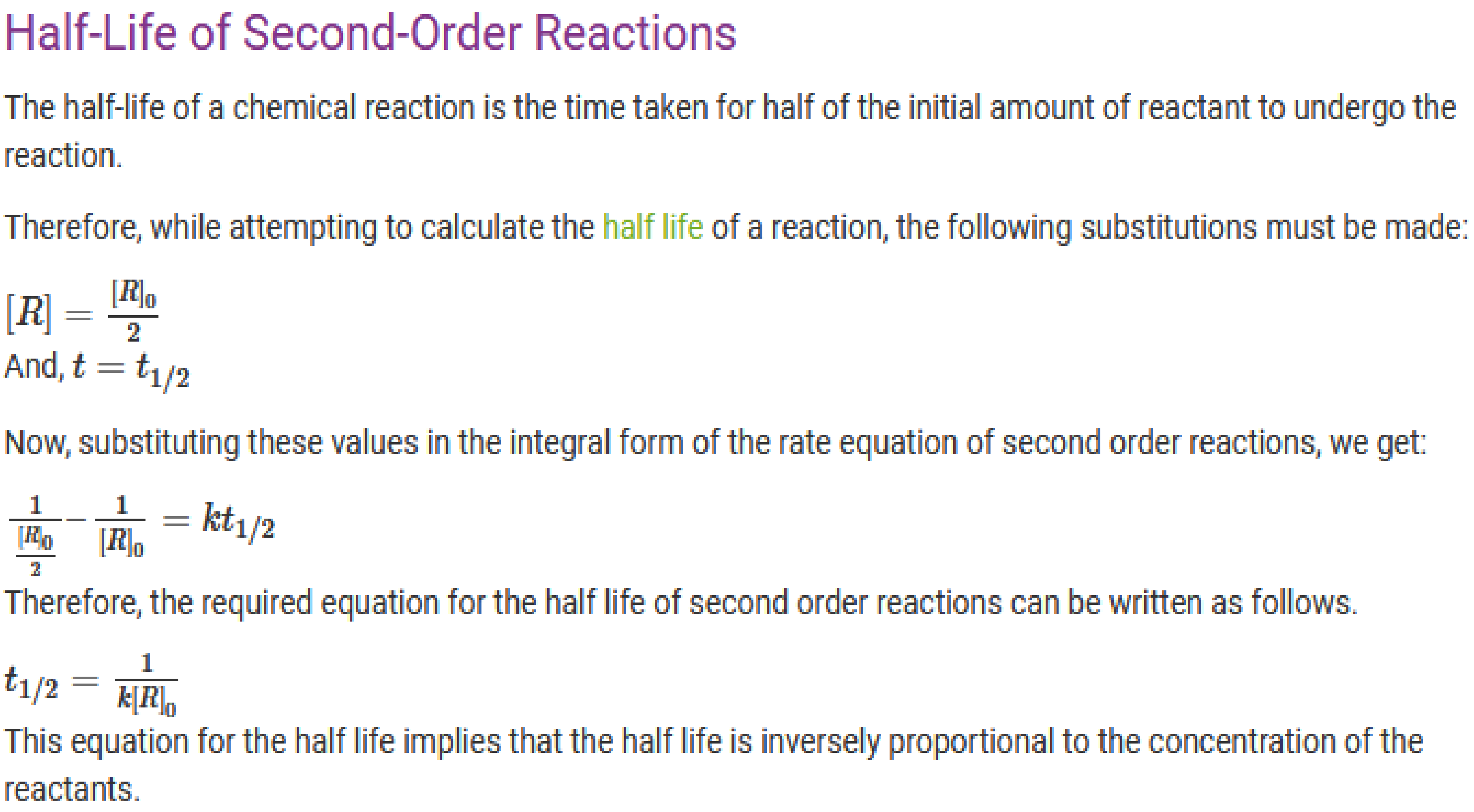
$$\frac{1}{[R]} = kt + \frac{1}{[R]_0}$$

Plotting a straight line (y=mx + c) corresponding to this equation (y = 1/[R] , x = t , m = k , c = $1/[R]_0$)

It can be observed that the slope of the straight line is equal to the value of the rate constant, k.

Types of reaction order

Second ORDER REACTION



Half-Life of Second-Order Reactions

The half-life of a chemical reaction is the time taken for half of the initial amount of reactant to undergo the reaction.

Therefore, while attempting to calculate the half life of a reaction, the following substitutions must be made:

$$[R] = \frac{[R]_0}{2}$$

And, $t = t_{1/2}$

Now, substituting these values in the integral form of the rate equation of second order reactions, we get:

$$\frac{1}{\frac{[R]_0}{2}} - \frac{1}{[R]_0} = kt_{1/2}$$

Therefore, the required equation for the half life of second order reactions can be written as follows.

$$t_{1/2} = \frac{1}{k[R]_0}$$

This equation for the half life implies that the half life is inversely proportional to the concentration of the reactants.

Determination of reaction order

- In order to determine the reaction order, the power-law form of the rate equation is generally used. The expression of this form of the rate law is given by $\mathbf{r = k[A]^x[B]^y}$.
-
- In the expression described above, ‘r’ refers to the rate of reaction, ‘k’ is the rate constant of the reaction, [A] and [B] are the concentrations of the reactants. The exponents of the reactant concentrations x and y are referred to as partial orders of the reaction. Therefore, the sum of all the partial orders of the reaction yields the overall order of the reaction.
- **How to Determine Reaction Order**
- There are several different methods which can be followed in order to determine the reaction order. Some of these methods are described in this subsection.

Determination of reaction order

1-Initial Rates Method

- **$r = k[A]^x[B]^y$**.
- First, the natural logarithm form of the power-law expression is obtained. It is given by: **$\ln r = \ln k + x.\ln[A] + y.\ln[B] + ….$**
- The partial order corresponding to each reactant is now calculated by conducting the reaction with varying concentrations of one reactant in the reaction and the concentration of the other reactants kept constant.
- If the partial order of A is being determined, the power-law expression of the rate equation now becomes **$\ln r = x.\ln[A] + C$**, where C is a constant.

Determination of reaction order

1-Initial Rates Method

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- First, the natural logarithm form of the power-law expression is obtained. It is given by: **$\ln r = \ln k + x.\ln[A] + y.\ln[B] + ….$**
- The partial order corresponding to each reactant is now calculated by conducting the reaction with varying the initial concentrations of one reactant in the reaction and the concentration of the other reactants kept constant.
- If the partial order of A is being determined, the power-law expression of the rate equation now becomes **$\ln r = x.\ln[A] + C$**, where C is a constant.
- A graph is now plotted by taking ‘ln r’ as a function of ln[A], the corresponding slope is the partial order, given by x.

Determination of reaction order

2- (Integrated rate law method)

- This method can be used when there is only one reactant (i.e the other are constant). By measuring the instantaneous rate for one reactant we can find the following

- If the plot of **log [A] vs t** is a straight line, the reaction follows first-order
- If the plot of **1/[A] vs t** is a straight line, the reaction follows second order.
- If the plot of **$1/[A]^2$ vs t** is a straight line , the reaction follows third order.
- Generally, for a reaction of (nth) order, a graph of **$1/[A]^{n-1}$ vs t** must be a straight line Expect first order.

Determination of reaction order

3-Graphical Method

- A graph is plotted between time t and the concentration of reactant (a-x) or product (x), slope of which gives the rate of reaction (dx/dt) for the selected time instant. (figure 1 & 2)The various values of the rate (dx/dt) are now plotted against the corresponding concentration (a-x) or $(a\text{-}x)^2$ or $(a\text{-}x)^3$ from which we draw the following graphical conclusions:

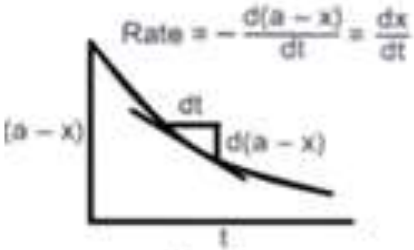


Fig. 1

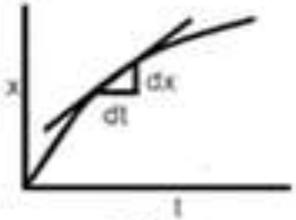


Fig. 2

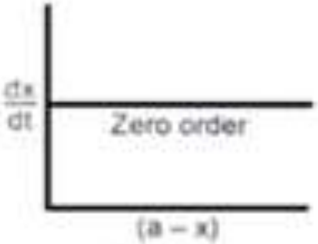


Fig. 3

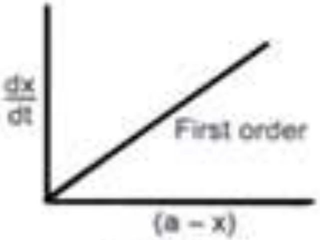


Fig. 4

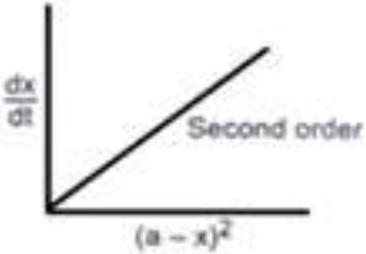


Fig. 5

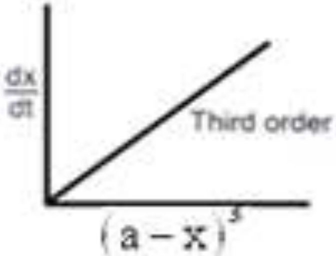


Fig. 6

Determination of reaction order

4-Half Life Method

- This method is used only when the rate law involved by only one concentration term.
- $\mathbf{t_{(1/2)} \;\infty\; a^{1-n}}$
- $\mathbf{t_{(1/2)} = k\, a^{1-n}}$
- $\mathbf{\log t_{(1/2)} = \log k' + (1-n) \operatorname{Log} a}$
- Graph of **$\log t_{1/2}$ vs $\log a$**, gives a straight line with slope (1-n) , where 'n' is the order of the reaction.
- Determining the slope we can find the order n.

Determination of reaction order

3-Half Life Method

- If half life at different concentrations is given then.

$$(t_{1/2})_1 \alpha \frac{1}{a_1^{n-1}}$$

and

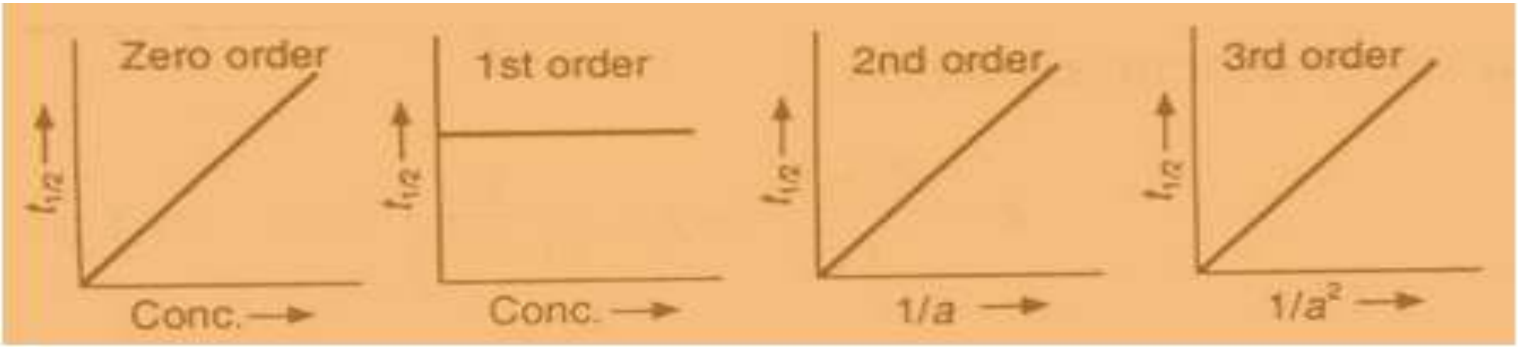
$$(t_{1/2})_2 \alpha \frac{1}{a_2^{n-1}}$$

$$\therefore \frac{(t_{1/2})_1}{(t_{1/2})_2} = (\frac{a_2}{a_1})^{n-1}$$

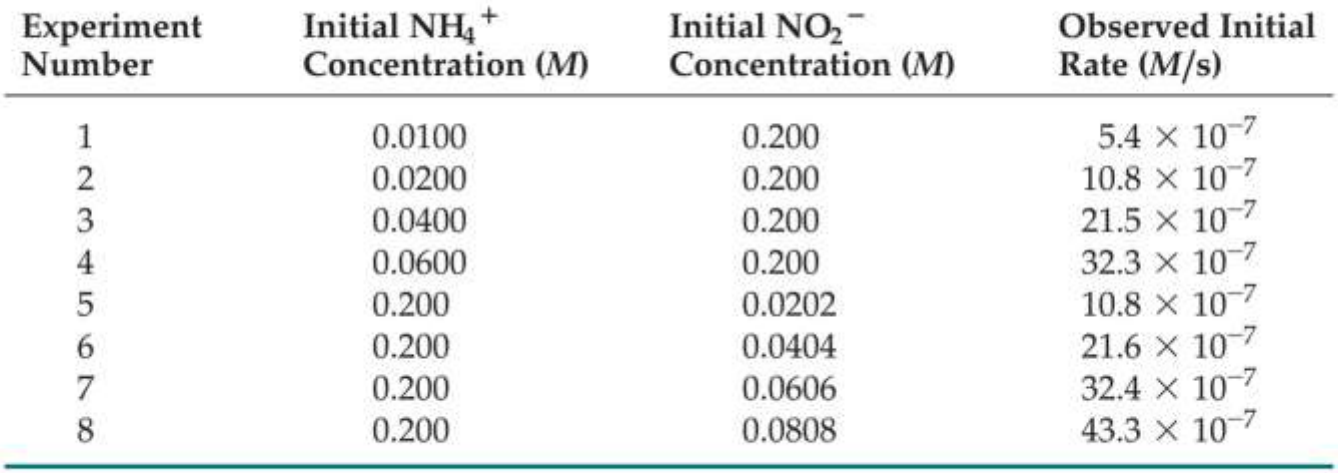
Taking logarithm and rearranging

$$n = 1 + \frac{log(t_{1/2}) - log(t_{1/2})_2}{log a_2 - log a_1}$$

- Plots of half-lives concentration ($t_{1/2}$ ∞ a^{1-a}):



Concentration and Rate



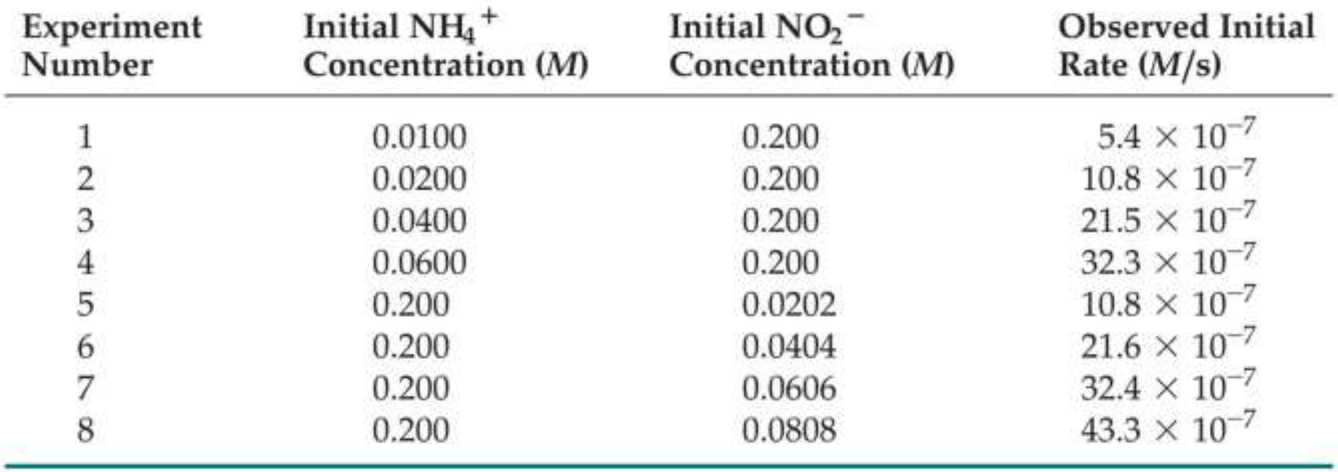
Experiment Number	Initial NH_4^+ Concentration (*M*)	Initial NO_2^- Concentration (*M*)	Observed Initial Rate (*M*/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Compare Experiments 1 and 2:

when $[NH_4^+]$ doubles, the initial rate doubles.

Concentration and Rate



Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Likewise, compare Experiments 5 and 6: when $[NO_2^-]$ doubles, the initial rate doubles.

مثال:

لديك التفاعل الافتراضي التالي

$$A + B \rightarrow P$$

فإذا علمت أن سرعة التفاعل تتغير مع التراكيز كما في الجدول التالي

رقم التجربة	1	2	3	4	5
[A]/M	0.1	0.2	0.4	0.1	0.1
[B]/M	0.1	0.1	0.1	0.2	0.4
rate/Ms^{-1}	1.2×10^{-2}	2.4×10^{-2}	4.8×10^{-2}	4.8×10^{-2}	1.9×10^{-1}

حدد رتبة التفاعل لكل مادة متفاعلة ورتبة التفاعل الكلية وقيمة ثابت السرعة للتفاعل.

الحل:

نقوم أولا بكتابة الصورة التفاضلية لقانون السرعة للتفاعل

$$\text{rate} = k[\text{A}]^x[\text{B}]^y$$

نقوم الآن بتحديد كل من x و y

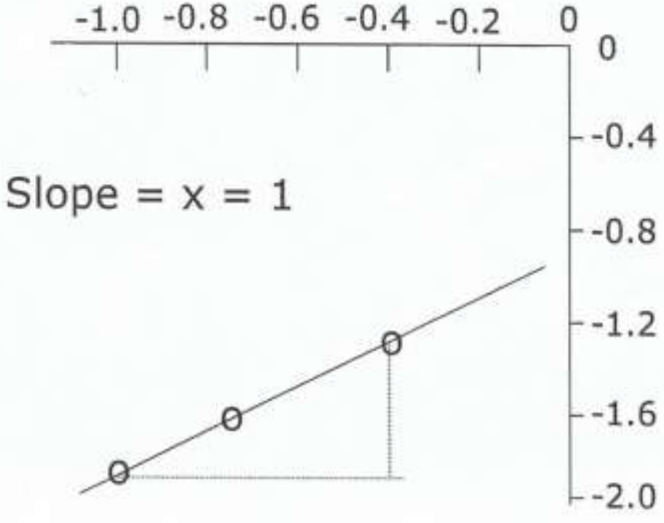
نحدد x أولا من الثلاث تجارب الأولى (التجارب التي يتغير فيها تركيز A مع بقاء تركيز المادة B ثابتا) بتمثيل log [A] ضد log rate حيث نحصل على خط مستقيم ميله يساوي x.

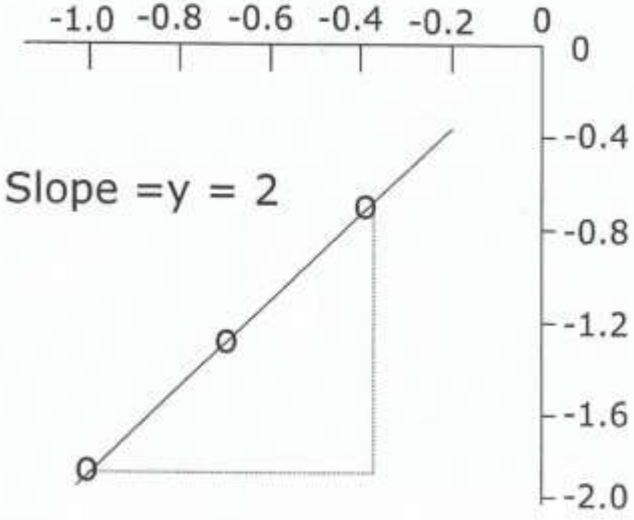
بعد ذلك نحدد y من الثلاث تجارب التي يتغير فيها تركيز المادة B مع ثبات تركيز المادة A (التجارب 1 و4 و5) بنفس الطريقة السابقة.

بعد تحديد كل من x و y نعوض في قانون السرعة بقراءات أي تجربة للحصول على قيمة k.

يمكن لنا الآن إعادة كتابة الجدول السابق مع إضافة ثلاثة صفوف أحدهم للمقدار log rate وآخر للمقدار log [A] والثالث للمقدار log [B].

رقم التجربة	1	2	3	4	5
[A]/M	0.1	0.2	0.4	0.1	0.1
[B]/M	0.1	0.1	0.1	0.2	0.4
rate/Ms^{-1}	1.2×10^{-2}	2.4×10^{-2}	4.8×10^{-2}	4.8×10^{-2}	1.9×10^{-1}
log [A]	-1	-0.7	-0.4	-1	-1
log [B]	-1	-1	-1	-0.7	-0.4
log rate	-1.92	-1.62	-1.32	-1.32	-0.72





بعد تحديد قيمتي x و y، واضح أن التفاعل من الرتبة الأولى بالنسبة للمادة A ومن الرتبة الثانية بالنسبة للمادة B، ونستطيع الآن كذلك حساب الرتبة الكلية للتفاعل (n) حيث $n = x + y = 1 + 2 = 3$. إذا التفاعل ككل من الرتبة الثالثة.

نحسب الآن قيمة ثابت السرعة k للتفاعل وذلك بالتعويض بقراءات أي تجربة في الجدول. فلو أخذنا قراءات التجربة رقم 1 في الجدول نجد أن

$$\text{rate} = k[\text{A}][\text{B}]^2$$

$$1.2 \text{ x } 10^{-2}\ (\text{Ms}^{-1}) = k(0.1\,\text{M})(0.1\,\text{M})^2$$

$$k = \frac{1.2 \text{ x } 10^{-2}\ (\text{Ms}^{-1})}{(0.1\,\text{M})(0.1\,\text{M})^2} = 12\ \text{M}^{-2}\text{s}^{-1} = 12\ \text{mol}^{-2}\text{L}^{2}\text{s}^{-1}$$

يمكن كذلك إيجاد رتبة التفاعل لكل مادة متفاعلة حسابيا ويكفي لذلك فقط قرائتي تجربتين.

كيف؟

نأخذ لوغارثم الطرفين لقانون السرعة ونعوض بعد ذلك بقراءات التجربتين للحصول على رتبة التفاعل للمادة المعنية كما يلي:

للتفاعل في المثال السايق

$$\text{A} + \text{B} \rightarrow \text{P}$$

دعنا نحدد x أولا. نحدد تجربتين يكون فيهما تركيز المادة A متغيرا وتركيز B ثابتا ولتكن التجربتين 1 و2 في الجدول من المثال السابق.

في التجربة الأولى

$$\log (\text{rate})_1 = \log k' + x \log [\text{A}]_1$$

وفي التجربة الثانية

$$\log (\text{rate})_2 = \log k' + x \log [\text{A}]_2$$

مع ملاحظة أن k' عبارة عن حاصل ضرب ثابت السرعة للتفاعل في التراكيز الثابتة للمواد المتفاعلة الأخرى (المادة B في هذا المثال) . نقوم الآن بطرح إحدى المعادلتين من الأخرى، المعادلة الأولى من الثانية مثلا لنحصل على

$$\log (\text{rate})_2 - \log (\text{rate})_1 = \cancel{\log k'} + x \log [\text{A}]_2 - \cancel{\log k'} - x \log [\text{A}]_1$$

$$\log \frac{(\text{rate})_2}{(\text{rate})_1} = x \log \frac{[\text{A}]_2}{[\text{A}]_1}$$

$$x = \frac{\log \dfrac{(\text{rate})_2}{(\text{rate})_1}}{\log \dfrac{[\text{A}]_2}{[\text{A}]_1}}$$

وبالتعويض بقراءات التجربتين الأولى والثانية في الجدول في المثال السابق نجد أن

$$x = \frac{\log \dfrac{2.4}{1.2}}{\log \dfrac{0.2}{0.1}} = \frac{\log 2}{\log 2} = 1$$

ونستطيع كذلك عمل نفس الشيء للمادة B. نختار تجربتين يكون فيهما تركيز B متغيرا وتركيز A ثابتا. فلو أخترنا التجربتين 1 و 4 في الجدول في المثال السابق نحصل على

$$y = \frac{\log \frac{(\text{rate})_4}{(\text{rate})_1}}{\log \frac{[\text{B}]_4}{[\text{B}]_1}}$$

وباتعويض بقراءات التجربتين نحصل على

$$y = \frac{\log \frac{4.8}{1.2}}{\log \frac{0.2}{0.1}} = \frac{\log 4}{\log 2} = 2$$

بعد تحديد رتب التفاعل بالنسبة لكل مادة متفاعلة نستطيع حساب الرتبة الكلية للتفاعل وكذلك حساب قيمة ثابت السرعة للتفاعل بالتعويض بقراءات أي تجربة من التجارب المعطاة بالضبط كما عملنا في المثال السابق.

Table 14.2 Initial Rates for the Reaction between A and B

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

[B] is kept constant for experiments 1 and 2, while [A] is doubled. Then [A] is kept constant while [B] is doubled.

Finding *m*, the order with respect to A:

We compare experiments 1 and 2, where [B] is kept constant but [A] doubles:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[A]_2^m \, \cancel{[B]_2^n}}{\cancel{k}[A]_1^m \, \cancel{[B]_1^n}} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

$$\frac{3.50 \times 10^{-3}\ \text{mol/L·s}}{1.75 \times 10^{-3}\ \text{mol/L·s}} = \left(\frac{5.00 \times 10^{-2}\ \text{mol/L}}{2.50 \times 10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get $2.00 = (2.00)^m$ so $m = 1$

Finding *n*, the order with respect to B:

We compare experiments 3 and 1, where [A] is kept constant but [B] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k[A]}_3^{m}\,[B]_3^{n}}{\cancel{k[A]}_1^{m}\,[B]_1^{n}} = \frac{[B]_3^{n}}{[B]_1^{n}} = \left(\frac{[B]_3}{[B]_1}\right)^{n}$$

$$\frac{3.50\text{x}10^{-3}\text{ mol/L}\cdot\text{s}}{1.75\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{6.00\text{x}10^{-2}\text{ mol/L}}{3.00\text{x}10^{-2}\text{ mol/L}}\right)^{m}$$

Dividing, we get $2.00 = (2.00)^n$ so $n = 1$

Table 14.3 Initial Rates for the Reaction between O_2 and NO

$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$ Rate = $k[O_2]^m[NO]^n$

Experiment	Initial Rate (mol/L·s)	Initial Reactant Concentrations (mol/L) $[O_2]$	$[NO]$
1	3.21×10^{-3}	1.10×10^{-2}	1.30×10^{-2}
2	6.40×10^{-3}	2.20×10^{-2}	1.30×10^{-2}
3	12.48×10^{-3}	1.10×10^{-2}	2.60×10^{-2}
4	9.60×10^{-3}	3.30×10^{-2}	1.30×10^{-2}
5	28.8×10^{-3}	1.10×10^{-2}	3.90×10^{-2}

Finding m, the order with respect to O_2:

We compare experiments 1 and 2, where [NO] is kept constant but $[O_2]$ doubles:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[O_2]_2^m \cancel{[NO]_2^n}}{\cancel{k}[O_2]_1^m \cancel{[NO]_1^n}} = \frac{[O_2]_2^m}{[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

$$\frac{6.40 \times 10^{-3}\ \text{mol/L·s}}{3.21 \times 10^{-3}\text{mol/L·s}} = \left(\frac{2.20 \times 10^{-2}\ \text{mol/L}}{1.10 \times 10^{-2}\ \text{mol/L}}\right)^m$$

Dividing, we get $1.99 = (2.00)^m$ or $2 = 2^m$, so $m = 1$

The reaction is first order with respect to O_2.

Finding *n*, the order with respect to NO:

We compare experiments 1 and 3, where $[O_2]$ is kept constant but [NO] doubles:

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[NO]_3}{[NO]_1}\right)^n \qquad \frac{12.8\text{x}10^{-3}\ \text{mol/L}\cdot\text{s}}{3.21\text{x}10^{-3}\text{mol/L}\cdot\text{s}} = \left(\frac{2.60\text{x}10^{-2}\ \text{mol/L}}{1.30\text{x}10^{-2}\ \text{mol/L}}\right)^n$$

Dividing, we get $3.99 = (2.00)^n$ or $4 = 2^n$, so $n = 2$.

Alternatively: $n = \dfrac{\log a}{\log b} = \dfrac{\log 3.99}{\log 2.00} = 2.00$

The reaction is second order with respect to NO.

The rate law is given by: rate = $k[O_2][NO]^2$

Sample Problem 14.5

Determining the Reactant Concentration after a Given Time

PROBLEM: At 1000°C, cyclobutane (C_4H_8) decomposes in a first-order reaction, with the very high rate constant of 87 s^{-1}, to two molecules of ethylene (C_2H_4).

(a) If the initial C_4H_8 concentration is 2.00 M, what is the concentration after 0.010 s?

(b) What fraction of C_4H_8 has decomposed in this time?

PLAN: We must find the concentration of cyclobutane at time *t*, $[C_4H_8]_t$. The problem tells us the reaction is first-order, so we use the integrated first-order rate law:

$$\ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt$$

Sample Problem 14.5

SOLUTION:

(a) $$\ln \frac{[C_4H_8]_0}{[C_4H_8]_t} = kt \qquad \ln \frac{2.00\ \text{mol/L}}{[C_4H_8]_t} = (87\ s^{-1})(0.010\ s) = 0.87$$

$$\frac{2.00\ \text{mol/L}}{[C_4H_8]_t} = e^{0.87} = 2.4$$

$$[C_2H_4] = \frac{2.00\ \text{mol/L}}{2.4} \boxed{= 0.83\ \text{mol/L}}$$

(b) Finding the fraction that has decomposed after 0.010 s:

$$\frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00\ M - 0.87\ M}{2.00\ M} \boxed{= 0.58}$$

في درجة حرارية معينة فإن فترات نصف العمر لتحلل الأمونيا بوجود العامل المساعد (المحفزات) كما يلي :

Pressure, mmHg	50	100	200
Half time ($t_{1/2}$), h	3.52	1.92	1.00

أوجد رتبة التفاعل.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} = \left(\frac{P_2}{P_1}\right)^{n-1}$$

$$\frac{3.52}{1.92} = \left(\frac{100}{50}\right)^{n-1}$$

$$1.833 = (2)^{n-1}$$

$$\log 1.83 = (n - 1)\log 2$$

$$n - 1 = \frac{\log 1.83}{\log 2}$$

$$n = \frac{\log 1.83}{\log 2} + 1$$

$$n = 1.872 \approx 2$$

مثال (٣)

إن فترات نصف العمر للتحلل الحراري للفوسفين في ضغوط مختلفة ثلاثة كما يلي :

Initial Pressure, mmHg	707	79	37.5
$t_{1/2}$ (s)	84	84	83.5

فما رتبة التفاعل؟

يتحلل الإيثيل أمين في عملية غير عكسية لتكوين الأمونيا والإيثيلين كما في المعادلة التالية :

$$C_2H_5NH_2(g) \longrightarrow C_2H_4(g) + NH_3(g)$$

فإذا علمت أن الضغط الإبتدائي ($a = P_0$) **يساوي** (55 mmHg).
ودرجة الحرارة (500 °C). وقد تم الحصول على النتائج التالية :

$P_0 = 55$ mmHg								
Time, min	1	2	4	8	10	20	30	40
$x = \Delta P$, mmHg	5	9	17	29	34	47	52	53.5
$(a - x) = (P_0 - \Delta P)$, mmHg	50	46	38	26	21	8	3	1.5
الرتبة الأولى : $k_1 = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) = \frac{2.303}{t}\log\left(\frac{P_0}{P_0-\Delta P}\right)$	9.53×10^{-2}	8.95×10^{-2}	9.24×10^{-2}	9.37×10^{-2}	9.62×10^{-2}	9.63×10^{-2}	9.70×10^{-2}	9.01×10^{-2}
الرتبة الثانية : $k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) = \frac{1}{t}\left(\frac{\Delta P}{P_0(P_0-\Delta P)}\right)$	1.82×10^{-3}	1.78×10^{-3}	2.03×10^{-3}	2.54×10^{-3}	2.94×10^{-3}	5.34×10^{-3}	10.51×10^{-3}	16.21×10^{-3}
الرتبة الثالثة $k_3 = \frac{1}{2t}\left(\frac{1}{(a-x)^2}-\frac{1}{a^2}\right) = \frac{1}{2t}\left(\frac{1}{(P_0-\Delta P)^2}-\frac{1}{P_0^2}\right)$	0.35×10^{-4}	0.36×10^{-4}	0.45×10^{-4}	0.72×10^{-4}	0.97×10^{-4}	3.82×10^{-4}	18.5×10^{-4}	55.5×10^{-4}

مما سبق يتضح أن قيم (k_1) تكاد تكون متقاربة جداً لذا فإن التفاعل من

$P_0 = 55$ mmHg								
Time, min	1	2	4	8	10	20	30	40
$x = \Delta P$, mmHg	5	9	17	29	34	47	52	53.5
$(a - x) = (P_0 - \Delta P)$, mmHg	50	46	38	26	21	8	3	1.5
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الرتبة الثانية : $k_2 = \frac{1}{t}\left(\frac{x}{a(a-x)}\right) = \frac{1}{t}\left(\frac{\Delta P}{P_0(P_0-\Delta P)}\right)$	1.82×10^{-3}	1.78×10^{-3}	2.03×10^{-3}	2.54×10^{-3}	2.94×10^{-3}	5.34×10^{-3}	10.51×10^{-3}	16.21×10^{-3}
الرتبة الثالثة $k_3 = \frac{1}{2t}\left(\frac{1}{(a-x)^2}-\frac{1}{a^2}\right) = \frac{1}{2t}\left(\frac{1}{(P_0-\Delta P)^2}-\frac{1}{P_0^2}\right)$	0.35×10^{-4}	0.36×10^{-4}	0.45×10^{-4}	0.72×10^{-4}	0.97×10^{-4}	3.82×10^{-4}	18.5×10^{-4}	55.5×10^{-4}

مما سبق يتضح أن قيم **(k_1)** تكاد تكون متقاربة جداً لذا فإن التفاعل من

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