PARTIAL FRACTION

Points to be covered in this topic

1. INTRODUCTION
2. PARTIAL FRACTION
3. POLYNOMIAL
4. RATIONAL FRACTION
5. METHOD OF RESOLVE INTO PARTIAL FRACTION
6. APPLICATION OF PARTIAL FRACTION IN CHEMICAL KINETICS AND PHARMACOKINETICS

❑ INTRODUCTION

- **A fraction is a symbol indicating the division of integers.**
- The **dividend (upper number)** is called the numerator N(x) and the divisor (lower number) is called the denominator, D(x).

$$\frac{13}{9} = \text{Fraction}$$

❑ PARTIAL FRACTIONS

- To express a **single rational fraction** into the **sum of two or more single rational fractions** is called Partial fraction resolution.

$$\frac{2x+x^2-1}{x(x^2-1)} = \frac{1}{x} + \frac{1}{x-1} - \frac{1}{x+1}$$

$\frac{2x+x^2-1}{x(x^2-1)}$ is the resultant fraction and

$\frac{1}{x} + \frac{1}{x-1} - \frac{1}{x+1}$ are its partial fraction.

❑ POLYNOMIAL

Any expression of the form $P(x) = a_n x^n + a_{n-1} x^n + a_{n-1} x^{n-1} + ...+ a_2 x^2 + a_1 x$
where a_n, a_{n-1}, a_2, a_1 are real constants
if $a_n \neq 0$ than $P(x)$ is called polynomial of degree n.

❑ RATIONAL FRACTION

Similarly the quotient of two polynomials where, $\frac{N(x)}{D(x)}$ where $D(x) \neq 0$ with **no common factors,** is called a rational fraction.

PROPER FRACTION

A rational fraction is called a proper fraction if the **degree of numerator N(x) is less than the degree of Denominator D(x).**

IMPROPER FRACTION

A rational fraction is called an improper fraction if the **degree of the Numerator N(x) is greater than or equal to the degree of the Denominator D(x)**

❑ METHOD OF RESOLVE INTO PARTIAL FRACTION

TYPE (i): When the factors of the denominator are all linear and distinct i.e., non repeating.

$$\text{Let } g(x) = (x-a_1)(x-a_2).....(x-a_n), \text{ then we assume that}$$

$$\frac{f(x)}{g(x)} = \frac{A_1}{x-a_1} + \frac{A_2}{x-a_2} + \frac{A_3}{x-a_3} + ...\frac{A_n}{x-a_n}$$

Where $A_1, A_2, A_3, ...A_4$ are constant and can be determined by comparing the coefficient of various power of x or by substituting $x = a_1, a_2, ...a_n$ in the LHS and RHS after simplification.

TYPE (ii): **When the factors of the denominator are all linear but some are repeated.**

Let $g(x) = (x-a)^k (x-a_1).....(x-a_r)$, *then we assume that*

$$\frac{f(x)}{g(x)} = \frac{A_1}{x-a} + \frac{A_2}{(x-a)^2} + \frac{A_3}{(x-a)^3} + ...\frac{A_k}{(x-a)}$$

TYPE (iii): **When the denominator contains ir-reducible quadratic factors which are non-repeated.**

$$\frac{1}{1+x^3} = \frac{1}{(1+x)(1+x^2-x)} = \frac{A}{1+x} + \frac{Bx+c}{1+x^2-x}$$

$$1 = A(1+x^2-x) + (bx+c)(1+x)$$

Put $x = -1$

$$1 = A(3)$$

$$A = \frac{1}{3}$$

Equating the coefficient of $x2$ *and cons* tan *t terms on the both side, we get*

$$0 = A + B$$

$$B = -\frac{1}{3}$$

$$1 = A + C$$

$$C = \frac{2}{3}$$

$$\frac{1}{1+x^3} = \frac{1}{3(1-x)} + \frac{\frac{1}{3}x + \frac{2}{3}}{1+x^2-x}$$

$$\frac{1}{1+x^3} = \frac{1}{3(x+1)} - \frac{1(x-2)}{3(1+x^2-x)}$$

TYPE (iv): **When the denominator has repeated Quadratic factors.**

$$\frac{f(x)}{(ax^2+bx+c)} = \frac{Ax+B}{(ax^2+bx+c)} + \frac{Cx+D}{(ax^2+bx+c)^2}$$

❑ APPLICATION OF PARTIAL FRACTION IN CHEMICAL KINETICS AND PHARMACOKINETICS

In second order kinetics

$$r = \frac{dx}{dt} = k_2 (a-x)(b-x)$$

$$or\ \frac{dx}{(a-x)(b-x)} = k_2 dt$$

$$\frac{1}{(a-x)(b-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)}$$

$$or\ 1 = A(b-x) + B(a-x)$$

$$put\ x = a, we\ get$$

$$1 = B(a-b)$$

$$B = \frac{1}{(a-b)}$$

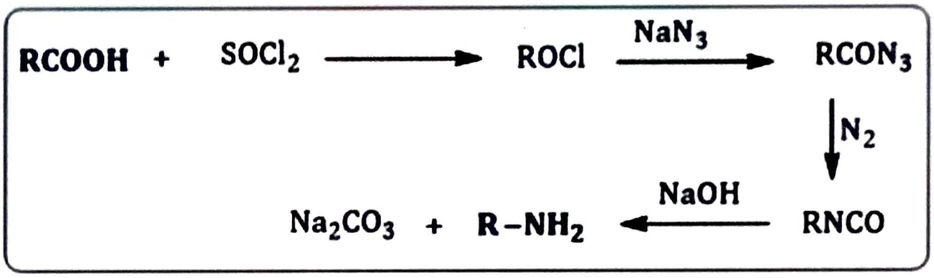
$$\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)(a-x)} + \frac{1}{(a-b)(b-x)}$$

$$\frac{1}{(a-x)(b-x)} = \frac{1}{a-b}'\left[\frac{1}{b-x} - \frac{1}{a-b}\right]$$

In two compartment model

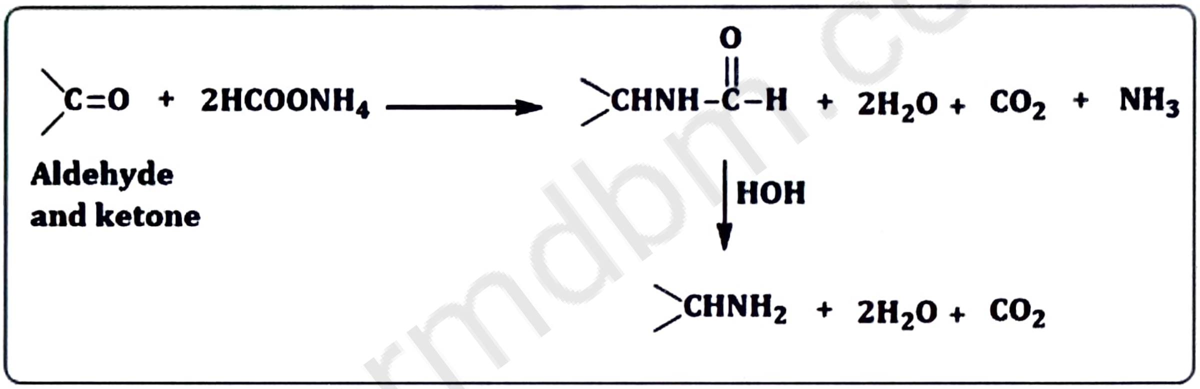
4. Curtius rearrangement

The Curtius Rearrangement is the thermal decomposition of **carboxylic azides** to produce an **isocyanate** further react with NaOH to form **primary amine**



5. By Leuckart reaction

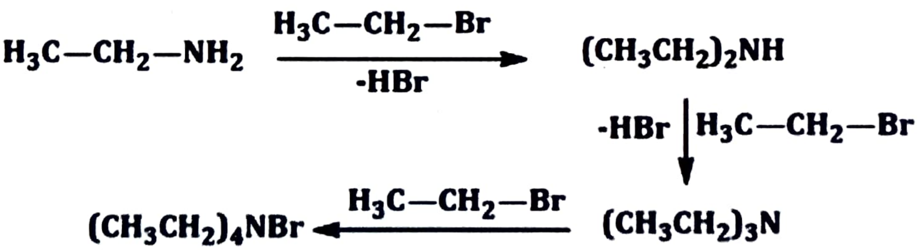
The Leuckart reaction is the chemical reaction that **converts aldehydes or ketones to amines** by **reductive amination** in the presence of heat.



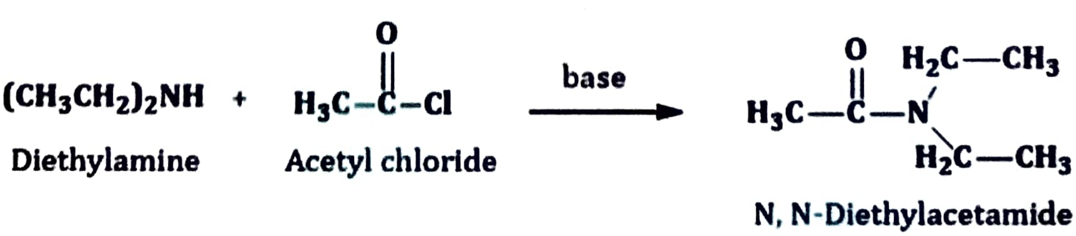
❑ CHEMICAL REACTION

Reaction of the lone pair of electrons

1. Alkylation



2. Acylation

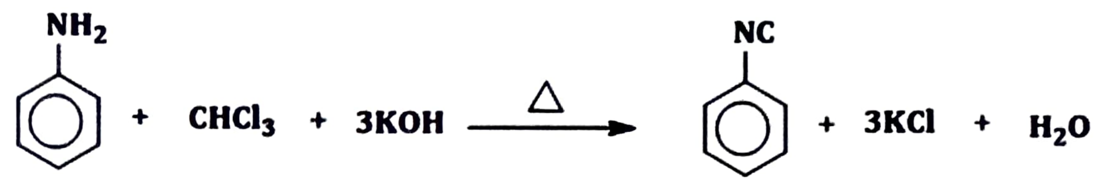


Reaction of nitrous acid

3. Reaction with chloroform (Carbylamine reaction)

Amines react with chloroform in the presence of a **base in alcohol** to give rise to **isocyanides.** This process is termed a Carbylamine reaction

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{\text{Alkyl carbyl amine}}{R{-}NC} + 3KCl + H_2O$$



Aniline

Phenyl isocynide

4. Reaction with nitrous acid

Reaction with nitrous acid helps in distinguishing between amines. Primary amines react with nitrous acid to form alcohols.

$$R{-}NH_2 + HONO \xrightarrow{NaNO_2/HCl} R{-}OH + N_2 + H_2O$$

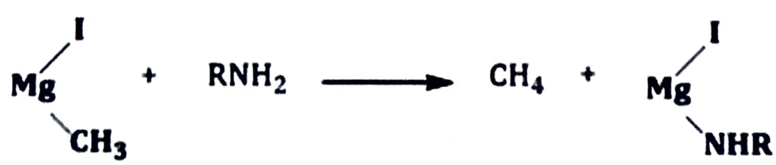
Secondary amines react with nitrous acid to form a yellow green oily layer of N-nitrosoamines.

$$R{-}NH_2 + HONO \xrightarrow{NaNO_2/HCl} R{-}OH + N_2 + H_2O$$

tert-Amines readily dissolve in nitrous acid forming crystalline trialkyl ammonium nitrite.

$$R_3N + HONO \longrightarrow \underset{\text{Trialkyl ammonium nitrite}}{R_3NHNO_2}$$

5. Reaction with Grignard reagent



Methyl magnesium iodide

Methane

6. Reaction with carbon disulphide

Primary amine forms alkyl **dithiocarbamic acid** which is decomposed with **mercuric chloride** to yield **alkyl isothiocyanate**, this is called **Hoffman's mustard oil reaction**

$$\underset{1^\circ \text{ Amine}}{RNH_2} + CS_2 \longrightarrow RNH-C(=S)-SH \xrightarrow[-Hgs,\ -2HCl]{HgCl_2} \underset{\text{Alkyl thio cyanate}}{RNCS}$$

Secondary amine forms dithiocarbamic acid but not decomposed by mercuric chloride

$$R_2NH + CS_2 \longrightarrow RNH-C(=S)-SH \xrightarrow{HgCl_2} \text{No reaction}$$

Tertiary amine will not react with carbon disulphide

$$R_3N + CS_2 \longrightarrow \text{No reaction}$$

7. Oxidation

Primary amine

$$\underset{1^\circ \text{ Amine}}{RCH_2NH_2} \xrightarrow{KMnO_4} RHC{=}NH \xrightarrow{H_2O} \underset{\text{Aldehyde}}{RCHO} + NH_3$$

$$\underset{1^\circ \text{ Amine}}{R_2CHNH_2} \xrightarrow{KMnO_4} R_2C{=}NH \xrightarrow{H_2O} \underset{\text{Aldehyde}}{R_2CO} + NH_3$$

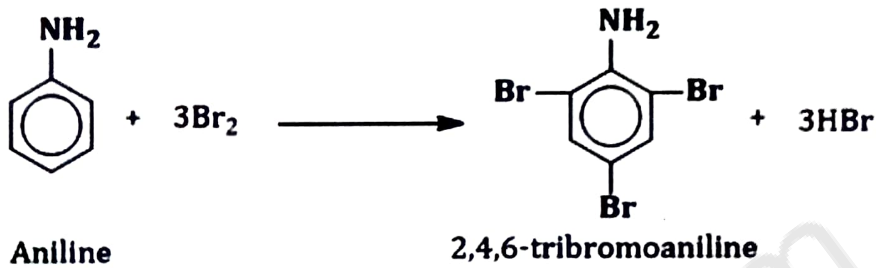
Secondary amine

$$\underset{\text{Dialkyl hydroxyl amine}}{R_2NOH} \longleftarrow R_2NH \longrightarrow \underset{\text{Tetra alkyl hydrazine}}{R_2NNR_2}$$

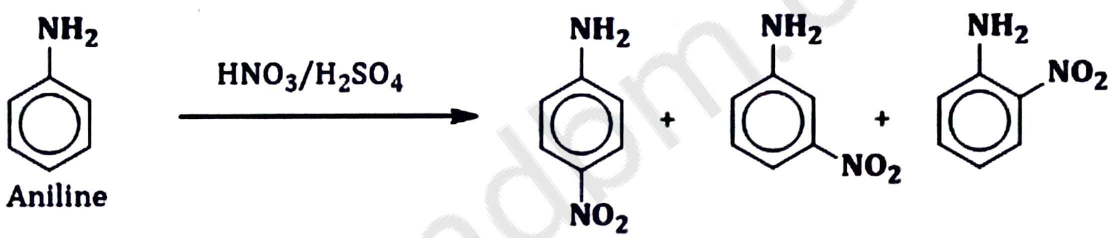
8. Electrophilic substitution reactions

Due to resonance, electron density increases at ortho and para positions as compared to meta positions.
Therefore, —NH2 group directs the incoming group to ortho and para positions

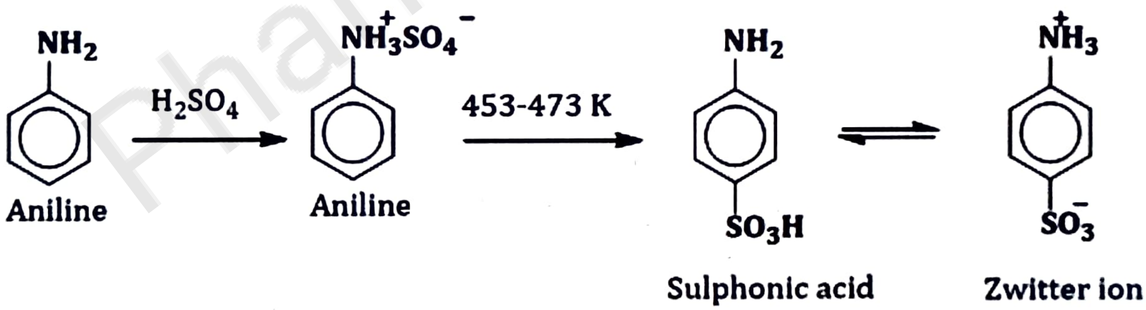
Bromination



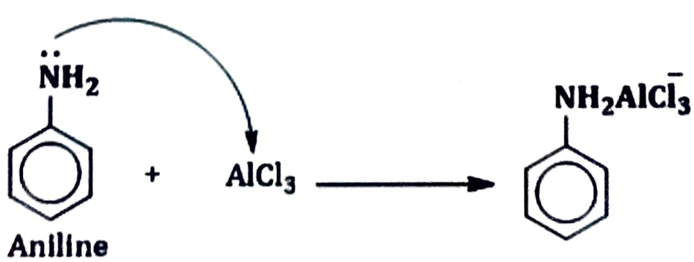
Nitration



Sulphonation



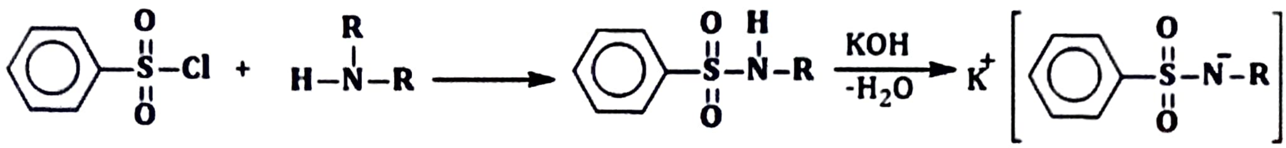
Friedel–Crafts reaction



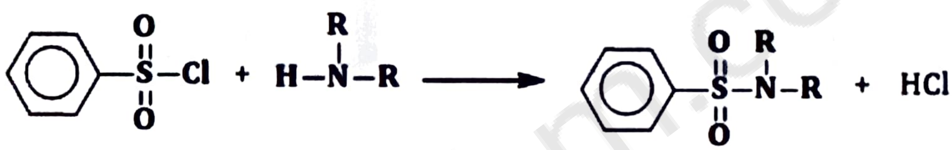
❑ QUALITATIVE TEST FOR AMINES

Hinsberg's test: In this test, the amine is first treated with Hinsberg's reagent (benzenesulphonyl chloride) and then shaken with aqueous KOH solution

1. Primary amine: A 1° amine gives a clear solution which on acidification gives an insoluble N-alkyl benzene sulphonamide.



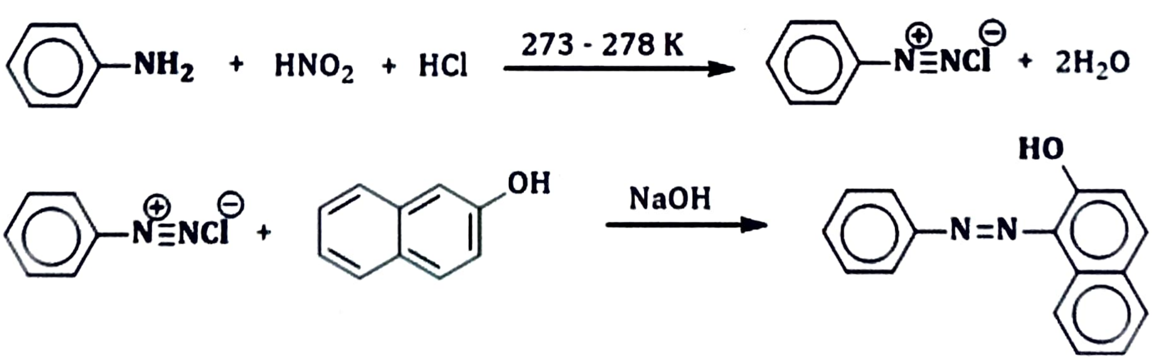
2. Secondary amine: A 2° amine gives an insoluble N, N-dialkyl benzene sulphonamide which remains unaffected on addition of acid.



3. Tertiary amine: A 3° amine does not react at all.

$$C_6H_5SO_2Cl + R_3N \xrightarrow{KOH} \text{No reaction}$$

Azo dye test: It involves the reaction of any **aromatic primary amine** with HNO_2 **($NaNO_2$ + dil. HCl)** at 273–278 K followed by treatment with an **alkaline solution of 2-naphthol**, where a brilliant yellow, orange or red coloured dye is obtained.



Solubility test: Amine are basic in nature they are easily dissolved in water and from corresponding salt

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3\overset{-}{Cl}$$

LOGARITHMS

Points to be covered in this topic

1. DEFINITION
2. PROPERTIES OF LOGARITHMS
3. COMMON LOGARITHMS
4. CHARACTERISTIC AND MANTISSA
5. APPLICATION OF LOGARITHM

❑ DEFINITION

- The logarithm is the **inverse operation** to exponentiation.
- The logarithm of any number $y > 0$, to a given base **$a > 0$ and $a \neq 0$** is the exponent to which the **base must be raised** in order to equal the given number
- Thus if $a^x = y$, then $\log_a y = x$

❑ PROPERTIES OF LOGARITHMS

1. $a^1 = a, b^1 = b$
   Than $\log_a a = 1$
   $\log_b b = 1$

2. $a^0 = 1, b^0 = 1$
   Than $\log_a 1 = 0$
   $\log_b 1 = 0$

3. $\log m.n = \log_a m + \log_a n$

4. $\log \frac{m}{n} = \log_a m - \log_a n$

5. $\log_a m^n = n\log_a m$
   or $\log_a a^n = n$

5. $\log_b a . \log_a b = 1$
   or $\log_b a = \frac{1}{\log_a b}$

6. $\log_b a = \log b \times \log_x a$

❑ COMMON LOGARITHMS

- Logarithms with a base of 10 are called common logarithms.

  For example

  $\log_{10}100 = \log_{10}10^2$

  the common logarithm of 100 is 2.

❑ CHARACTERISTIC AND MANTISSA

- The **integral part of logarithm** is called the characteristic and the **fraction (decimal) part** is mantissa.

❑ RULE TO DETERMINE THE LOGARITHIM OF ANY NUMBER

- The characteristics of a logarithm (base 10) of a number **greater than one** is **less by one** than the **number of digits in the integral part** is positive.
- The characteristics of a logarithm (base 10) of a number **greater than one** is **less by one** than the **number of digits in the integral part** is positive.
- The characteristic of the **logarithm of a positive decimal fraction** less than one, is greater by unit than the **numbers of consecutive zeros** immediately after the decimal point and is negative.
- Example: The characteristics of log 0.537, log 30.174 and 0.0023 are -1, 1 and -3 respectively.

❑ APPLICATION OF LOGARITHM

Question: One microgram of Na-24 is injected into a body of a patient. How long will it take radioactivity to full to 10% of initial value? ($t_{1/2}$ for Na-24 is 10 hours).

$$t_{1/2} = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda}$$

$$\lambda = \frac{\log_e 2}{t_{1/2}} = \frac{0.693}{10}$$

$$t = \frac{1}{\lambda} \times 2.303 \log\left(\frac{N_0}{N}\right) \text{ and } \frac{N_0}{N} = \frac{100}{10} = 10$$

$$t = \frac{10}{0.6930} \times 2.303 \log 10$$

$$t = \frac{10 \times 2.303}{0.6930}$$

Taking logarithm of both side of equation we get

$$\log t = \log 10 + \log 2.3030 - \log 0.6930$$

$$\log t = \log (1 \times 10^{0}) + \log (2.303 \times 10^{0}) - (\log 6.930 \times 10^{-1})$$

$$\log t = 0 + 0.3623 - (1.8407)$$

$$\log t = -1.4784$$

Taking antilog of both sides we get

$$t = \text{antilog}(1.4784) = 0.3384 \times 10$$

$$t = 3.3 \text{ hours}$$

Question: Calculate the half life period of a nucleus if at the end of 4.2 days, $N = 0.798\ N_0$. Given $N = N_0 e^{-\lambda t}$

Here it is given that

$$N = N_0 e^{-\lambda t}$$

$$e^{-\lambda t} = \frac{N}{N_0}$$

Taking log both side, we get

$$-\lambda t = \log \left(\frac{N}{N_0}\right)$$

$$\lambda = -\frac{1}{t} \log_e \left(\frac{N}{N_0}\right)$$

$$\lambda = -\frac{1}{4.2} \times 2.3030 \times \log_{10} \left(\frac{N}{N_0}\right)$$

$$\lambda = -0.5483 . \log_{10}(0.798)$$

$$\lambda = -0.5483 \times (\bar{1}.9020)$$

$$\lambda = -0.5483 . (-1 + 0.9020)$$

$$\lambda = 0.0537$$

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

$$t_{1/2} = \frac{0.693}{0.0537}$$

Taking log of both the sides we get

$$\log t_{1/2} = \log (6.93 \times 10^{-1}) - \log (5.37 \times 10^{-2})$$

$$\log t_{1/2} = \bar{1} + 0.8407 + 2 - 0.7300$$

$$\log t_{1/2} = 1.1107$$

$$\log t_{1/2} = \text{Antilog}\,(1.1107)$$

$$\log t_{1/2} = 1.290 \times 10 = 12.90 \text{ days}$$

FUNCTION

Points to be covered in this topic

1. REAL VALUED FUNCTION
2. CLASSIFICATION OF REAL VALUED FUNCTIONS

❑ REAL VALUED FUNCTION

- If the domain and range of a function f are subsets of R (the set of real number) than it is said to be real valued function
- A function is said to be real if its values are real.

❑ CLASSIFICATION OF REAL VALUED FUNCTION

Identity function: Let R be the set of real number and $f : R \longrightarrow R$ s.t.y = f(x) = x. each element of R be mapped on itself. Then f is called the identity function. The graph of such function is a straight line passing through origin

Constant function: Define the function $f : R \longrightarrow R$ by $f(x) = k, \forall x \in R$ and K is a constant. f(x) is known as constant function.

Polynomial function: A function $f : R \longrightarrow$ is said to be polynomial function, if $\forall x \in R$, $y = f(x) = a_0 + a_1x^1 + a_2x^2 + \ldots + a_nx^n$ where n is non – negative integer and $a_0 + a_1 + a_2 + a_n$ are real constants.

Rational function: The function of the type $\frac{f(x)}{g(x)}$ where f(x) and g(x) are polynomial functions $\forall x \in R$ and $g(x) \neq 0$

Modulus function: The function $f : R \longrightarrow R$ defined by $y = f(x) |x| \forall x \in R$ is called modulus function.

Exponential function: A function f : R ⟶ R said to be exponential if y = f(x) = e^x ∀x∈ R

logarithm function: A function f : R ⟶ R s.t.y = f(x) = log said to be exponential if y = f(x) = e^x ∀x∈ R x ∈ R^+ (Positive real number)

Even function: A function f(x) is said to be even function if f(x) = f(x) ∀x∈ domain of f.

Odd function: A function f(x) is said to be an odd function if f(-x) = -f(x) ∀x∈ domain of f.

EXCERCISE

Question: If $f(x) = \frac{\sin x}{1+\sin x}$, find $f\left(\frac{\pi}{2}\right)$

Solution:

Here $f(x) = \frac{\sin x}{1+\sin x}$

$$f\left(\frac{\pi}{2}\right) = \frac{\sin\frac{\pi}{2}}{1+\sin x} = \frac{1}{1+1} = \frac{1}{2}$$

LIMITS AND CONTINUITY

Points to be covered in this topic

1. INTRODUCTION
2. LIMIT OF A FUNCTION
3. DEFINITION OF LIMIT OF A FUNCTION
4. CONTINUITY

❑ LIMIT OF A FUNCTION

- The limit of a function f(x) is said to L at $x = x_o$ if f(x) gets closer and closer to L as x moves closer and closer to x_o.
- There are two ways x could approach a number x_o either from left or from right, i.e. all the values of x near to xo could to less or could be greater than xo.
- This naturally leads to two limits the right hand limit and the left hand limit.
- Thus right hand limit of a function f(x) is that value of f(x) which is determined by value of f(x) when $x \longrightarrow x_o$ from the right.

❑ ε – δ DEFINITION OF LIMIT OF A ACTION

- The limit of a function f(x) is l at x = a if for a, ε > 0 ∍ a d > 0 s. t.

$$|f(x) - l| < 2\varepsilon$$

$$\textit{and } |x - a| < \delta$$

Symbiolically written as

$$\lim_{x \to a} f(x) = l$$

PROPERTIES OF LIMIT

Let $\lim_{x\to a} f(x) = l$ and $\lim_{x\to a} g(x) = m$, then

(i) $\lim_{x\to a}\{f(x) \pm g(x)\} = \lim_{x\to a} f(x) \pm \lim_{x\to a} g(x) = l \pm m.$

(ii) $\lim_{x\to a}\{f(x).g(x)\} = \lim_{x\to a} f(x).\lim_{x\to a} g(x) = l.m$

in partivular.

$\lim_{x\to a}\{f(x)\}^n = \{\lim_{x\to a} f(x)\}^n$

(iii) $\lim_{x\to a}\left\{\frac{f(x)}{g(x)}\right\} = \frac{\lim_{x\to a} f\, f(x)}{\lim_{x\to a} g(x)} = \frac{l}{m}$ *provided* $\neq 0.$

(iv) $\lim_{x\to a}\{K\ f(x)\} = K\{\lim_{x\to A} f(x)\} = Kl$, *where k is constant*

(v) $\lim_{x\to a}\{f(x)\}^{g(x)} = l^m.$

(vi) $\lim_{x\to a}|f(x)| = |\lim_{x\to a} f(x)| = |l|.$

INDETERMINATE FORM

- There are seven meaningless form known as indeterminate form, they are

$$\frac{0}{0}, \frac{\infty}{\infty}, 0\times\infty, \infty-\infty, 0^0, \infty^0 \text{ and } 1^\infty$$

- L hospital's rule: suppose we have one of the following case:

$\lim_{x\to 0}\left\{\frac{f(x)}{g(x)}\right\} = \frac{0}{0}$ *(Form) or* $\lim_{x\to 0}\left\{\frac{f(x)}{g(x)}\right\} = \frac{\infty}{\infty}$

then in these cases we have

$\lim_{x\to 0}\left\{\frac{f(x)}{g(x)}\right\} = \lim_{x\to 0}\left\{\frac{f'(x)}{g'(x)}\right\}$

Some starndard limits

(i) $\lim_{x\to 0}\frac{e^x - 1}{x} = 1$ (ii) $\lim_{x\to 0}(1+px)^{1/x} = e^p$

(iii) $\lim_{x\to 0}\left(1+\frac{p}{x}\right)^x = e^p$ (iv) $\lim_{x\to a}\frac{x^n - a^n}{x-a} = na^{n-1}$, *n is +ve intenger*

(v) $\lim_{x\to 0}\frac{\sin\theta}{\theta} = 1$ (vi) $\lim_{x\to 0}\frac{(1+x)^n - 1}{x} = n$ (vii) $\lim_{x\to 0}\frac{x}{\sin x} = 1$

EXCERCISE

Question: Evaluate the $\lim_{x\to 1}(x^3+x^2-1)$

Solution: we have, $\lim_{x\to 1}(x^3+x^2-1)=1^3+1^2=1.$

Question: Evaluate the $\lim_{x\to a}(4x^2-6x+7)$

Solution: we have, $\lim_{x\to a}(4x^2-6a+7)=4a^2-6a+7$

Question: Evaluate the $\lim_{x\to 3}\frac{x^2-9}{x-3}$

Solution: we have $\lim_{x\to 3}\frac{x^2-9}{x-3}\left[\text{Form}\frac{0}{0}\right]$

$$=\lim_{x\to 3}\frac{(x-3)(x-3)}{(x-3)}=\lim_{x\to 3}(x+3)=3+3=6$$

Question: Evaluate the $\lim_{x\to 0}\frac{a^x-1}{x}$

Solution: we have $\lim_{x\to 0}\frac{a^x-1}{x}\left[\text{Form}\frac{0}{0}\right]$

$$=\lim_{x\to 0}\frac{e^{\log a^x}-1}{x}=\frac{e^{x\log a}-1}{x}\times\frac{\log a}{\log a}$$

$$=\log a.\lim_{x\to 0}\frac{e^{x\log a}-1}{x\log a} \qquad \text{put } x\log a=y$$

$$=\log a.\left[\lim_{x\to 0}\frac{e^y-1}{y}\right] \qquad x\to 0\ y\to 0$$

$$=\log a.1$$

Question: Evaluate the $\lim_{x\to 0}\left(\frac{x}{\tan x}\right)$

Solution:

$$y=\lim_{x\to 0}\left(\frac{x}{\tan x}\right)$$

$$=\lim_{x\to 0}\frac{x.\cos x}{\sin x}$$

$$=\lim_{x\to 0}\frac{x}{\sin x}.\lim_{x\to 0}\cos x$$

$$=1.\cos 0=1.1=1$$

❑ PROPERTIES OF LIMIT

- A function f(x) is said to be continuous at a point $x = x_0$ of its domain

$$R.H.L. = L.H.L = f(x_0)$$

$$\lim_{x \to x_0} + f(x) = \lim_{x \to x_0} + f(x) = f(x_0)$$

$f(x_0)$ is known as functional value of f(x) at $x = x_0$

EXCERCISE

Question: Evaluate the

$$f(x) = \sum \frac{e^{\sin x-1}}{x}$$

$$0 \ (x=0)$$

Determine wheather the function f(x) is continuous at $x = 0$

Solution:

We have $f(0) = 0$ given

$$L.H.L. = \lim_{h \to 0} f(0-h) = \lim_{h \to 0} \left\{ \frac{e^{\sin(0-h)}-1}{0-h} \right\}$$

$$= \lim_{h \to 0} \frac{e^{\sin(0-h)}-1}{0-h} = \lim_{h \to 0} \frac{e^{\sin(0-h)}-1}{-\sin h} \left(\frac{-\sin h}{-h} \right)$$

$$= \lim_{h \to 0} \frac{e^{\sin(0-h)}-1}{-\sin h} . \lim_{h \to 0} \left(\frac{\sin h}{h} \right)$$

$$= 1.1 = 1$$

$$L.H.L. \neq 0$$

f(x) is not continuous at $x = 0$