Ministry of Higher Education and Scientific Research
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Department of Biochemistry

Physical Chemistry

Lecture 3

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First semester

Kinetic of First Order Reaction

By

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Integrated Rate Equations

Zero Order Reactions

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

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

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

Integrated Rate Equations

Integrating both sides between proper limits

$$\int_{R_0}^{R} d[R] = -k \int_{0}^{t} dt$$

$$[R] - [R_o] = -kt$$

Or

$$[R_o] - [R] = kt$$

Or

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

Integrated Rate Equations

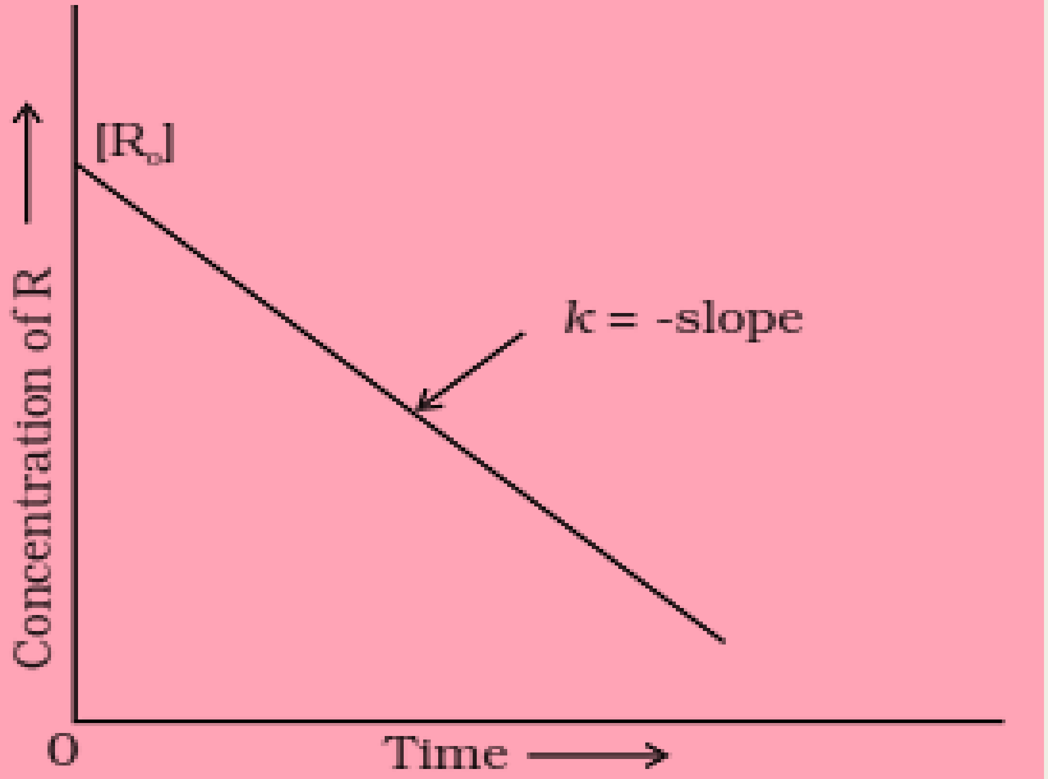


Fig. [illegible] Variation in the concentration vs time plot for a zero order reaction

Integrated Rate Equations

First Order Reactions

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

$$R \longrightarrow P$$

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

$$\text{or} \quad \frac{d[R]}{[R]} = -k\,dt$$

Integrated Rate Equations

Integrating both sides between proper limits

$$\int_{R_0}^{R} \frac{d[R]}{R} = -k \int_{0}^{t} dt$$

$$\ln[R] - \ln[R_o] = -kt$$

Or

$$\ln[R_o] - \ln[R] = kt$$

Or

$$kt = \ln \frac{[R_0]}{[R]}$$

Or

$$k = \frac{1}{t} \ln \frac{[R_0]}{[R]}$$

Or

$$\boxed{k = \frac{2.303}{t} \log_{10} \frac{[R_0]}{[R]}}$$

Integrated Rate Equations

$$k = \frac{2.303}{t} \log_{10} \frac{[Ro]}{[R]}$$

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

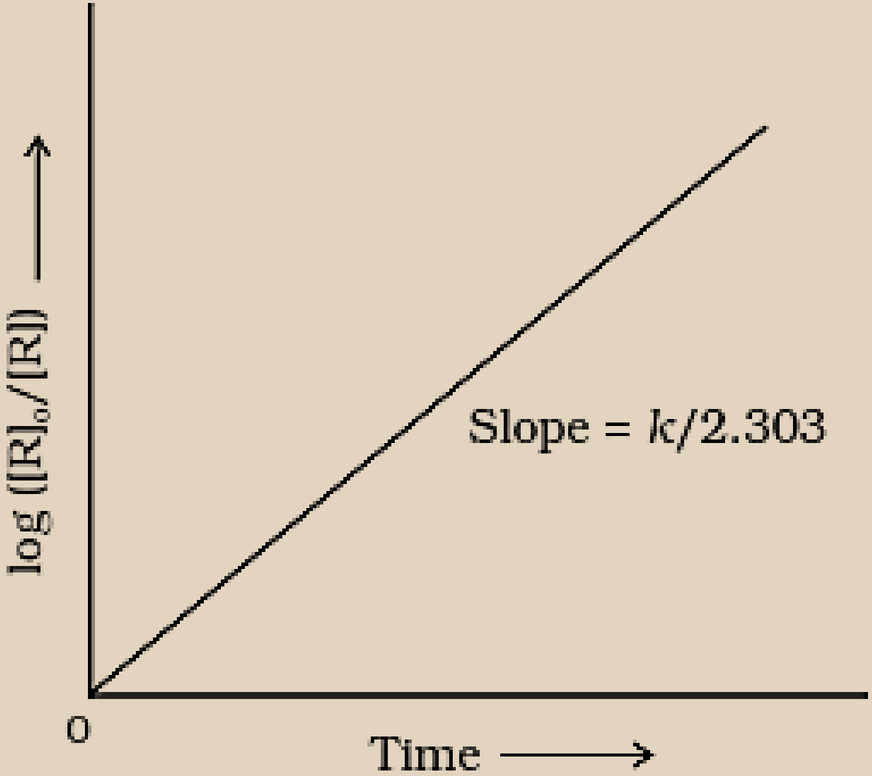
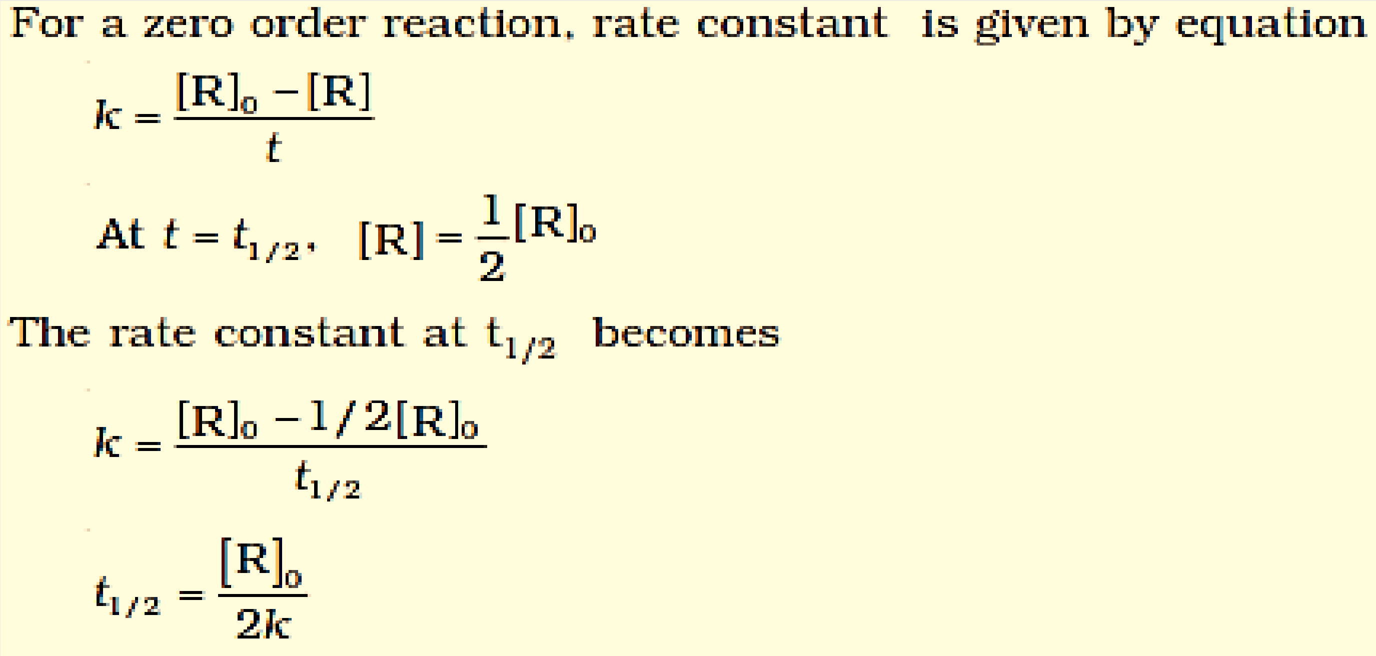


Fig. 4.5: *Plot of log [R]$_0$/[R] vs time for a first order reaction*

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 $t_{1/2}$

$t_{1/2}$ for a Zero Order Reactions



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

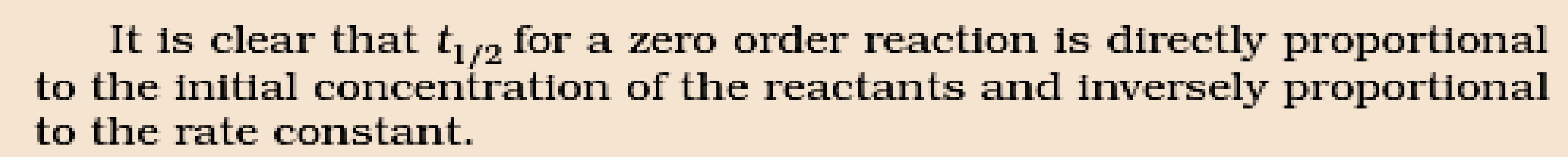
$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, \quad [R] = \frac{1}{2}[R]_0$$

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.

Half-Life of a Reaction

$t_{1/2}$ for a First Order Reactions

For the first order reaction,

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

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

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

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

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

Thus for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species.

Pseudo - first order reaction

Reactions which are not truly of the first order but under certain conditions reactions become that of first order are called pseudo unimolecular reaction.

For example: Hydrolysis of ester in presence of acid

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

From this reaction, the rate expression should be

$$r = k\,[ester]\,[H_2O]$$

Since, hydrolysis takes place in the excess of H_2O and concentration change of H_2O is negligible practically.

therefore, $r = k'\,[ester]$

Where $k' = k[H_2O]$.

Methods of determining the order of a reaction

1- Integrated method

The equation which gives a constant value of k decides the order of reaction

2- Graphical method

The data are plotted acc to different integrated rate equations so as to yield a straight line .Slope gives the value of rate constant

3- Initial rate method

Concentration of one of the reactant is varied

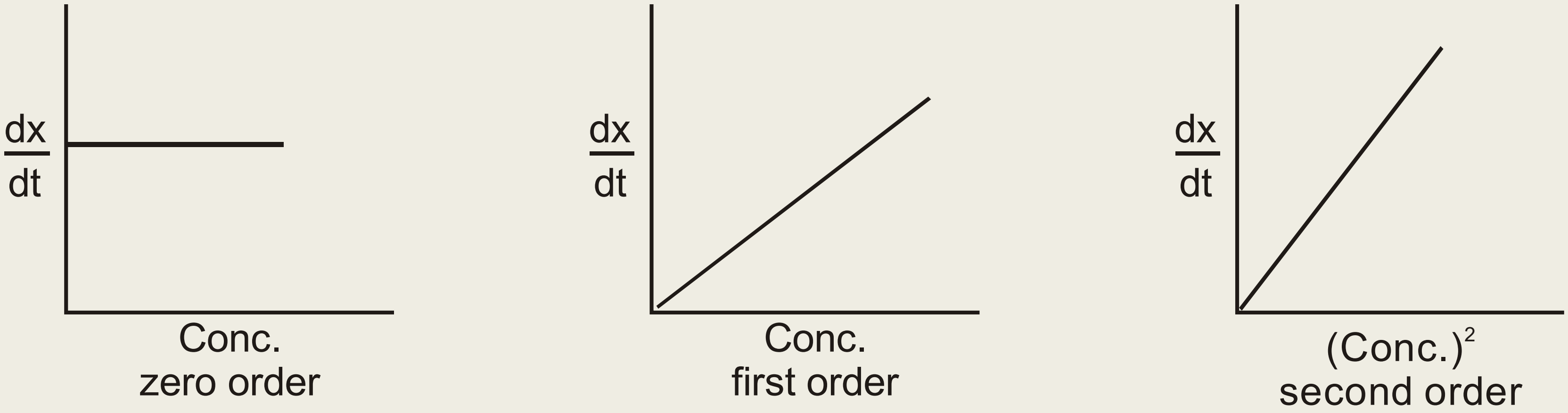
4- Half life method

In this method we plot half life of the reactant versus conc. of the reactant.

Methods of determining the order of a reaction

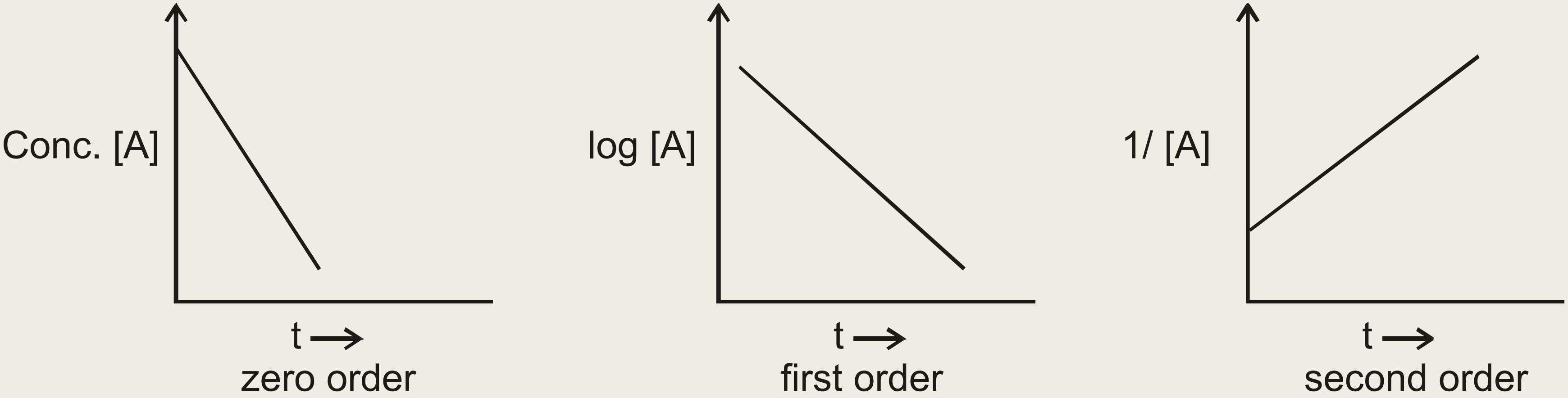
Reaction Order	Differential rate law	Integrated rate law	Characteristic kinetics Plot	Slope of kinetics plot	Units of rate constant
Zero	$\frac{-d[A]}{dt} = k$	$[A]=[Ao]-kt$	[A] vs t	-k	$\text{Mole l}^{-1}\ \text{sec}^{-1}$
First	$\frac{-d[A]}{dt} = k[A]$	$[A]=[Ao]e^{-kt}$	In[A] vs t	-k	sec^{-1}
Second	$\frac{-d[A]}{dt} = k[A]^2$	$A = \frac{[Ao]}{1+k+[A]}$	1/[A] vs t	k	$\text{L mole}^{-1}\ \text{sec}^{-1}$

Graphical Representation



Graphical representation of rate versus concentrations

Graphical Representation



zero order first order second order

Graphical representation for concentration of integrated rate equation versus time

Initial rate method

- This method involves the determination of the order of each reactant separately.

- To determine the order of a particular reactant, its concentration is varied keeping the concentrations of other reactants constant.

- In every experiment, we determine the initial rate of the reaction and observe the dependence of rate on that particular reactant.

$$r \propto [A]^m [B]^n$$

Keeping [B] constant

$$\frac{r_1}{r_2} = \frac{[A_1]^m [B]^n}{[A_2]^m [B]^n}; \quad \frac{r_1}{r_2} = \left[\frac{[A_1]}{[A_2]}\right]^m$$

Illustrative Example

Rate of the reaction; A + B = products; is given below as a function of the initial concentration of ‘A’ and ‘B’.

[A](mol L^{-1})	[B](mol L^{-1})	rate($\text{mol L}^{-1}\text{min}^{-1}$)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to ‘A’ and

Solution:

For first two experiments, the concentration of the reactant ‘B’ is constant.

Rate of the reaction depend linearly on reactant ‘A’.

Now, taking experiments first and third, the concentration of the reactant ‘A’ is constant.

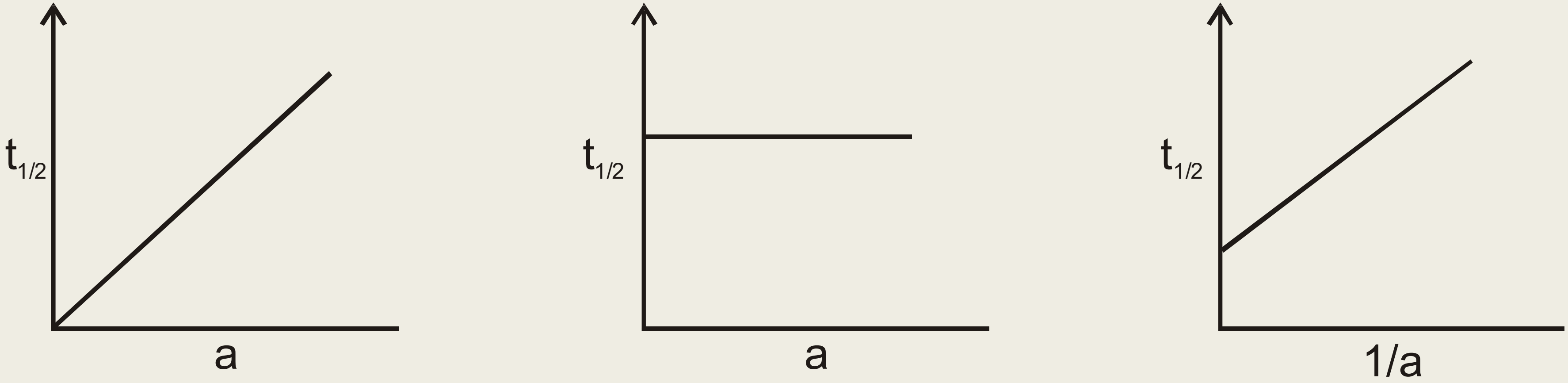
Therefore, rate of the reaction is independent of ‘B’.

Thus, order of the reaction with respect to ‘A’ = one.

Order of the reaction with respect to ‘B’ = zero.

Half life method

$$t_{1/2} \; \alpha \; \frac{1}{[A]_0^{n-1}}$$



zero order   first order   second order

Graphical representation for half lives versus concentration

Illustrative Example

The half-life of a particular chemical reaction at two different initial concentrations 5 x 10^{-4} and 25 x10^{-5} M are 2 and 16 hours. Calculate the order of reaction.

Solution:

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left\{ \frac{\left([A]_0 \right)_1}{\left([A]_0 \right)_2} \right\}^{n-1}$$

$$\Rightarrow \frac{16}{2} = \left(\frac{5 \times 10^{-4}}{25 \times 10^{-5}} \right)^{n-1} = (2)^{n-1}$$

$$\Rightarrow 8 = (2)^{n-1}$$

$$\Rightarrow n - 1 = 3$$

$$\Rightarrow n = 4$$

Integrated method

In this method, we put the data into the integrated form of the rate laws and calculate the values of the rate constants for different kinetics of the reaction.

The order of the reaction is that one for which the value of rate constant is constant.

Example: The activation energy of a first order reaction is 50.2 kJ/mol at 25°C. At what temperature will the rate constant double?

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(1) $k_2 = 2k_1$

(2) $$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) \;=\; \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(3) $$\frac{E_a}{R} = \frac{50.2\ \text{kJ/mol} \times \dfrac{10^3\,\text{J}}{1\,\text{kJ}}}{8.314\,\dfrac{\text{J}}{\text{mol}\cdot\text{K}}} \;=\; 6.04 \times 10^3\,\text{K}$$

(4) $$\ln(2) = 0.693 \;=\; 6.04 \times 10^3\,\text{K} \times \left(\frac{1}{298\text{K}} - \frac{1}{T_2}\right)$$

A 10°C change of temperature doubles the rate!!

(5) $$\frac{1}{T_2} = 3.24 \times 10^{-3}\,\text{K}^{-1} \longrightarrow \boxed{T_2 = 308\ \text{K}}$$

Example/ Using the data for 25C° and 65C° in table, calculate Ea, the energy of activation for the decomposition of Nitrogen pentoxide N_2O_5.

25+273 = 298 k
65+273 = 338 k
K1 = 3.46*10-5
K2 = 4.87*10-3

$$\mathrm{Log}\ \frac{K2}{K1} = \frac{Ea}{2.303R} * \frac{T2-T1}{T1-T2}$$

$$\mathrm{Log}\ \frac{4.87*10\text{-}3}{3.46*10\text{-}5} = \frac{Ea}{2.303R}\ \frac{338-298}{338-298}$$

Ea = 24.800 cal


Thank you