4. CHEMICAL KINETICS

Synopsis:

- The study of rates of chemical reactions mechanisms and factors affecting rates of reactions is called chemical kinetics.
- Spontaneous chemical reaction means, the reaction which occurs on it's own without any external reagent. A spontaneous chemical reaction may be slow or fast (instantaneous).

  For spontaneous reaction ΔG = – ve.

  Spontaneity deals with feasibility.
- Based on the speed of reactions, the chemical reactions are of 3 types.

  i) Very slow reactions: Ex. Rusting of iron, Formation of H_2O from H_2 and O_2 at room temperature]

  ii) Very fast reactions (instantaneous reactions) :

  a) Discharge of pink color of $KMnO_4$ by oxalic acid in acid medium.

  b) $H_2 + F_2 \xrightarrow{\text{sun light}} 2HF$

  c) $H_2 + Cl_2 \xrightarrow{\text{sun light}} 2HCl$

  Al ionic reactions and neutralisation reactions are fast.

  iii) Slow reactions: These reactions occur with optimum speeds.

  Rates of very slow and very fast reactions can not be determined.

  Rate of these slow reactions can be measured

  Ex: a) $2H_2O_2 \rightarrow 2H_2O + O_2$

  b) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

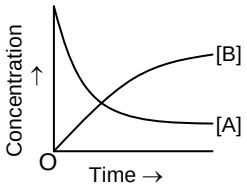
c) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Reaction rate or rate of a reaction:

- The change in concentration per unit time is called rate of reaction.
- Unit of rate of reaction : mol. $lit^{-1}.sec^{-1}$.
- Rate of reaction can be expressed with respect to reactants or products.

  Rate = $-\frac{dc}{dt}$ (-sign indicates decrease in the concentration of reactants)

  Rate = $+\frac{dc}{dt}$ (+sign indicates increase in the concentration of products)
- The rate of reaction will not remain constant and it changes with time.
- Average rate of reaction is the rate of reaction measured in long time interval.
- Instantaneous rate of reaction is the rate of reaction measured in infinitesimally small time interval. For reaction A $\rightarrow$B graphical representation of rate is as follows.



- The rate reaction changes with time exponentially.
- No reaction takes place uniformly through out the course of the reaction.

Expressing the rate of reaction:

- General equation : $mA + nB \rightarrow pC + qD$

  Rate of reaction = $-\frac{1}{m}\frac{d[A]}{dt} = -\frac{1}{n}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$

Example :

1) $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$\text{rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

$$= -\frac{d[N_2O_5]}{dt} = -\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{2\times d[O_2]}{dt}$$

2) $2SO_2 + O_2 \rightarrow 2SO_3$

$$\text{rate} = -\frac{1}{2}\frac{d[SO_2]}{dt} = -\frac{d[O_2]}{dt} = +\frac{1}{2}\frac{d[SO_3]}{dt}$$

$$= -\frac{d[SO_2]}{dt} = -\frac{2\times d[O_2]}{dt} = +\frac{d[SO_3]}{dt}$$

- The decrease in the concentration of the reactant per unit time or increase in the concentration of the product per unit time is called rate of the reaction.
- The rates of chemical reactions differ form one another, since the number and the nature of the bonds are different in the different substances (reactants products or both)
- $A \rightarrow B$

  $$\text{rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$
- The unit for the rate of the reaction is
  moles – lit^{-1} – sec^{-1}.
- $N_2 + O_2 \rightarrow 2NO$

  $$\text{rate} = -\frac{d[N_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} \text{ (or)}$$

  $$\text{rate} = \frac{2d[N_2]}{dt} = -\frac{2d[O_2]}{dt} = +\frac{d[NO]}{dt}$$

- $pP + qQ \rightarrow rR + sS$

  $$\text{the rate} = -\frac{1}{p}\frac{d[P]}{dt} = -\frac{1}{q}\frac{d[Q]}{dt} = +\frac{1}{r}\frac{d[R]}{dt}$$

  $$= +\frac{1}{s}\frac{d[s]}{dt}$$
- The rate of the reaction measured with respect to the decrease in the concentration of the reactants decreases.
- The rate of the reaction measured with respect to the increase in the concentration of the products increases.
- The rate of a reaction at any particular instant of time during the course of a reaction is the rate of change of concentration of a reactant or a product at that instant of time.
- The rate of the reaction varies with time of the reaction.
- The concentration of the reactants in a reaction varies exponentially with time.
- No reaction takes place with uniform rate throughout the course of the reaction.

Factors influencing rate of reaction:

1) Nature of the reactants :

- The rate of reaction depends on the nature of reactants.

- Reactants which require less activation energy react faster than the reactants which require higher activation energy.
- Ionic reactions and neutralisation reactions are very fast in solution as they involve simple exchange of ions.
- Reactions between covalent molecules are generally slow as they involve shuffling of bonds.

  The reactions which involve greater bond rearrangements are slow and the reactions involving lesser bond rearrangements are fast.

Fast reactions	**Slow reactions**
i) $H^+ + OH^- \rightarrow H_2O$	$2H_2O + O_2 \rightarrow 2H_2O$
ii) $2NO + O_2 \rightarrow 2NO_2$	$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

2) Effect of concentration of reactants :

- According to law of mass action, the rate of a chemical reaction is directly proportional to the product of concentration of reactants.
- In case of gaseous reactions, rate is directly proportional to the product of partial pressures of reactants.
- If concentration is higher, the number of molecules per unit volume is, more and the number of active collisions increases. According to collision theory, rate of reaction increases with increase in the number of collisions.
- The dependence of rate of reaction on the concentration of reactants can be mathematically expressed as $-\frac{dc}{dt} = k.C^n$ (n can take any simple value including zero)

3) Effect of temperature :

- With increase in temperature rate of reaction increases because the number of active collisions or activated molecules increases.

- According to Arhenious for most of the reactions rate of reaction doubles or triples for every 10° rise in temperature.

  Temperature coefficient (μ) = $\frac{K_{T+10}}{K_T}$ = 2 (or) 3

- Arhenious suggested a simple empirical relation between specific rate and temperature.

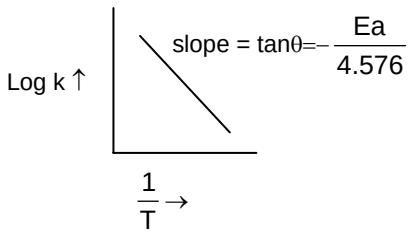
  $K = A.e^{-Ea/RT}$

  $\ell n\, K = \ell n\, A - Ea/RT$

  $2.303\, \ell og\, K = 2.303\, \ell og\, A - Ea/RT$

  $\ell og\, K = \ell og\, A - \frac{Ea}{2.303R} \times \frac{1}{T}$

  Plot of log k Vs $\frac{1}{T}$ gives a linear graph with –ve slope.



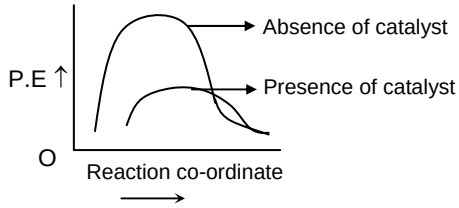
- Slope gives the activation energy and intercept gives frequency factor.

4) Effect of catalyst :

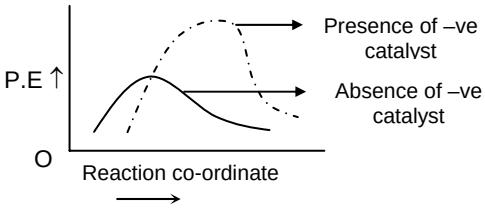
- Catalyst alters the speed of reaction by changing the activation energy.
- Catalyst alters the activation energy by changing the path of the reaction or mechanism of reaction.
- A positive catalyst increases the rate of reaction by decreasing the activating energy.

  In case of some reactions, rate is proportional to the concentration of catalyst.

  Ex : Acid catalysed hydrolysis of ester.



- A negative catalyst decreases the rate of reaction by increasing the activation energy.



- Enzymes are biocatalysts for biochemical reactions.

5) Effect of radiation :

- Some chemical reactions take place very fast by absorbing sunlight. Such chemical reactions are called photocatalysed or photoaccelerated or photosensitized reactions.

6) Physical state of reactants :

- In heterogeneous system, collisions are not much effective as that of in homogeneous system. There fore reactions are much faster in gaseous and liquid states.

  Rate of reaction :

  Gaseous state > Liquid state >Solid state

7) Physical size of reactants;

- In case of solids, rate increases with decrease in the size of particle. Rate is faster in powdered state than that of undivided state because surface area increases and the possibility of contact between reactant molecules increases.

Rate law and rate constant :

- The equation which relates the rate of the reaction and the concentration of the reactants is known as rate equation or rate law.
- Rate equation is written after the experiment only. It is not related to coefficients of reactants in balanced equation.
- Rate of reaction does not depend on the reactant if it's concentration is large excess.
- "Isolation" methods are usually followed to study rate of the reaction.
- $nA + mB \rightarrow$ products

  rate $r \alpha [A]^n [B]^m$; rate $= K[A]^n [B]^m$
- K is called rate constant or specific rate or rate per unit concentration of the reactants.

  i) $CH_3COOC_2H_{5(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + C_2H_5OH_{(aq)}$

  The rate equation :

  $K[CH_3COOC_2H_5]^1 [NaOH]^1$

  ii) $2H_2O_2 \rightarrow 2H_2O + O_2$

  rate $\alpha [H_2O_2]^1$

  iii) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

  rate $\alpha [N_2O_5]^1$

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

  rate α [ester]^1 $[H_2O]^0$

  v) $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

  rate α [ester]^1 $[NaOH]^1$

Order of the reaction:

- The sum of the powers of the concentration terms of reactants in the rate equation is called order of the reaction.
- Order of reaction may be zero or fraction or negative or a whole number (n).
- Order of the reaction can be determined experimentally.

Molecularity of the reaction:

- Molecularity of a reaction is the number of reactant molecules taking part in rate determining step.
- A chemical reaction may take place in one or more steps. Different steps may proceed with different speeds. The slowest step is rate determining step.
- Molecularity of simple reactions is equal to the stoichiometric coefficients in balanced equation.
- Molecularity is a theoretical concept.
- Molecularity is related to mechanism of reaction.
- Molecularity is always a whole number.
- Molecularity cannot be zero, –ve, fractional, infinite and imaginary.
- Generally, moleclarity of a reaction can not be greater than three because more than 3 molecules may not mutually collide with each other.

  Examples :

  i) $2\ H_2O_2 \rightarrow 2H_2O + O_2$ uni molecular

  ii) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ uni molecular

  iii) $PCl_5 \rightarrow PCl_3 + Cl_2$ uni molecular

  iv) $2HI \rightarrow H_2 + I_2$ Bimolecular

  v) $CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$
  Bimolecular

  vi) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
  Bimolecular

  vii) $2SO_2 + O_2 \rightarrow 2SO_3$ Termolecular

  viii) $2CO + O_2 \rightarrow 2CO_2$ Termolecular

  ix) $2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$ Termolecular

Order of reaction : zero, $A \rightarrow$ products

The concentration of reactant decreases linearly with time. The rate of reaction is uniform. The time required for the completion of reaction is zero.

- Equation for rate constant : $K_o = \frac{x}{t}$.
- Units for rate constant : moles– lit^{-1}– sec^{-1}.
- Half life : $t_{1/2} \ \alpha$ a.

  a = initial conc. of the reactants

  Examples :

  $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

  $2NH_3 \xrightarrow[M_0]{w(or)} N_2 + 3H_2$

  $2HI \xrightarrow{Au} H_2 + I_2$
- Order of reaction : First

  $A \rightarrow$ products

  $r = k_1 [A]^1$

  equation for rate constant :

$$k_1 = \frac{2.303}{t}\log\frac{a}{a-x}$$

- Units for rate constant: sec^{-1}
- The exponential form of the above equation is,

  $(a - x) = a.e^{-kt}$

  $x = a(1-e^{-kt})$

  Half life : It is the time taken for 50% completion of reaction or the time taken for concentration of reactant to become half of it's initial value.
- For 1^{st} order reactions, $t_{1/2}$ is independent of initial concentration of reactant.
- The concentration of the reactant left after 'n' half lifes, $(a-x) = \frac{a}{2^n}$.
- Rate constant, k depends on the
  i) Nature of reactant
  ii) Temperature of reaction
  iii) Catalyst
- Rate constant, k is independent of
  i) Initial concentration of reactant
  ii) Time
- Half life time : $t_{1/2} \alpha a^0$.

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

  Examples :

  1. $N_2O_5 \underset{(g)}{\rightarrow} N_2O_4 \underset{(g)}{+} \frac{1}{2} O_2$
  2. $SO_2Cl_{2(g)} \rightarrow SO_{2(g} + Cl_{2(g)}$
  3. $H_2O_{2(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)}$
  4. Acid hydrolysis of ester.

     $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
  5. $NH_4NO_{2(aq)} \rightarrow N_2O + 2H_2O_{(l)}$
  6. Disintegration of radio active elements.
  7. $NH_4NO_3 \rightarrow N_2O + 2H_2O$
  8. Inversion of canesugar.

  $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

  Order of reaction - second order :

  $2A \rightarrow$ products (or) $A + B \rightarrow$ products

  $r = k_2[A]^2$ (or) $r = k_2 [A]^1[B]^1$

- Equation for rate constant $k_2 = \frac{1}{at}.\frac{x}{a-x}$
- Units for rate constant : lit. $mole^{-1}.sec^{-1}$.
- Half life time : $t_{1/2} \alpha \frac{1}{a}$

$$t_{1/2} = \frac{1}{k_2 a}$$

Examples:

1) $2O_3 \rightarrow 3O_2$
2) $2N_2O \rightarrow 2N_2 + O_2$
3) $2Cl_2O \rightarrow 2Cl_2 + O_2$
4) $CH_3COOH + NaOH \rightarrow CH_3COONa + C_2H_5OH$
5) $2NO_2 \rightarrow 2NO + O_2$
6) $C_2H_4 + H_2 \xrightarrow{Ni} C_2H_6$
7) $2HI \rightarrow H_2 + I_2$

Order of reaction : Third order :

$3A \rightarrow$products (or) $2A + B \rightarrow$ products (or)

$A + B + C \rightarrow$ products.

$r = K_3[A]^3$ (or) $r = K_3[A]^2[B]^1$ (or) $r=K_3[A]^1[B]^1[C]^1$

equation for rate constant :

$$k_3 = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$$

Units for rate constant : $lit^2.mole^{-2}.sec^{-1}$.

Half life time : $t_{1/2} \alpha \frac{1}{a^2}$

Examples :

$2NO + O_2 \rightarrow 2NO_2$

$2NO + Cl_2 \rightarrow 2NOCl$

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

(aq) (aq) (aq) (aq)

Order of reaction : n^{th} order

Units for rate constant : $lit^{n-1}.mole^{1-n}.sec^{-1}$. (or)

$(atm)^{1-n}.\ sec^{-1}$

Half life : $t_{1/2} \alpha \frac{1}{a^{n-1}}$

Order of reaction : Fractional order

Examples :

Decomposition of acetaldehyde is 3/2 order

$CH_3CHO \rightarrow CH_4 + CO$

$r = k\,[CH_3CHO]^{3/2}$

Reaction between Hydrogen and Bromine

$H_2 + Br_2 \rightarrow 2HBr$

$r = k[H_2]^1\,[Br_2]^{1/2}$ order $= 1+\frac{1}{2}=\frac{3}{2}$

Order of reaction : negative order :

When the concentration of the reactants increases, rate decreases.

Decomposition of zone.

$2O_3 \rightarrow 3O_2$.

$r = -\frac{1}{2}\frac{d(O_3)}{dt} = \frac{k[O_3]^2}{[O_2]} = k[O_3]^2[O_2]^{-1}$

The order of reaction w.r.t oxygen is –1.

Pseudo unimoelcuar reactions :

The reactions with molecularity greater than or equal to 2 but order is one are called Pseudo unimolecular or Pseudo first order reactions.

Eg : i) Hydrolysis of ethyl acetate in acid medium.

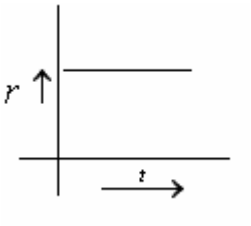
ii) Inversion of cane sugar.

Difference between molecularity and order of reaction:

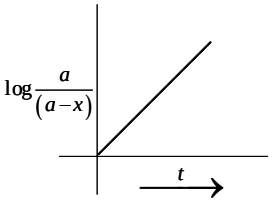
Molecularity	Order of reaction
The number of atoms or ions or molecules participating in the rate determining step of the reaction or activated complex of the reaction is called molecularity.	The sum of the powers of the concentration terms of the reactants in the rate equation is called order of the reaction.
Molecularity is always whole number or integer. It cannot become zero or fraction or negative.	Order can becomes negative or fraction or whole number.
This is theoretically elucidated from the mechanism of the reaction.	This is determined experimentally.
All reactions involve elementary steps, it may be one step or more steps.	All reactions need not have order. Only those reactions for which is in the form $r = K.C_A^m.C_{B.}^n$ can have order.
Molecularity of a complex reaction has no meaning. It is expressed only for elementary steps.	Order is the same for the whole reaction whether it involves a single step or more steps.
Molecularity does not exceed 3.	Order usually does not exceed 3.

METHODS OF DETERMINATION OF ORDER OF REACTION.

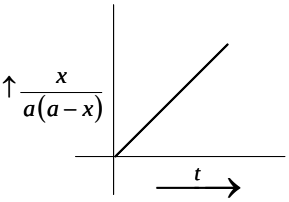
- **TRAIL AND ERROR METHOD OR INTEGRATED FORM OF RATE EQUATION METHOD.**
- Zero order $R \rightarrow P^0$



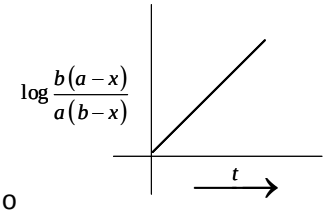
- $x = kt \quad (or) \qquad K = \frac{x}{t} = \frac{a-(a-x)}{t}$
- First order $R \rightarrow P$
- $K = \frac{2.303}{t} \log \frac{a}{(a-x)}$



- Second order $2R \rightarrow P$
- $K = \frac{1}{at} \times \frac{x}{(a-x)}$



- Second order $R_1 + R_2 \rightarrow P$
- $K = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$



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- **HALF-TIME** $(t_{1/2})$ **METHOD**
- $t_{1/2} \alpha \frac{1}{a^{n-1}}$

- $\left(\frac{t'_{1/2}}{t''_{1/2}}\right)=\left(\frac{a''}{a'}\right)^{n-1}$

- where n = order of reaction

- **Van't Hoff Differential Method**
- $\frac{-dc}{dt}=KC^n$
  - For two initial concentrations we C_1, C_2 have
- $\frac{-dc_1}{dt}=KC_1^n; \qquad \frac{-dc_2}{dt}=KC_2^n$
- $\therefore n=\frac{\log\left(\frac{-dc_1}{dt}\right)-\log\left(\frac{-dc_2}{dt}\right)}{\left(\log c_1-\log c_2\right)}$

- **Ostwald's Isolation Method**
- This method is useful to determine the order w.r.t each reactant of a reaction separately by taking other reactants in excess quantity.
- A + B + C products
- Then order with respect to A is n_A
- Order with respect to B is n_B
- Order with respect to C is n_C
- overall order of the reaction = $n_A + n_B + n_C$

Collision theory of reaction rates :

- Collision theory was proposed by Arrhenius.

  The main postulates of collision theory are
- Collisions must occur between the molecules of reacting gases for a reaction to occur.
- All collisions do not lead to the formation of products. (only fruitful collisions leads to formation of products)
- The minimum amount of energy possessed by the colliding molecules to the formation of products or reaction to occur is known as threshold energy.
- The energy possessed by the molecules at STP is known as normal energy or internal energy.
- Normal energy possessed by normal molecules is always less than threshold energy.
- The minimum excess energy required by the normal molecules during the collision to convert into products is known as activation energy or energy of activation.
- Activation energy = Threshold energy – energy of normal colliding molecules.
- Higher the activation energy, lower is the rate of reaction. Lower the activation energy, higher is the rate of reaction.

  $\Delta H = H_p - H_R$

  ΔH= difference in the activation energies between reactants and products.

- The activation energy for nuclear reaction is zero.

  Arrhenius rate equation : $K = A.\ e^{-Ea/RT}$

  K = Specific rate

  A = Frequency factor (constant)

  Ea = Activation energy

  R = Gas constant; T = Absolute temperature
- The fraction of activated collisions is always smaller than the total number of collisions.

  $\therefore$ Actual rate of reaction is much smaller than the rate of the reaction calculated on the basis of the normal collisions.
- Reacting molecules must be properly oriented to make effective collisions.

First order reaction:

- Rate equation for first order A $\rightarrow$Product is

  $\frac{dx}{dt} = K[A]^1$ or $\frac{dx}{dt} = K(a-x)$
- The specific rate constant

  $K = \frac{2.303}{t}\log\frac{a}{(a-x)}$

  a = initial concentration of the reactant.

  (a-x) = remaining concentration of the reactant.

  x = the concentration of the product at time 't'

  $x = a\left(1-e^{-kt}\right)$ or $c_t = c_0 e^{-kt}$
- The unit for first order rate constant is sec^{-1}.
- The time required for the initial concentration of 'a' of the reactant to become half of its value namely (a/2) is known as half life ($t_{1/2}$) or half time of the reaction.
- $t_{1/2} = \frac{0.693}{k}$
- The half life of a first order reaction is independent of the initial concentration.

  The equation for half life period for a reaction of

  'n' th order can be written as $t_{1/2}\ \alpha\ \frac{1}{a^{(n-1)}}$.
- For the decomposition of $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$.

  The volume of O_2 is measured. Then the rate constant $K = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

  Here $V_\infty = a$, $V_\infty - V_t = (a-x)$.
- Not only the time taken for the initial concentration is to reach half its value but the time taken for it to reach any fraction (1/4 or 3/4) of the initial concentration is independent of initial concentration. This is one of the main characteristics of a first order reaction.
- For a first order reaction it can be shown that

  a) $t_{1/2} : t_{3/4} : t_{7/8} = 1 : 2 : 3$

b) $t_{90\%} : t_{99\%} = 1 : 2$

c) $t_{50\%} : t_{90\%} = 3 : 10$

d) $t_{50\%} : t_{99.9\%} = 1 : 10$

- In a first order reaction the graph between log(a-x) and t is a straight line with negative slope.

