

Lecture 22

We will continue to learn about “Chemical Kinetics”

Suggested book: Physical Chemistry by Ira Levine

Integrated Rate Laws:

First-order reaction:

Let us suppose the reaction $aA \rightarrow \text{Product}$

The rate law for this first order reaction

$$r = (-) \frac{1}{a} \frac{d[A]}{dt} = k [A]$$

$$\Rightarrow \frac{d[A]}{[A]} = (-) k \times a \times dt = (-) k_a \times dt \quad [k_a = k \times a]$$

At $t = 0$, $[A] = [A]_0$ and at $t = t$, $[A] = [A]$

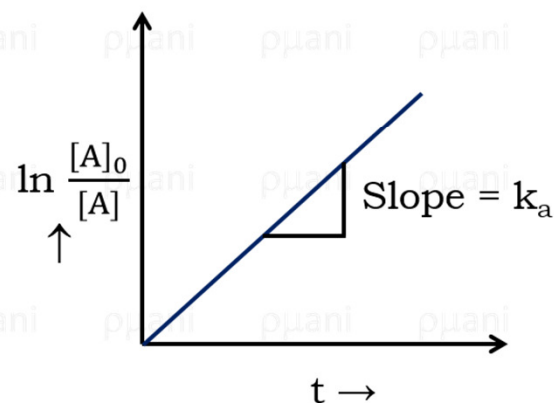
Integrating the above equation,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = (-) k_a \times \int_0^t dt$$

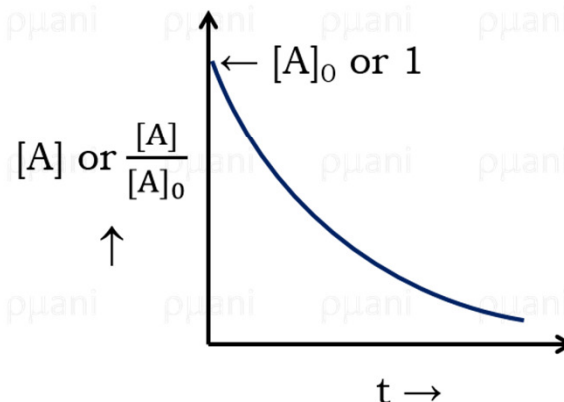
$$\Rightarrow \boxed{\ln \frac{[A]}{[A]_0} = (-) k_a \times t} \dots\dots\dots (i)$$

$$\Rightarrow \boxed{[A] = [A]_0 \times e^{-k_a \times t}} \dots\dots\dots (ii)$$

When you plot $\ln \frac{[A]}{[A]_0}$ vs. t



When you plot $[A]$ or $\frac{[A]}{[A]_0}$ vs. t



Half-life ($t_{\frac{1}{2}}$) is defined as the time required for $[A]$ to drop to $\frac{1}{2} [A]_0$ i.e. $[A] = \frac{1}{2} [A]_0$

Putting the value in equation (i)

$$\ln \frac{1}{2} = (-) k_a \times t_{\frac{1}{2}}$$

$$\Rightarrow k_a \times t_{\frac{1}{2}} = (-) \ln \frac{1}{2} = \ln 2 = 0.693$$

$$\Rightarrow \boxed{t_{\frac{1}{2}} = \frac{0.693}{k_a}}$$

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

Unit of 1st order rate constant = (time)⁻¹

Second-order reaction:

Single reactant case:

Let us suppose the chemical reaction to be



Rate law taken the form

$$r = (-) \frac{1}{a} \frac{d[A]}{dt} = k [A]^2$$
$$\Rightarrow \frac{d[A]}{[A]^2} = (-) k \times a \times dt = (-) k_a \times dt$$

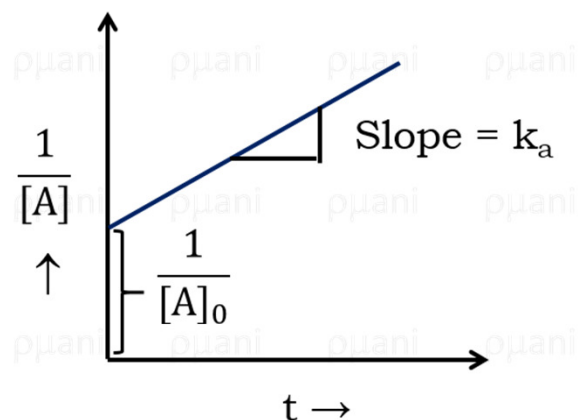
Integrating the above equation,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = (-) k_a \times \int_0^t dt$$
$$\Rightarrow \frac{1}{[A]_0} - \frac{1}{[A]} = (-) k_a \times (t - 0) = (-) k_a \times t$$

$$\Rightarrow \boxed{\frac{1}{[A]} - \frac{1}{[A]_0} = k_a \times t} \dots\dots\dots(i)$$

$$\Rightarrow \boxed{[A] = \frac{[A]_0}{(1 + k_a \times t \times [A]_0)}} \dots\dots\dots(ii)$$

Thus by plotting $\frac{1}{[A]}$ against t we get,



To get half-life, we put $[A] = \frac{1}{2} [A]_0$ in equation (i), thus we get

$$\frac{1}{\frac{[A]_0}{2}} - \frac{1}{[A]_0} = k_a \times t_{\frac{1}{2}}$$

$$\Rightarrow \frac{1}{[A]_0} = k_a \times t_{\frac{1}{2}}$$

$$\Rightarrow \boxed{t_{\frac{1}{2}} = \frac{1}{[A]_0 \times k_a}}$$

For second order reaction $t_{\frac{1}{2}}$ depends on initial concentration (contrary to first order reaction)

Thus, it takes twice as long time to go from 50% to 75% completion as from 0 to 50% completion.

Suggested work:

(1) Make a chart of (a) final integrated rate equation, (b) expression and unit of (i) rate, (ii) rate constant and (iii) $t_{\frac{1}{2}}$, for zero, 1st, 2nd and nth order reactions.

How does the rate of decay of $\frac{[A]}{[A]_0}$ compare for 1st order and 2nd order reaction?

Generally for a 2nd order reaction the rate of decay of the reactant is comparatively faster for a for a 2nd order reaction.

However, let us see what happens under a special situation when $k_a \ll 1$ and $[A]_0 < 1$]. If we assume both reactions start with same initial concentration and has same k_a value then,

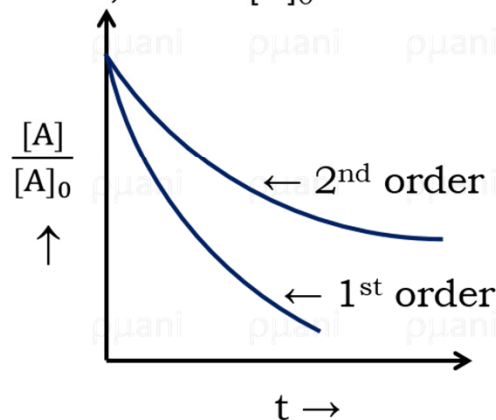
For second order reaction,

$$\frac{[A]}{[A]_0} = \frac{1}{(1 + k_a \times [A]_0 \times t)} = [1 + k_a \times [A]_0 \times t]^{-1} = [1 - k_a \times [A]_0 \times t] \quad [\text{when } k_a \ll 1]$$

For first order reaction,

$$[A] = [A]_0 \times e^{-k_a \times t} = [A]_0 [1 - k_a \times t] \quad [\text{when } k_a \ll 1] \quad , \text{ So, } \frac{[A]}{[A]_0} = [1 - k_a \times t]$$

Thus, when $[A]_0 < 1$ then for first order reaction $\frac{[A]}{[A]_0}$ will fall off much rapidly than for 2nd order reaction.



This means for 1st order reaction, $\frac{[A]}{[A]_0}$ falls off comparatively much rapidly than in 2nd order reaction .

Second order reaction with two reactants:

Let us suppose the reaction $aA + bB \rightarrow \text{Product}$

Then rate law is $r = (-) \frac{1}{a} \frac{d[A]}{dt} = (-) \frac{1}{b} \frac{d[B]}{dt} = k [A] [B]$ (i)

In this equation there are three unknown $[A]$, $[B]$, and t . To integrate we must find relations between $[A]$ and $[B]$ so that we can eliminate one of them.

The amounts of A and B that react are proportional to their coefficients a , b in the reaction so that

$$\frac{\Delta n_B}{\Delta n_A} = \frac{b}{a}$$

Dividing by volume we get,

$$\frac{b}{a} = \frac{\Delta[B]}{\Delta[A]} = \frac{[B] - [B]_0}{[A] - [A]_0}$$

$$\Rightarrow [B] = [B]_0 - \frac{b}{a} [A]_0 + \frac{b}{a} [A] \quad \text{..... (ii)}$$

Substituting value of $[B]$ from equation (ii) in equation (i) we get,

$$\int_1^2 \frac{1}{[A] \times ([B]_0 - \frac{b}{a} [A]_0 + \frac{b}{a} [A])} \times d[A] = - \int_1^2 a k dt$$

[Mathematically, We know, $\int \frac{1}{x(p + sx)} dx = -\frac{1}{p} \ln \frac{(p + sx)}{x}$ (for $p \neq 0$)]

$$p = [B]_0 - \frac{b}{a} [A]_0, \quad s = \frac{b}{a}$$

Thus we get,

$$\frac{1}{[B]_0 - \frac{b}{a} [A]_0} \ln \frac{([B]_0 - \frac{b}{a} [A]_0 + \frac{b}{a} [A])}{[A]} \Bigg|_1^2 = a k (t_2 - t_1)$$

$$\Rightarrow \frac{1}{a [B]_0 - b [A]_0} \times \ln \frac{[B]}{[A]} \Bigg|_1^2 = k (t_2 - t_1)$$

$$\Rightarrow \frac{1}{a [B]_0 - b [A]_0} \times \ln \frac{[B]/[B]_0}{[A]/[A]_0} = k t \quad \text{..... (iii)}$$

Where $[A]$, $[B]$ are concentration at time 't' and $[A]_0$ and $[B]_0$ are concentrations at $t = 0$ time.

A plot of L.H.S. of equation (iii) against 't' will give a straight line with slope = k

Let us now consider a Special case:

A special case can be considered where $\frac{[B]_0}{[A]_0} = \frac{b}{a}$

Then equation (iii) will not apply as $(a [B]_0 - b [A]_0) = 0$. Then we consider at any point of time $\frac{[B]}{[A]} = \frac{b}{a}$

This follows from equation (ii) with $[B]_0 = \frac{b}{a} \times [A]_0$. Equation (i) becomes

$$\left(\frac{1}{b \times [A]^2} \right) d[A] = -k \times dt \quad \text{..... (iv)}$$

Integrating this equation (iv) we get,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = b \times k \times t \quad \text{..... (v)}$$

Let us now consider a general n^{th} order reaction:

Let us consider the following rate law

$$\frac{d[A]}{dt} = (-) k_a \times [A]^n$$

$$\Rightarrow \int_1^2 \frac{d[A]}{[A]^n} = (-) k_a \times \int_1^2 dt$$

$$\Rightarrow \frac{[A]^{-n+1} - [A]_0^{-n+1}}{-n+1} = (-) k_a \times t \quad [n \neq 1]$$

Multiplication of both sides by $(1 - n) [A]_0^{n-1}$ gives

$$\left(\frac{[A]}{[A]_0}\right)^{1-n} = 1 + [A]_0^{n-1} \times (n - 1) \times k_a \times t \quad [n \neq 1] \quad \text{..... (A)}$$

Setting $[A] = \frac{1}{2} [A]_0$ and thus $t = t_{\frac{1}{2}}$

$$\boxed{t_{\frac{1}{2}} = \frac{2^{n-1} - 1}{(n - 1) \times [A]_0^{n-1} \times k_a}} \quad (\text{for } n \neq 1) \quad \text{..... (B)}$$

Equations (A) and (B) holds for all except $n = 1$. It is true for $n = 0$, $n = \frac{1}{2}$, $\frac{3}{2}$ etc.

Zero-order reaction:

Assume a zero order reaction as $aA \rightarrow \text{Product}$

$$r = (-) \frac{1}{a} \frac{d[A]}{dt} = k [A]^0$$

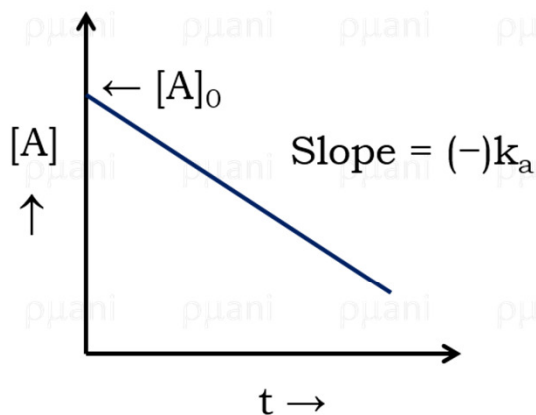
$$\Rightarrow -d[A] = k \times a \times dt = k_a \times dt$$

Integrating,

$$-\int_{[A]_0}^{[A]} d[A] = k_a \times \int_0^t dt$$

$$\Rightarrow \boxed{[A] = [A]_0 - k_a \times t} \quad \text{..... (i)}$$

Plotting $[A]$ vs. t we get



Unit of rate constant = $\text{moles lit}^{-1} \text{sec}^{-1}$

$$\text{When } [A] = \frac{[A]_0}{2}$$

$$\text{Then, } k_a \times t_{\frac{1}{2}} = [A]_0 - \frac{[A]_0}{2}$$

$$\text{So, } \boxed{t_{\frac{1}{2}} = \frac{1}{k_a} \times \left(\frac{[A]_0}{2}\right)}$$

Important series expansion:

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 - \dots$$

$$e^{+x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots$$

Question: What are the expressions and unit of rate constant and $t_{\frac{1}{2}}$ for zero, first and 2nd and nth order reactions?

Question: Calculate the time required for ϕ fraction of the reactant to undergo reaction for zero, first, second order reaction.