Chemical Kinetics - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following:

- Derive Integrated Rate Equations for the Zero and First Order Reactions
- Determine the Rate Constants for Zeroth and First Order Reactions
- Determine the Half-life of a Reaction

Contents Outline

- Integrated Rate Equations
- Zero Order Reactions
- First Order Reactions
- Half-life of a Reaction
- Pseudo First Order Reactions
- Summary

Integrated Rate Equations

We have already noted in the last module that the concentration dependence of rate is called differential rate equation. It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point '*t*' in concentration vs time plot. This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, i.e., concentrations at different times and rate constant.

The integrated rate equation is used to determine the rate constant of the reaction. Also, it is helpful to calculate the exact time when reaction is either complete or at any intermediate position (i.e. 25% or 50% or 90% completion) and vice versa. The integrated equations are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

Zero Order Reactions

A reaction with zero order means that the rate of the reaction is proportional to zero power of the concentration of reactants, i.e. independent of the concentration of the reactants. Consider the reaction,

$R \rightarrow P$

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

As any quantity raised to power zero is unity

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

$$d[R] = - k.dt$$

Integrating both sides

$$[R] = - kt + I \qquad (1)$$

where I is the constant of integration.

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

Substituting in equation (1)

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

$$[R]_0 = I$$

Substituting the value of I in the equation (1)

$$[R] = - kt + [R]_0 \qquad (2)$$

Comparing (2) with equation of a straight line,

$y = mx + c$, if we plot [R] against *t*, we get a straight line (Fig.1) with slope = – k and intercept equal to $[R]_0$.

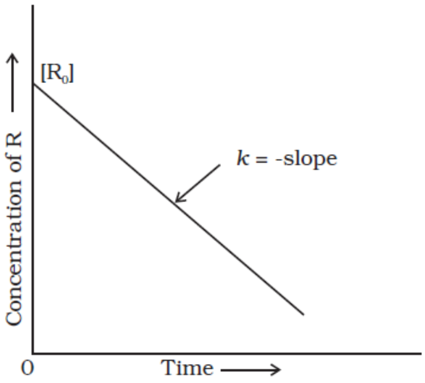


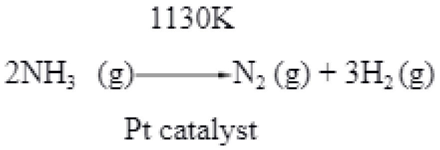
Fig. 1: Variation in the concentration vs time plot for a zero order reaction

(Source: Fig 4.3, page no. 104, Chapter 4: Chemical Kinetics, NCERT Textbook)

Further simplifying equation (2), we get the rate constant, k as

$$k = \frac{[R]_0 - [R]}{t} \qquad (3)$$

All zero order reactions obey the equation (3). If the values for $[R]_0$, [R] and t are known then the value of rate constant can be easily evaluated. 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. These types of reactions generally occur in heterogeneous systems. For example, the decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.



$$2NH_3\ (g) \xrightarrow[\text{Pt catalyst}]{1130K} N_2\ (g) + 3H_2\ (g)$$

Rate of the reaction is given as:

Rate = $k\,[NH_3]^0 = k$

In this reaction, platinum metal acts as a catalyst. At high pressure, the finely divided metal surface, i.e. platinum surface gets saturated with ammonia gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making the rate of the reaction independent of its concentration. The thermal decomposition of HI on the gold surface is another example of zero order reaction.

First Order Reactions

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

$R \rightarrow P$

The rate of the reaction is given as:

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

or

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

Integrating this equation, we get

$$ln[R] = -\ kt + I \qquad (4)$$

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) can be written as

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

$$ln[R]_0 = I$$

Substituting the value of I in equation (4), we get

$$ln[R] =- kt + ln[R]_0 \qquad (5)$$

On rearranging the equation (5), we get

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

$$\text{or } k = \frac{1}{t} ln\frac{[R]_0}{[R]} \qquad (6)$$

At time $t_{1,}$ from equation (4)

$$ln[R]_1 =- kt_1 + ln[R]_0 \qquad (7)$$

At time t_2,

$$ln[R]_2 =- kt_2 + ln[R]_0 \qquad (8)$$

where $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting equation (8) from equation (7),

$$ln[R]_1 - ln[R]_2 =- kt_1 - \left(- kt_2\right)$$

$$ln\frac{[R]_1}{[R]_2} =- k\left(t_1 - t_2\right) = k\left(t_2 - t_1\right)$$

$$k = \frac{1}{\left(t_2 - t_1\right)} ln\frac{[R]_1}{[R]_2} \qquad (9)$$

Equation (5) can also be written as

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

Taking antilog of both sides, we get

$$[R] = [R]_0 e^{-kt} \qquad (10)$$

Comparing equation (5) with y = mx + c, if we plot ln [R] against t (Fig. 2), we get a straight line with slope = – k and intercept equal to $\ln[R]_{0.}$

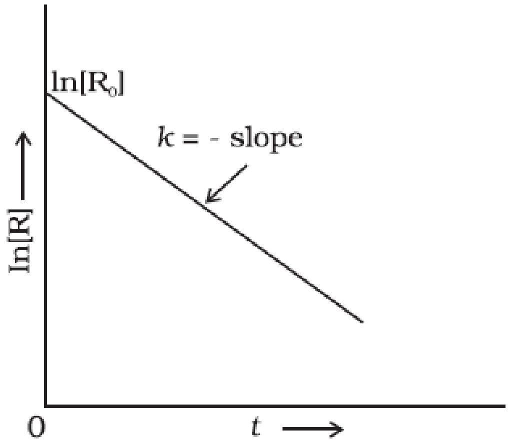


Fig. 2: A plot between ln [R] and t for a first order reaction.

(Source: Fig. 4, page no. 106, Chapter 4: Chemical Kinetics, NCERT Textbook)

The first order rate equation (6) can also be written in the form

$$k = \frac{2.303}{t} log \frac{[R]_0}{[R]} \tag{11}$$

$$log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

If we plot a graph between log $[R]_0/[R]$ vs t, (Fig. 3), the slope = (k / 2.303).

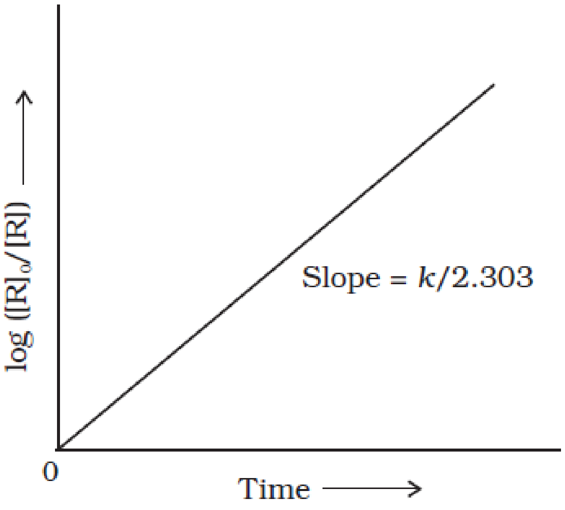


Fig. 3: A plot of log ($[R]_0$/ [R]) vs time for a first order reaction.

(Source: Fig 5, page no. 106, Chapter 4: Chemical Kinetics, NCERT Textbook)

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4\,(g) \;+\; H_2\,(g) \rightarrow C_2H_6\,(g)$$

$Rate\ =\ k\,[C_2H_4]$

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

$$^{226}_{88}Ra \rightarrow\ ^{4}_{2}He +\ ^{222}_{86}Rn$$

Rate = k [Ra]

Decomposition of N_2O_5 and N_2O are some more examples of first order reactions.

Let us consider a typical first order gas phase reaction

$$A\,(g) \rightarrow B\,(g)\ +\ C\,(g)$$

Let p_i be the initial pressure of A and p_t the total pressure at time 't'. Integrated rate equation for such a reaction can be derived as

Total pressure, $p_t\ =\ p_A\ +\ p_B\ +\ p_C$ (pressure units)

where p_A, p_B and p_C are the partial pressures of A, B and C, respectively. If x atm be the decrease in pressure of A at time t and one mole each of B and C is being formed, the increase in pressure of B and C will also be x atm each.

	$A\,(g)$	$\rightarrow$ $B\,(g)$	$+$ $C\,(g)$
At t = 0,	p_i atm	0 atm	0 atm
At time t,	$(p_i – x)$ atm	x atm	x atm

where p_i is the initial pressure at time t = 0.

$$p_t = (pi - x)\ +\ x\ +\ x\ =\ p_i + x$$

$$x\ =\ (p_t - p_i)$$

where $p_A\ =\ p_i - x\ =\ p_i - (p_t - p_i)$

$= 2\,p_i - p_t$

$$k\ = \left(\frac{2.303}{t}\right)\left(log\frac{p_i}{p_A}\right) \qquad (12)$$

$$= \left(\frac{2.303}{t}\right)log\frac{p_i}{\left(2p_i - p_t\right)}$$

Example 1: The initial concentration of N_2O_5 in the following first order reaction

$N_2O_5\,(g) \rightarrow 2\,NO_2\,(g)\ +\ ½O_2\ (g)$

was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

Solution: For the first order reaction, we have

$$log\frac{[R]_1}{[R]_2} = \frac{k(t_2-t_1)}{2.303}$$

$$k = \frac{2.303}{(t_2-t_1)}log\frac{[R]_1}{[R]_2}$$

$$= \frac{2.303}{(60\ min-0\ min)}log\frac{1.24\times10^{-2}\ mol\ L^{-1}}{0.20\times10^{-2}\ mol\ L^{-1}}$$

$$= \frac{2.303}{60}log6.2\ min^{-1}$$

$$k = 0.0304\ min^{-1}$$

Example 2: The following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume:

$$2\ N_2O_5\ (g) \rightarrow 2\ N_2O_4\ (g)\ +\ O_2\ (g)$$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

Solution: Let the pressure of N_2O_5 (g) decrease by $2x$ atm. As two moles of N_2O_5 decompose to give two moles of N_2O_4 (g) and one mole of O_2 (g), the pressure of N_2O_4 (g) increases by $2x$ atm and that of O_2 (g) increases by x atm.

	$2\ N_2O_5\ (g)$	$\rightarrow$	$2\ N_2O_4\ (g)$	$+$	O_2 (g)
At t = 0,	0.5 atm		0 atm		0 atm
At time t,	$(0.5 - 2x)$ atm		$2x$ atm		x atm

$$p_t = p_{N_2O_5} + p_{N_2O_5} + p_{O_2}$$

$$= (0.5 - 2x) + 2x + x = 0.5 + x$$

$$= x = p_t - 0.5$$

$$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$$

At t = 100 s, $p_t = 0.512$ atm

$$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476\ atm$$

Using equation (12)

$$k = \left(\frac{2.303}{t}\right)\left(log\frac{p_i}{p_A}\right)$$

$$k = \left(\frac{2.303}{100s}\right)\left(log\frac{0.5atm}{0.476atm}\right) = \frac{2.303}{100s} \times 0.0216 = 4.98 \times 10^{-4}s^{-1}$$

Example 3: For a first order reaction, calculate the time required to reduce the concentration of a reactant from 10 g to 3 g. (Given: the first order reaction rate constant is $2.51 \times 10^{-3}\ s^{-1}$)

Solution: Initial concentration of reactant, $[R]_0 = 10$ g

Final concentration of reactant, $[R]_t = 3$ g

Rate constant = $2.51 \times 10^{-3}\ s^{-1}$

For a first order reaction, we have

$$k = \frac{2.303}{t}log\frac{[R]_0}{[R]}$$

or

$$= \frac{2.303}{2.51\times10^{-3}} \times 0.523\ s$$

$$t = \frac{2.303}{k}log\frac{[R]_0}{[R]} = \frac{2.303}{2.51\times10^{-3}}log\frac{10}{3}$$

$$t = 0.48 \times 10^{3}s$$

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. In other words, half-life is the time required for the completion of half of the reaction. It is represented as $t_{1/2}$.

Half-Life for zero order reaction: For a zero order reaction, rate constant is given as:

$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $[R] = [R]_0/2$

Hence, the rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - \left(\frac{1}{2}[R]_0\right)}{t_{\frac{1}{2}}}$$

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

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.

Half-Life for first order reaction: For the first order reaction we,

$$k = \frac{2.303}{t} log \frac{[R]_0}{[R]} \tag{13}$$

At t = $t_{1/2}$, [R] = $[R]_0/2$

S.No.	Time/s	Total Pressure/(atm)
1.	0	0.5
2.	100	0.512

Hence, the rate constant at $t_{1/2}$ becomes

$$k = \frac{2.303}{t_{1/2}} log \frac{[R]_0}{\left(\frac{1}{2}[R]_0\right)} \tag{14}$$

$$t_{1/2} = \frac{2.303}{k} log 2 = \left(\frac{2.303}{k}\right) \times 0.301$$

$$t_{1/2} = \frac{0.693}{k} \tag{15}$$

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 $[R]_0$.

Example 4: A first order reaction is found to have a rate constant, k = 5.5×10^{-14} s^{-1}. Find the half-life of the reaction.

Solution: Half-life for a first order reaction is

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

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} s^{-1}}$$

$$t_{1/2} = 1.26 \times 10^{13} s$$

Example 5: Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

Solution: When reaction is completed 99.9%, $[R] = [R]_0 - 0.999[R]_0$

$$k = \frac{2.303}{t} log \frac{[R]_0}{[R]}$$

$$k = \frac{2.303}{t} log \frac{[R]_0}{[R]_0 - 0.999[R]_0}$$

$$k = \frac{2.303}{t} log10^{3}$$

$$t = \frac{6.909}{k}$$

For half-life of the reaction, we know

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

$$\frac{t}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} = 10$$

Example 6: The half-life period of a first order reaction is 200 sec. Calculate the rate constant for this reaction.

Solution: For a first order reaction, half-life is given as

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

Therefore,

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

We have, $t_{1/2}$ = 200 sec

$$k = \frac{0.693}{200\, s} = 3.465 \times 10^{-3} s^{-1}$$

Example 7: The half-life period for a first order reaction is 45 minutes. Calculate the percentage of the reactant left after 180 minutes.

Solution: For a first order reaction, it is given that

$t_{1/2}$ = 45 min

The rate constant for the reaction will be

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{45\, min} = 1.54 \times 10^{-2}\, min^{-1}$$

The rate expression for first order is given by

$$k = \frac{2.303}{t} log\frac{[R]_0}{[R]} \quad \text{or} \quad \frac{[R]_0}{[R]} = exp(kt) \quad \text{or} \quad \frac{[R]}{[R]_0} = exp(-\, kt)$$

At t =180 min

$$\frac{[R]}{[R]_0} = exp\left(-\ 1.54 \times 10^{-2} \times 180\right) = 0.0625$$

Therefore, after 180 minutes only 6.25% of the reactant is left.

Example 8: For a zero order reaction, the rate constant is 0.14 mol L^{-1} s^{-1}. If after two minutes the concentration of the reactant is 0.15 mol L^{-1}, calculate its initial concentration.

Solution: For a zero order reaction we have,

$$k = \frac{[R]_0 - [R]}{t}$$

Given: k =0.14 mol L^{-1} s^{-1}; [R] = 0.15 mol L^{-1}; t = 2 min = 2 × 60 sec = 120 sec

$[R]_0 = (k \times t) + [R]$

$= \{(0.14 \times 120) + 0.15\}$ mol L^{-1}

$= (16.8 + 0.15)$ mol L^{-1}

$= 16.95$ mol L^{-1}

Table 1 summarises the mathematical features of integrated laws of zero and first order reactions.

Table 1: Integrated Rate Laws for the Reactions of Zero and First Order Reactions

Order	**Reaction type**	**Differential rate law**	**Integrated rate law**	**Straight line plot**	**Half-Life**	**Units of *k***
0	R → P	$\frac{d[R]}{dt} = -k$	$kt = [R]_0 - [R]$	[R] vs t	$[R]_0/2k$	conc $time^{-1}$ or $molL^{-1}$ s^{-1}
1	R → P	$\frac{d[R]}{dt} = -k[R]$	$[R] = [R]_0 \exp(-kt)$ or $kt = \ln\{[R]_0/[R]\}$	ln[R] vs t	ln2/k or 0.693/k	$time^{-1}$ or s^{-1}

Pseudo First Order Reactions

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning (*t* = 0) and at the completion (*t*) of the reaction are given as under.

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

t = 0	0.01 mol	10 mol	0 mol	0 mol
t = t	0 mol	9.9 mol	0.01 mol	0.01 mol

The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

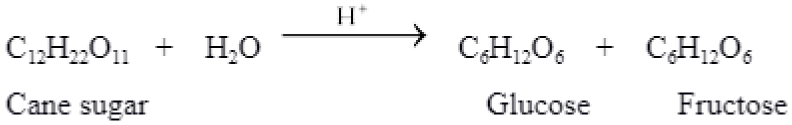
$$Rate\ =\ k\,[CH_3COOC_2H_5]\,[H_2O]$$

The term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$Rate\ =\ k'\,[CH_3COOC_2H_5]$$

where $k'\ =\ k\,[H_2O]$

and the reaction behaves as a first order reaction. Such reactions are called pseudo first order reactions. Another example of pseudo first order reaction is inversion of cane sugar.



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Rate = k $[C_{12}H_2 2O_{11}]$

Example 9: Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below.

t/min	0	30	60	90
C/mol L^{-1}	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction, as the concentration of water remains nearly constant (55 mol L^{-1}), during the course of the reaction. What is the value of k in this equation?

$$Rate\ =\ k\,[CH_3COOCH_3][H_2O]$$

Solution: For pseudo first order reaction, the reaction should be first order with respect to ester when $[H_2O]$ is constant. The rate constant k' for pseudo first order reaction is

$$k'\ = \frac{2.303}{t}\,log\frac{C_0}{C}$$

where k’ = k $[H_2O]$

From the above data we note

t/min	C/mol L^{-1}	k’/min^{-1}
0	0.8500	-
30	0.8004	2.004×10^{-3}
60	0.7538	2.002×10^{-3}
90	0.7096	2.005×10^{-3}

It can be seen that $k' = k[H_2O]$ is constant and equal to 2.004×10^{-3} min^{-1} and hence, it is a pseudo first order reaction. We can now determine k from

$k\,[H_2O] = 2.004 \times 10^{-3}\ min^{-1}$

$k\,[55\ mol\ L^{-1}] = 2.004 \times 10^{-3}\ min^{-1}$

$k = 3.64 \times 10^{-5}\ mol^{-1}\ L\ min^{-1}$

Example 10: In a pseudo first order hydrolysis of ester in water the following results were obtained:

t/ min	0	30	60	90
[Ester]/ M	0.55	0.31	0.17	0.085

a) Calculate the average rate of the reaction between the time interval 30 to 60 seconds.

b) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Solution:

a) Average rate of the reaction between time interval 30 to 60 seconds is given by:

$$Average\ Rate\ = \frac{C_2 - C_1}{\Delta t} = \frac{(0.17 - 0.31)}{(60 - 30)} = \frac{-0.14}{30} = -\ 4.67\ \times 10^{-3} M\, s^{-1}$$

Negative sign indicates that as the concentration of ester decreases with passage of time, the rate of reaction also decreases with time.

b) Pseudo first order rate constant is given as

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

where a: initial concentration and (a – x): concentration after time *t*.

Here, a = 0.55 M. The rate constant at different instant of time is tabulated below:

t/ min	**C/ mol L^{-1}**	**k'/ s^{-1}**
30	0.31	1.91×10^{-2}
60	0.17	1.95×10^{-2}
90	0.085	2.06×10^{-2}

The values of rate constant at every instant of time is almost the same which confirms that the reaction is of first order. The actual value for rate constant will be:

$$k = \frac{(1.91+1.95+2.06)}{3} \times 10^{-2} s^{-1} = 1.97 \times 10^{-2} s^{-1}$$

Summary

In this module we have learnt about the integrated forms of the rate law equations for zero and first order reactions. A reaction with zero order means that the rate of the reaction is proportional to zero power of the concentration of reactants. In first order reactions (like R → P), the rate of the reaction is proportional to the first power of the concentration of the reactant R. The integrated rate equations for zero and first order reactions were derived. 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. For zero and first order reactions, the half-life periods were derived. There are also some reactions called pseudo first order reactions. These reactions appear to be of higher order but actually follow first order kinetics.