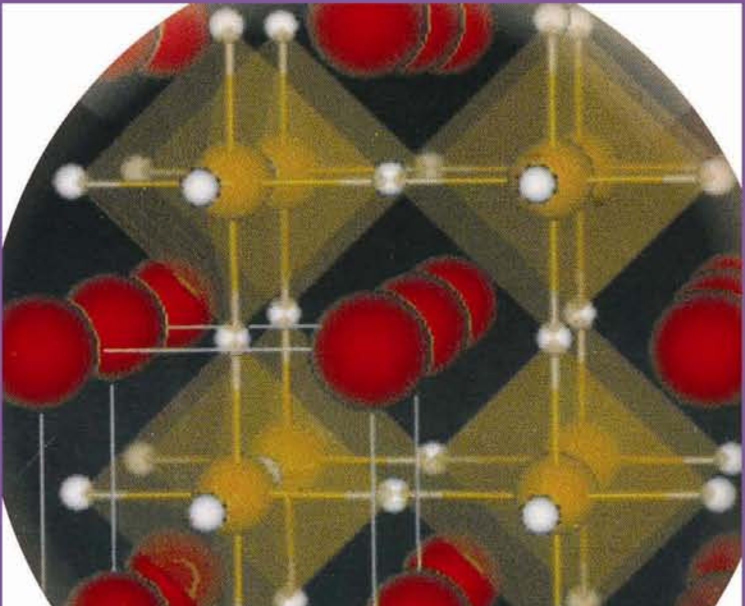
PHYSICAL CHEMISTRY

VOL-I



Pragati's

PHYSICAL CHEMISTRY

Vol. I

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Revised Edition *2010*

ISBN : 978–93–5006–047–6

Published by K.K. Mittal for Pragati Prakashan, Meerut – 250 001 and Photocomposing by : Pragati Laser Type Setters Pvt. Ltd., Meerut (Phone 2661657) Printed at Arihant Electric Press, Meerut.

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Chapter 1

MATHEMATICAL CONCEPTS

1·1. LOGARITHMS

Definition

If $a^b = c$; then exponent **'*b*'** is called the logarithm of number **'*c*'** to the base **'*a*'** and is written as **$\log_a c = b$, *e.g.*,**

$3^4 = 81 \Rightarrow$ logarithm of 81 to the base 3 is 4, *i.e.*, $\log_3 81 = 4$.

Note : $a^b = c$, is called the *exponential form* and $\log_a c = b$ is called the *logarithmic form, i.e.,*

(i) $2^{-3} = 0.125$ (Exponential form)

$\Rightarrow$ $\log_2 0.125 = -3$ (Logarithmic form)

(ii) $\log_{64} 8 = \frac{1}{2}$ (Logarithmic form)

$\Rightarrow$ $(64)^{1/2} = 8$ (Exponential form)

Laws of Logarithms

[I] First law (Product law) :

The logarithm of a product is equal to the sum of logarithms of its factors.

$$\therefore \quad \log_a (m \times n) = \log_a m + \log_a n$$

$$\log_a (m \times n \times p) = \log_a m + \log_a n + \log_a p$$

Remember :

$$\log_a (m + n) \neq \log_a m + \log_a n$$

[II] Second law (Quotient law) :

The logarithm of a fraction is equal to the difference between the logarithm of numerator and the logarithm of denominator.

$$\log_a \frac{m}{n} = \log_a m - \log_a n$$

Remember :

$$\frac{\log_a m}{\log_a n} \neq \log_a m - \log_a n$$

[III] Third law (Power law)

The logarithm of a power of a number is equal to the logarithm of the number multiplied by the power.

$$\log_a (m)^n = n \log_a m$$

Corollary : Since $\sqrt[n]{m} = m^{1/n}$, so

$$\log_a \sqrt[n]{m} = \log_a m^{1/n} = \frac{1}{n} \log_a m$$

Note :

(a) Logarithms to the base 10 are known as *common logarithms.*
(b) If no base is given, the base is always taken as 10.

(c) Logarithm of a number to the same base is always one, *i.e.*,

$\log_a a = 1$; $\log_{10} 10 = 1$ and so on.

(d) The logarithm of 1 to any base is zero, *i.e.*,

$\log_a 1 = 0$; $\log_5 1 = 0$; $\log_{10} 1 = 0$ and so on.

(e) $\log_{10} 1 = 0$; $\log_{10} 10 = 1$;

$\log_{10} 100 = 2$ $[\because \log_{10} 100 = \log_{10} 10^2 = 2 \log_{10} 10 = 2 \times 1 = 2]$

Similarly, $\log_{10} 1000 = 3$; $\log_{10} 10000 = 4$ and so on.

Problem 1. ***If log 2 = 0.3010 and log 3 = 0.4771; find the values of :***
(i) log 6 ***(ii) log 5*** ***(iii) log √24***

Solution.

(i) $\log 6 = \log (2 \times 3) = \log 2 + \log 3 = 0.3010 + 0.4771 = \mathbf{0.7781}$

(ii) $\log 5 = \log \frac{10}{2} = \log 10 - \log 2 = 1 - 0.3010 = \mathbf{0.6990}$ $(\because \log 10 = 1)$

(iii) $\log \sqrt{24} = \log (24)^{1/2} = \frac{1}{2} \log (2^3 \times 3)$

$$= \frac{1}{2} [3 \log 2 + \log 3] = \frac{1}{2} [3 \times 0.3010 + 0.4771] = \mathbf{0.69005}$$

1·2. COMMON LOGARITHMS AND USE OF FOUR FIGURE LOG TABLES

[I] Common Logarithms

Logarithms to the base 10 are known as *common logarithms.* If no base is given, the base is always taken as 10.

[II] Characteristic and Mantissa

The logarithm of a number consists of two parts :

(i) Characteristic : It is the integral part of the logarithm.

(ii) Mantissa: It is the fractional or decimal part of the logarithm.

For example, in log 273 = 2.4362, the integral part is 2 and the decimal part is .4362. Therefore, characteristic = 2 and mantissa = .4362.

[III] How to Find the Characteristic?

(i) ***The characteristic of the logarithm of a number greater than one is positive and is numerically one less than the number of digits before the decimal point.***

In number 475.8; the number of digits before the decimal point is three.

∴ Characteristic of log 475.8 = 2, *i.e.*, (3 − 1 = 2)

Similarly, Characteristic of log 4758 = 3, *i.e.*, (4 − 1 = 3)

Characteristic of log 47.58 = 1, *i.e.*, (2 − 1 = 1)

Characteristic of log 4.758 = 0, *i.e.*, (1 − 1 = 0)

(ii) ***The characteristic of the logarithm of a number less than one is negative and is numerically one more than the number of zeros immediately after decimal point.***

The number 0.004758 is less than one and the number of zeros immediately after decimal point in it are two.

∴ Characteristic of log 0.004758 = − (2 + 1) = −3, which is also written as $\bar{3}$.

To find the characteristic of the logarithm of a number less than one, count the number of zeros immediately after the decimal point and add one to it. The number so obtained with negative sign gives the characteristic.

∴ Characteristic of log 0.3257 = − 1 = $\bar{1}$

[Since, the number of zeros after decimal point = 0]

Characteristic of log 0.03257 = − 2 = $\bar{2}$

[Since, the number of zeros after decimal point = 1]

Characteristic of log 0.0003257 = −4 = $\bar{4}$ and so on.

[IV] How to Find the Mantissa?

The mantissa of the logarithm of a number can be obtained from the logarithmic table.

A *logarithmic table* consists of three parts :

(1) A column at the extreme left contains two digit numbers starting from 10 to 99.

(2) Ten columns headed by the digits 0, 1, 2, 3, 4, 5, 6, 7, 8, 9.

(3) Nine more columns headed by digits 1, 2, 3, 4, 5, 6, 7, 8, 9.

A part of the logarithmic table is given below : (Difference to be added)

	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 8	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	6 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	6 7 8	9 11 12

(a) To find the mantissa of the logarithm of one digit number.

Let the number be 3.

∴ Mantissa of log 3 = Value of the number 30 under 0.

= 0.4771.

(b) To find the mantissa of the logarithm of two digit number.

Let the number be 32.

∴ Mantissa of log 32 = Value of the number 32 under 0.
= 0.5051.

(c) To find the mantissa of the logarithm of three digit number.

Let the number be 325.

∴ Mantissa of log 325 = Value of 32 under 5
= 0.5119

(d) To find the mantissa of the logarithm of a four digit number.

Let the number be 3257.

∴ Mantissa of log 3257 = Value of 32 under 5 plus the difference under 7
= 0.5128 [5119 + 9 = 5128]

(e) To find the logarithm of a number from the logarithm table.

First, find the characteristic and then mantissa.

Suppose the number is 3257.

Characteristic of log 3257 = 3
Mantissa of log 3257 = 0.5128
Therefore, log 3257 = 3.5128

[**Note :** The mantissa of the logarithms of all the numbers having the same significant digits is the same. While finding the mantissa, ignore the decimal point.]

For example : log 3257 = 3.5128
log 325.7 = 2.5128
log 3.257 = 0.5128
log 0.3257 = $\bar{1}.5128$
log 0.003257 = $\bar{3}.5128$, and so on]

Note :

(1) $\bar{3}.4682$ is equivalent to (–3 + 0.4682) and –3.4682 = – (3 + 0.4682) = –3 – 0.4682, *i.e.*, in $\bar{3}.4682$, the mantissa is **positive,** while in –3.4682, the mantissa is **negative**.

(2) Remember, the *mantissa* should always be written positive.

(3) To make the mantissa positive, subtract 1 from the integral part and add 1 to the decimal part. Thus,

$$\begin{aligned} -3.4682 &= -3 - 0.4682 \\ &= (-3 - 1) + (1 - 0.4682) \\ &= -4 + 0.5318 \\ &= \bar{4}.5318 \end{aligned}$$

Problem 1. ***Find out the values of the following :***

(i) $\bar{3}.8321 + 1.4307$ ***(ii)*** $1.9256 - 4.5044$

(iii) $\bar{1}.7544 \times 2$ ***(iv)*** $\bar{2}.3206 \div 3$

Solution :

(i) $\bar{3}.8321$

$\underline{1.4307}$ Since, after adding decimal parts, we have 1 to carry.

$\underline{\bar{1}.2628}$ ∴ $1+\bar{3}+1=1-3+1=-1=\bar{1}$.

(ii) $$\begin{array}{r} 1.9256 \\ \underline{-4.5044} \\ \underline{\bar{3}.4212} \end{array}$$ Since, $1-4=-3=\bar{3}$

(iii) $$\begin{array}{r} \bar{1}.7544 \\ \underline{\times 2} \\ \underline{\bar{1}.5088} \end{array}$$ Since, $\bar{1}\times 2+1=\bar{2}+1=\bar{1}$

(iv) $\bar{2}.3206 \div 3$

$$=\frac{\bar{2}.3206}{3}$$

$$=\frac{\bar{3}+1.3206}{3}$$ To make the integral part $\bar{2}$ divisible by 3.

$$=\frac{\bar{3}+1.3206}{3}$$ Take $\bar{2}=\bar{3}+1$

$$=\bar{1}+0.4402=\bar{1}.4402$$

1·3. ANTILOGARITHMS

If log 5274 = 3.7221, then 5274 is called the *antilogarithm* of 3.7221.

We write, antilog 3.7221 = 5274.

To find an antilogarithm, the antilogarithm tables are used.

The antilogarithm tables are used in the same way as the logarithm tables. The only difference between the two tables is that the column at the extreme left of the log table contains all two digit numbers starting from 10 to 99; whereas an antilog table contains numbers from .00 to .99 (*i.e.*, all fractional numbers with only two digits after decimal) in the extreme left column of it.

x	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
0.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1 1 2	2 3 3	4 4 5
0.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1 1 2	2 3 3	4 4 5
0.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1 1 2	2 3 4	4 5 5
0.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1 1 2	2 3 4	4 5 5

[**Note :**

(i) Antilog tables are used only to find the antilogarithm of decimal part.

(ii) The antilog of 2.368 means to find the number whose log is 2.368].

Problem1. ***If log x = 2.368, find the value of x.***

Solution. $\log x = 2.368$

$\Rightarrow$ x = antilog 2.368

Antilog 2.368 = the number characteristic of whose log is 2 and mantissa is 368.

From antilog table, the value of .36 under 8 is 2333.

Since the characteristic of log of the number is 2.

∴ The number has 2 + 1 = 3 digits in its integral part (*i.e.*, 3 digits before the decimal point).

∴ Antilog 2.368 = **233.3.**

Problem 2. ***Find the antilog of $\bar{2}$.3536***

Solution. From the antilog table, find the value of .35 under 3 and add to it the *mean difference* under 6. The number thus obtained is 2257.

Now place the decimal point so that the characteristic of its log is 2.

$\therefore$ Antilog $\bar{2}.3536 = \mathbf{0.02257}$

[**Note :**

(i) Antilog 0.5362 = 3.438 Antilog $\bar{1}.5362 = 0.3438$

(ii) Antilog 2.5362 = 343.8 Antilog $\bar{3}.5362 = 0.003438$

(iii) Antilog 4.5362 = 34380 Antilog $\bar{5}.5362 = 0.00003438$ and so on].

Problem 3. ***Find the value of*** $\log_3 343$.

Solution. Suppose $\log_3 343 = x$. Thus, according to definition,

$$3^x = 243 = 3 \times 3 \times 3 \times 3 \times 3 = 3^5$$

$$\therefore \quad x = 5$$

Therefore, $\log_3 343 = \mathbf{5}$.

Problem 4. ***Find the logarithon of 104976 to the base*** $3\sqrt{2}$.

Solution. Suppose $\log_{3\sqrt{2}} (104976) = x$. Thus, according to definition

$$(3\sqrt{2})^x = 104976 = 16 \times 6561 = 2^4 \times 3$$

$$\text{or} \quad (3\sqrt{2})^x = [(\sqrt{2})^2]^4 \times 3^8 = (3\sqrt{2})^8$$

$$\therefore \quad x = 8$$

Therefore, $\log_{3\sqrt{2}} (104976) = \mathbf{8}$

Problem 5. Prove that, $\log_a m = \log_b m \times \log_a b$

Solution : Suppose $\log_a m = x$ and $\log_b m = y$

$$\therefore \quad a^x = m \quad \text{and} \quad b^y = m$$

$$\text{or} \quad a^x = b^y \Rightarrow (a^x)^{1/y} = b$$

$$\therefore \quad \log_a b = \frac{x}{y} = \frac{\log_a m}{\log_b m}$$

$$\text{or} \quad \log_a m = \log_b m \times \log_a b \text{ (Proved)}$$

Problem 6. ***Simplify the factor*** $\log_a \dfrac{x^m y^n}{z^p u^q}$.

Solution. $\log_a \dfrac{x^m y^n}{z^p u^q} = \log_a (x^m y^n) - \log_a (z^p u^q)$

$$= \log_a x^m + \log_a y^n - \log_a z^p - \log_a u^q$$

$$= m \log_a x + n \log y - p \log_a z - q \log_a u$$

1·4. LINEAR GRAPH AND SLOPES

[I] Inclination of a Line and Slope of a Line

The angle which a straight line makes with the positive direction of x-axis, measured in anti-clockwise direction is known as its *inclination* or *angle of inclination*. It is usually denoted by θ [Fig. (1)]. It is to be noted that:

(i) The inclination of a line parallel to x-axis or the x-axis itself is 0°, and

(ii) The inclination of a line parallel to y-axis or the y-axis itself is 90°.

If the inclination of a line is θ ($\neq 90^\circ$), then $\tan\theta$ is called the **slope** or **gradient.** It is usually denoted by m, *i.e.*, $m = \tan\theta$.

We know that after painstaking and strenuous research, we obtain the scientific data. It can be well understood or appreciated by plotting graphs. Linear graphs are mentioned by the appropriate equation of a straight line. There are several equations of a straight line, which are all first degree in x and y.

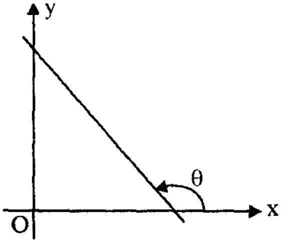


Fig. 1. Inclination of a straight line.

(1) The ***general equation of a straight line*** is,

$$ax + by + c = 0 \qquad \dots (1)$$

where a and b are not equal to zero and a, b, c are real numbers.

(2) The ***slope-intercept form of a straight line*** is,

$$y = mx + b \qquad \dots (2)$$

where m is the slope of the line and b is the intercept of the line on y-axis.

(3) The ***slope-point form of a straight line*** is,

$$y - y_1 = m\,(x - x_1) \qquad \dots (3)$$

where m is the slope of the line and the line passes through a point (x_1, y_1).

(4) The ***two-point form of a straight line*** is,

$$y - y_1 = \frac{y_2 - y_1}{x_2 - x_1}(x - x_1);\ x_1 \neq x_2 \qquad \dots (4)$$

where the line passes through two points (x_1, y_1) and (x_2, y_2).

(5) The ***intercept form of a straight line*** is

$$\frac{x}{a} + \frac{y}{b} = 1 \qquad \dots (5)$$

where x-intercept of the line is a and y-intercept is b.

[I] Slope of a Line

The slope (m) of a straight line is the ratio of the change in y compared with the change in x. Thus,

$$m = \frac{\text{Change in } y}{\text{Change in } x} = \frac{dy}{dx} \qquad \dots (6)$$

where dy is the infinitesimal change in y corresponding to infinitesimal change in x, *i.e.*, dx. If the two points on a line are represented by (x_1, y_1) and (x_2, y_2) and m is the slope of the line, then

$$m = \frac{y_2 - y_1}{x_2 - x_1};\ x_1 \neq x_2 \qquad \dots (7)$$

[II] Parallel and Perpendicular Lines

The two non-vertical lines are parallel if and only if the slopes of the two lines are equal, *i.e.*,

$$m_1 = m_2$$

The two non-vertical lines are perpendicular if and only if the product of their slopes is -1, *i.e.*,

$$m_1\, m = -1$$

Problem 1. ***Write the equation of a line passing through the points A (1, − 3) and B (3, 4).***

Solution. According to equation (4),

$$y - y_1 = \frac{y_2 - y_1}{x_2 - x_1}(x - x_1)$$

or $$y + 3 = \frac{4 - (-3)}{3 - 1}(x - 1)$$

or $$y + 3 = \frac{7}{2}(x - 1)$$

or $$2(y + 3) = 7(x - 1)$$

or $$2y + 6 = 7x - 7$$

or $$7x - 2y - 13 = 0 \quad \text{or} \quad 7x - 2y = 13$$

Problem 2. ***Write the equation of a straight line with a slope $-\frac{1}{2}$ and intercept = 5.***

Solution. $m = -\frac{1}{2}$ and $b = 5$

According to equation (2),

$$y = \frac{-1}{2}x + 5$$

or $$2y = -x + 10$$

or $$x + 2y = 10$$

Problem 3. ***Mention whether the line containing the points R* and *S is parallel or perpendicular to the line containing the points P* and *Q.***

(i) *R* (2, 4), *S* (3, 8), *P* (5, 1) and *Q* (4, − 3)

(ii) *R* (2, − 3), *S* (− 4, 5), *P* (0, −1) and *Q* (− 4, − 4).

Solution. (i) $m_1 = \frac{8 - 4}{3 - 2} = 4, m_2 = \frac{-3 - 1}{4 - 5} = 4$

As $m_1 = m_2$, the lines RS and PQ are parallel.

(ii) $$m_1 = \frac{5 - (-3)}{-4 - 2} = \frac{8}{-6} = \frac{-4}{3}, \quad m_2 = \frac{-4 - (-1)}{-4 - 0} = \frac{-3}{-4} = \frac{3}{4}$$

As $m_1 m_2 = \left(\frac{-4}{3}\right)\left(\frac{3}{4}\right) = -1$, the lines RS and PQ are perpendicular.

1·5. CURVE SKETCHING

[I] Concave and Convex Curves

If P is any point on a curve and AB is any given line which does not pass through this point P then the curve is said to be *concave* (Fig. 1), at P with respect to the line AB, if the small are of the curve containing P lies entirely within the acute angle between the tangent at P to the curve and the line AB. The curve is said to be ***convex*** at P if the arc of the curve containing *P* lies wholly outside the acute angle between that tangent at P and the line AB (Fig. 2).

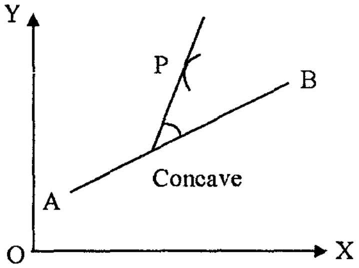


Fig. 2.

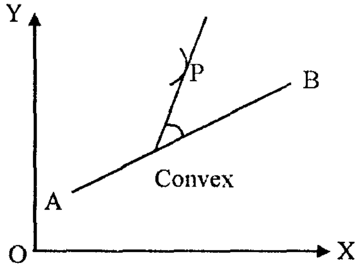


Fig. 3.

[II] Point of Inflexion

A point P on the curve is said to the point of inflexin if the curve on one side of P is concave and other side of P convex with respect to the line AB which does not pass through the point *P* as shown in figure (3).

[III] Inflexion Tangent

The tangent at the point of inflexion to a curve is known as inflexion tangent. The line PQ in figure (3) is the inflexion tangent.

When we study the motion of a particle, the valocity-time graphs and the displacement-time graphs are considered to be the simplest graphs. The shortest distance between the initial and the final positions of a particle (or object) is called its displacement $\vec{s}$. The velocity is the rate of change of displacement, *i.e.*, $\vec{v} = d\vec{s}/dt$. The acceleration is the rate of change of velocity, *i.e.*, $\vec{a} = d\vec{v}/dt$.

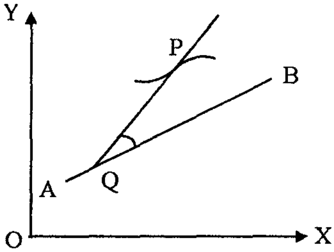
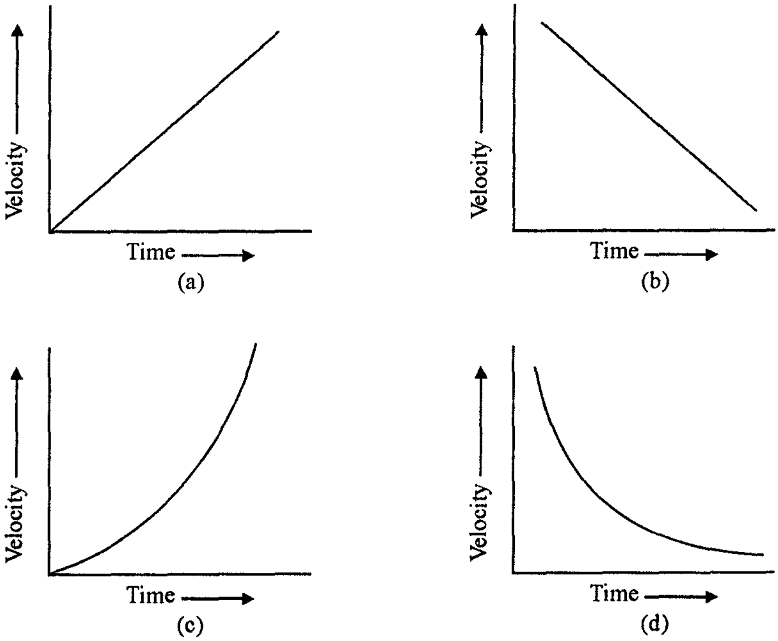


Fig. 4.



(a) (b) (c) (d)

Fig. 5. Velocity versus time graphs.

Figure (2) shows the commonly seen velocity versus time graphs

Figure 2 (a) shows uniform positive aceeleration while fig. 2(b) shows uniform negative acceleration (or retardation). Fig. 3(c) shows variable positive acceleration, while fig. 3(d) shows variable negative acceleration (retardation).

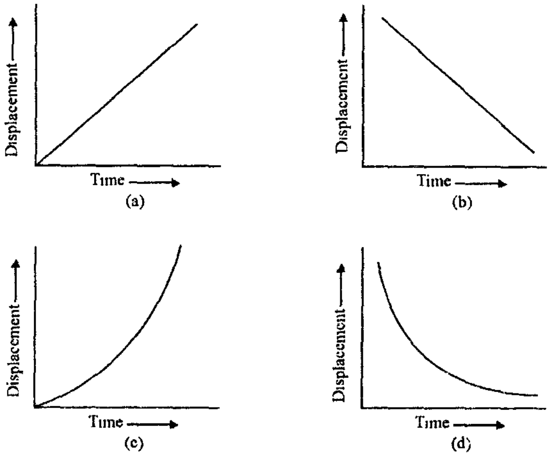


Fig.6. Displacement versus time graphs.

Figure (3) shows the commonly seen displacement versus time graphs.

Figure 3 (a) shows uniform positive velocity, while figure 3 (b) shows uniform negative velocity. Fig. 3(c) shows variable positive velocity, while fig. 3 (d) shows variable negative velocity.

[IV] Graphs of Linear Equation

The equation $y = mx + b$ is the equation of a straight line. The graph of such an equation can be achieved easily as shown in the following problem.

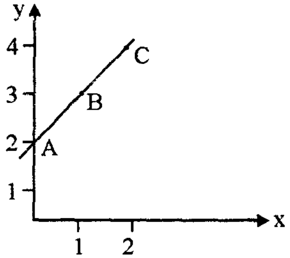


Fig. 7. Graph of the equation $y = x + 2$

Problem 4. ***Draw the graph of the equation*** $y = x + 2$.

Solution. The following value table is drawn.

x	0	1	2
y	2	3	4

We now plot the points A(0, 2), B(1, 3) and C(2, 4) on a graph paper. The points A, B and C are joined and produced on either side. The line ABC is the required graph of the equation $y = x + 2$.

1·6. FUNCTIONS OF A REAL VARIABLE

A variable y is said to be a function of another variable x, written as $y = f(x)$, if there is a rule which connects one value of y with value of x in its range of values. For example, if $f(x) = x^2 + 3x$, then $f(1) = 4$, *i.e.*, there is only one value of y corresponding to a single value of x. So, the function $f(x)$ is known as a *single-valued function.* The variable y whose value depends on the chosen value of x is known as *dependent variable*, while x is known as *independent variable.* A function $f(x)$ may have more than one value associated with it corresponding to a siangle value of x. such a function is known as *multivalued function.* For example, if $y^2 = x + 3$ then $y = \pm (x + 3)^{1/2}$ which shows that corresponding to a single value of x, the function $y = f(x)$ is a *double-valued function.* The interval or range of the independent variable is known as the *domain* of the function. A function is said to be defined on an interval if it is defined on every point of the interval. Following are some frequently used elementary functions :

(i) Polynomials : A polynomial is a function.

$$f(x) = a_0 + a_1 x + a_2 x^2 + \ldots\ldots + a_n x^n$$

where $a_0, a_1, a_2, \ldots\ldots, a_n$ are constants and the exponent x, which is a positive integer is known as the degree of the polynomial. If the polynomial equation $f(x) = 0$, then the equation has exactly n equal roots. So, $x^3 - 9x^2 + 27x - 27$, *i.e.* $(x - 3)^3 = 0$, has three equal roots.

(ii) Exponential functions : *e.g.*, $f(x) = e^x$, where $e = 2.7182818\ldots\ldots$ The algebraic operations with respect to exponential functions are :

$$e^x - e^y = e^{x+y} \quad ; \quad e^x/e^y = e^{x-y} \quad ; \quad \frac{1}{e^{+x}} = \ln x \qquad \ldots (7)$$

The inverse of e^x is known as natural logarithm, $\ln x$. The factor e is called the base of the logarithm. When the base e is replaced by 10, then $1/10^x = \log x$. Then $\log x$ is known as common logarithm of x. The values of $\ln x$ and $\log x$ are related by $\ln x = 2.303 \log x$. The fundamental equations satisfied by the natural and also the common logarithms are

[Product formula] $\ln (xy) = \ln x + \ln y$

[Quotient formula] $\ln (x/y) = \ln x - \ln y$

[Power formula] $\ln x^y = y \ln x$

(iii) Trigonometric functions : Tignometric munctions Such as $f(x) = \sin x$, $\cos x$, $\tan x$, $\cot x$, $\sec x$ and $\operatorname{cosec} x$ are periodic, *i.e.*, they satisfy the relation

$$f(x + k) = f(x) \qquad \ldots (8)$$

where k in radians is the period for all the periodic functions. For example, $\sin x$ and $\cos x$ have the period 2π. Note that $\sin(-x) = -\sin x$ and $\cos(-x) = \cos x$. Therefore, $\sin x$ is known as an *odd function,* whereas $\cos x$ is known as an *even function.* Some important relations among trigonometric functions are as follow :

(a) $\sin^2 x + \cos^2 x = 1, \quad \sec^2 x = 1 + \tan^2 x, \quad \operatorname{cosec}^2 x = 1 + \cot^2 x$

(b) $\sin (x \pm y) = \sin x \cos y \pm \cos x \sin y$

(c) $\cos (x \pm y) = \cos x \cos y \pm \sin x \sin y$

(d) $\sin 2x = 2 \sin x \cos x = \dfrac{2 \tan x}{1 + \tan^2 x}$

(e) $\cos 2x = \cos^2 x - \sin^2 x$

(f) $\sin^2 x = \dfrac{1 - \cos 2x}{2}$

(g) $\cos^2 x = \dfrac{1 + \cos 2x}{2}$

(iv) Inverse trigonometric functions : Function as $f(x) = \sin^{-1} x, \cos^{-1} x, \tan^{-1} x$, etc are the inverse of the corresponding trigonometric functions. For example, if $x = \sin y$, then $y = (-1)^x \sin^{-1} x + n\pi$, where $n = 0, 1, 2, \ldots\ldots$ and

$$\frac{-\pi}{2} \le \sin^{-1} x \le \frac{\pi}{2}$$

When $x = 0, y = \sin^{-1} x$ is the principal value of the angle y.

(v) Hyperpolic functions : Hyperbolic functions are defined in terms of the exponential functions as

$$\sinh x = \frac{1}{2}(e^x - e^{-x}) \quad ; \quad \cosh x = \frac{1}{2}(e^x + e^{-x})$$

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad ; \quad \coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}}$$

(vi) Explicit and implicit functions : A function $f(x)$ is said to be explicit if it can be expressed directly in terms of the independent variable (or variables).

For example, (i) $y = x^2$ (ii) $y = e^x x^3$

A function $f(x)$ is said to be implicit if it cannot be expressed directly in terms of the independent variable or variables.

For example, (i) $x^2 f y^2 = k$ (ii $x^2 + y^2 + 5xy + 7x - 3y + 6 = 0$)

Note : If the relation between x and y is of the form $f(x, y) = 0$ then y is called an implicit function of x.

(vii) Parametric functions : If the value of x and y can be expressed in terms of another variable 't' *i.g.*, $x = f(t)$, $y = g(t)$, then the function is defined as a parametric function.

1·7. DIFFERENTIATION

In differential calculus, a new word *'increment'* is used. Increment is used to show a small change (increase or decrease) in the value of any variable. So, if x is a variable, then a small change (increase or decrease) in the value of x is called the increment in x and it is usually represented by δx (read as 'delta x'). The term δx is not a product of δ and x and it represents a single small quantity which starts for the increment in x.

Suppose $y = f(x)$ is a function of the variable x. Let δy be the increment in y corresponding to an increment δx in x.

$\therefore$ $$y + \delta y = f(x + \delta x)$$

We have $$\delta y = f(x + \delta x) - f(x)$$

or $$\frac{\delta y}{\delta x} = \frac{f(x + \delta x) - f(x)}{\delta x}$$

The value $\frac{\delta y}{\delta x}$ gives the average rate of change of y with respect to x in the interval $(x, x + \delta x)$.

[I] Differential Coefficient

Let $y = f(x)$ be a function of the variable x. The differential coefficient of $f(x)$ with respect to x is defined as

$$\frac{dy}{dx} = \lim_{\delta x \to 0} \frac{\delta y}{\delta x} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} \qquad \ldots (1)$$

provided the limit exists.

The differential coefficient is also known as ***derivative.*** The differential coefficient of $y = f(x)$ with respect to x is generally denoted by any one of the following symbols :

$$\frac{dy}{dx}, \frac{d}{dx}(y), y^1, y_1, Dy, \frac{d}{dx}[f(x)], f'x \text{ or } Df(x).$$

The differential coefficient is the average rate of change of y with respect to x average is taken on a very-very small interval (as $\delta x \to 0$). Thus, it gives instantaneous rate of change of y with respect to x.

Note : (i) The differential coefficient of $f(x)$ at the point $x = a$ is denoted by,

$$f'(a) \quad \text{or} \quad \left[\frac{d}{dx} f(x)\right]_{x = a}$$

(ii) The value $\frac{dy}{dx}$ gives the limit of ratio of the change in y to the change in x.

(iii) $\frac{dy}{dx}$ means the differential coefficient of y with respect to x.

(iv) The process of finding the derivative by using this definition, is called the *differentiation from the first principle.*

By using the above definition, we will find differential coefficients of some standard functions.

(1) Differential coefficient of a constant

Let $y = f(x) = k$, be a constant function.

$$\therefore \quad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{k - k}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{0}{\delta x} = \lim_{\delta x \to 0} (0) = 0.$$

$$\therefore \quad \mathbf{\frac{d}{dx}(constant) = 0.} \qquad \ldots (2)$$

(2) Differential coefficient of x^n

Let $y = f(x) = x^n$. $\quad \therefore f(x + \delta x) = (x + \delta x)^n$.

$$\therefore \quad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{(x + \delta x)^n - x^n}{\delta x}$$

$$= \lim_{\delta x \to 0} x^n . \left[\frac{\left(1 + \frac{\delta x}{x}\right)^n - 1}{x}\right]$$

$$= \lim_{\delta x \to 0} x^n \left[\frac{1 + n . \frac{\delta x}{x} + \frac{n(n-1)}{2!}\left(\frac{\delta x}{x}\right)^2 + \ldots - 1}{\delta x}\right]$$

[Expanding $(1 + \delta x/x)^n$ by binomial theorem]

$$= \lim_{\delta x \to 0} x^n \cdot \frac{\delta x}{\delta x} \cdot \left[\frac{n}{x} + \text{the terms involving } \delta x \right] = x^n \cdot \frac{n}{x} = n \cdot x^{n-1}$$

$$\therefore \qquad \frac{\mathbf{d}}{\mathbf{dx}} (\mathbf{x^n}) = \mathbf{n} \cdot \mathbf{x^{n-1}}. \qquad \ldots (3)$$

(3) Differential coefficient of the product of constant and a function.

Let $y = kf(x)$, where k is a constant.

$$\therefore \qquad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{kf(x + \delta x) - kf(x)}{\delta x} = k \cdot \lim_{\delta x \to 0} \frac{f(x + \delta x) - fx}{\delta x}$$

$$= k \cdot \frac{d}{dx} [f(x)].$$

$$\therefore \qquad \frac{\mathbf{d}}{\mathbf{dx}} [\mathbf{kf(x)}] = \mathbf{k} \frac{\mathbf{d}}{\mathbf{dx}} [\mathbf{f(x)}]. \qquad \ldots (4)$$

(4) Differential coefficient of e^x.

Let $y = f(x) = e^x, \ \therefore \ f(x + \delta x) = e^{x + \delta x}.$

$$\therefore \qquad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{e^{x + \delta x} - e^x}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{e^x \cdot e^{\delta x} - e^x}{\delta x} = \lim_{\delta x \to 0} \frac{e^x (e^{\delta x} - 1)}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{e^x \left[1 + \delta x + \frac{(\delta x)^2}{2!} + \frac{(\delta x)^3}{3!} + \ldots - 1 \right]}{\delta x}$$

[Expanding $e^{\delta x}$ by exponential series]

$$= \lim_{\delta x \to 0} e^x \frac{\delta x}{\delta x} \cdot \left[\frac{\delta x}{2!} + \frac{(\delta x)^2}{3!} + \ldots \right]$$

$$= \lim_{\delta x \to 0} e^x \cdot [\text{terms involving } \delta x] = e^x.$$

$$\therefore \qquad \frac{\mathbf{d}}{\mathbf{dx}} (\mathbf{e^x}) = \mathbf{e^x}. \qquad \ldots (5)$$

(5) Differential coefficient of sin x.

Let $y = f(x) = \sin x, \ \therefore \ f(x + \delta x) = \sin (x + \delta x).$

$$\therefore \qquad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{\sin (x + \delta x) - \sin x}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{2 \cos \left(x + \frac{\delta x}{2} \right) \cdot \sin \frac{\delta x}{2}}{\delta x} = \lim_{\delta x \to 0} \cos \left(x + \frac{\delta x}{2} \right) \cdot \frac{\sin \frac{\delta x}{2}}{\frac{\delta x}{2}}$$

[Using the formula of sin C – sin D]

$$= \lim_{\delta x \to 0} \cos\left(x + \frac{\delta x}{2}\right) . \lim_{\delta x \to 0} \frac{\sin \frac{\delta x}{2}}{(\delta x/2)}$$

$$= \cos x \,.\, 1 = \cos x \qquad \left(\because \lim_{\theta \to 0} \frac{\sin \theta}{\theta} = 1\right)$$

$$\mathbf{\frac{d}{dx}(\sin x) = \cos x.} \qquad \dots (6)$$

(6) Differential coefficient of cos x.

Let $y = f(x) = \cos x$; $f(x + \delta x) = \cos (x + \delta x)$.

$$\therefore \quad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{\cos (x + \delta x) - \cos x}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{2 \sin\left(x + \frac{\delta x}{2}\right) . \sin\left(-\frac{\delta x}{2}\right)}{\delta x}$$

[Using the formula for $\cos C - \cos D$]]

$$= \lim_{\delta x \to 0}\left[-\sin\left(x + \frac{\delta x}{2}\right)\right] . \lim_{\delta x \to 0} \frac{\sin \frac{\delta x}{2}}{\left(\frac{\delta x}{2}\right)} = -\sin x \,.\, 1 = -\sin x.$$

$$\therefore \qquad \mathbf{\frac{d}{dx}(\cos x) = -\sin x.} \qquad \dots (7)$$

(7) Differential coefficient of $\log_e$ x.

Let $y = f(x) = \log_e x$; $\therefore$ $f(x + \delta x) = \log_e (x + \delta x)$.

$$\therefore \quad \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{\log_e (x + \delta x) - \log_e x}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\log_e\left[x\left(1 + \frac{\delta x}{x}\right)\right] - \log_e x}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\log_e x + \log_e\left(1 + \frac{\delta x}{x}\right) - \log_e x}{\delta x} = \lim_{\delta x \to 0} \frac{\log_e\left(1 + \frac{\delta x}{x}\right)}{\delta x}$$

[$\because$ $\log mn = \log m + \log n$]

$$= \lim_{\delta x \to 0} \frac{\frac{\delta x}{x} - \frac{1}{2} . \left(\frac{\delta x}{x}\right)^2 + \frac{1}{3}\left(\frac{\delta x}{x}\right)^3 - \dots}{\delta x}$$

[Expanding $\log_e (1 + \delta x/x)$ by logarithmic series]

$$= \lim_{\delta x \to 0}\left[\frac{1}{x} - \text{terms involving } \delta x\right] = \frac{1}{x}.$$

$$\therefore \qquad \mathbf{\frac{d}{dx}(\log_e x) = \frac{1}{x}.} \qquad \dots (8)$$

(8) Differential coefficient of $\log_a x$.

Remember :

We know $\log_a x = (\log_a x) \,.\, \log_a (e)$.

$$\therefore \quad \frac{d}{dx}(\log_a x) = \log_a (e) \,.\, \frac{d}{dx}(\log_e x) \qquad [\because \log_a (e) \text{ is constant}]$$

$$\mathbf{\frac{d}{dx}(\log_a x) = \frac{1}{x} \,.\, \log_a (e)} \qquad \dots (9)$$

(9) Differential coefficient of a^x.

Let $y = f(x) = a^x = e^{x \log a}$.

$\therefore \quad f(x + \delta x) = e^{(x + \delta x) \log a}$

$$\frac{dy}{dx} = \lim_{\delta x \to 0} \frac{f(x+\delta x) - f(x)}{\delta x} = \lim_{\delta x \to 0} \frac{e^{(x+\delta x)\log a} - e^{x \log a}}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{e^{x \log a} \,.\, e^{\delta x \log a} - e^{x \log a}}{\delta x} = \lim_{\delta x \to 0} \frac{e^{x \log a}\,[e^{\delta x \log a} - 1]}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{e^{x \log a} \,.\left[1 + \frac{(\delta x \log a)}{1\,!} + \frac{(\delta x \log a)^2}{2\,!} + \dots - 1\right]}{\delta x}$$

$$= \lim_{\delta x \to 0} e^{x \log a}\left[\log a + \frac{\delta x\,(\log a)^2}{2\,!} + \dots\right]$$

$$= e^{x \log a} \,.\, \log a = a^x \,.\, \log a.$$

$$\therefore \quad \mathbf{\frac{d}{dx}(a^x) = a^x \,.\, \log a.} \qquad \dots (10)$$

(10) Differential coefficient of the sum (or difference) of the two functions.

Let $y = F(x) = f_1(x) + f_2(x)$.

$\therefore \quad F(x + \delta x) = f_1(x + \delta x) + f_2(x + \delta x)$.

$$\frac{dF(x)}{dx} = \frac{dy}{dx} = \lim_{\delta x \to 0} \frac{F(x+\delta x) - F(x)}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\{f_1(x+\delta x) + f_2(x+\delta x)\} - \{f_1(x) + f_2(x)\}}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\{f_1(x+\delta x) - f_1(x)\} + \{f_2(x+\delta x) - f_2(x)\}}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{f_1(x+\delta x) - f_1(x)}{\delta x} + \lim_{\delta x \to 0} \frac{f_2(x+\delta x) - f(x)}{\delta x}$$

$$= \frac{d}{dx} f_1(x) + \frac{d}{dx} f_2(x)$$

$$\frac{d}{dx}\{f_1(x) + f_2(x)\} = \frac{d}{dx} f_1(x) + \frac{d}{dx} f_2(x). \qquad \dots (11)$$

Thus, the differential coefficients of the sum of the two functions
= The sum of their respective differential coefficients.

In general, $\frac{d}{dx}\{a_1f_1(x) + a_2f_2(x) + \ldots + a_nf_n(x)\}$

$$= a_1\frac{d}{dx}f_1(x) + a_2\frac{d}{dx}f_2(x) + \ldots + a_n\frac{d}{dx}f_n(x).$$

Similarly, $\frac{d}{dx}\{f_1(x) - f_2(x)\} = \frac{d}{dx}f_1(x) - \frac{d}{dx}f_2(x).$ ... (12)

(11) Differential coefficient of the product of two functions.

Let $F(x) = f_1(x) \cdot f_2(x).$

$\therefore \quad F(x + \delta x) = f_1(x + \delta x) \cdot f_2(x + \delta x).$

$$\therefore \quad \frac{dF(x)}{dx} = \lim_{\delta x \to 0} \frac{F(x+\delta x) - F(x)}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{f_1(x+\delta x)\,f_2(x+\delta x) - f_1(x)\,f_2(x)}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\{f_1(x+\delta x)\,f_2(x) - f_1(x)\,f_2(x)\} + \{f_1(x+\delta x)\,f_2(x+\delta x) - f_1(x+\delta x)\,f_2(x)\}}{\delta x}$$

[Adding and subtracting the terms $f_1(x + \delta x), f_2(x)$ in the numerator]

$$= \lim_{\delta x \to 0} \frac{f_1(x+\delta x)\,\{f_2(x+\delta x) - f_2(x)\} + \{f_1(x+\delta x) - f_1(x)\}\,f_2(x)}{\delta x}$$

$$= \lim_{\delta x \to 0} f_1(x+\delta x)\left\{\frac{f_2(x+\delta x) - f_2(x)}{\delta x}\right\} + \lim_{\delta x \to 0} \frac{f_1(x+\delta x) - f_1(x)}{\delta x} \cdot f_2(x)$$

$$= f_1(x)\frac{d}{dx}f_2(x) + \frac{d}{dx}f_1(x) \cdot f_2(x).$$

Thus, $\frac{d}{dx}\{f_1(x) \cdot f_2(x)\} = f_1(x)\frac{d}{dx}f_2(x) + \frac{df_1(x)}{dx} \cdot f_2(x).$ ... (13)

In words,

The differential coefficient of the product of two functions = **1st** function × diff. coeff. of the second function + diff. coeff. of the 1st function × 2nd function.

(12) Differential coefficient of the quotient of two functions.

Let $F(x) = \frac{f_1(x)}{f_2(x)}$ and hence $F(x + \delta x) = \frac{f_1(x+\delta x)}{f_2(x+\delta x)}$

$$\frac{dF(x)}{dx} = \lim_{\delta x \to 0} \frac{F(x+\delta x) - F(x)}{\delta x} = \lim_{\delta x \to 0} \frac{\frac{f_1(x+\delta x)}{f_2(x+\delta x)} - \frac{f_1(x)}{f_2(x)}}{\delta x}$$

$$= \lim_{\delta x \to 0} \frac{\frac{f_1(x+\delta x)}{f_2(x+\delta x)} - \frac{f_1(x)}{f_2(x+\delta x)} + \frac{f_1(x)}{f_2(x+\delta x)} + \frac{f_1(x)}{f_2(x)}}{\delta x}$$

$\left[\text{Adding and subtracting the term } \frac{f_1(x)}{f_2(x+\delta x)} \text{ in the numerator}\right]$

$$= \lim_{\delta x \to 0} \left\{ \frac{1}{f_2(x+\delta x)} \; \frac{f_1(x+\delta x) - f_1(x)}{\delta x} \right\}$$

$$- \lim_{\delta x \to 0} \left\{ \frac{f_1(x)}{f_2(x)\, f_2(x+\delta x)} \; \frac{f_2(x+\delta x) - f_2(x)}{\delta x} \right\}$$

$$= \frac{1}{f_2(x)} \; \frac{d}{dx} f_1(x) - \frac{f_1(x)}{f_2(x)\, f_2(x)} \; \frac{d}{dx} f_2(x)$$

$$\frac{d}{dx}\left[\frac{f_1(x)}{f_2(x)}\right] = \frac{f_2(x)\, \frac{d}{dx} f_1(x) - f_1(x) \frac{d}{dx} f_2(x)}{[f_2(x)]^2} \qquad \ldots (14)$$

or

$$\frac{d}{dx}\left[\frac{f_1(x)}{f_2(x)}\right] = \frac{\text{(Denominator)} \times \text{(Diff. coeff. of numerator)} - \text{(Numerator} \times \text{Diff. coeff. of denominator)}}{\text{(Denominator)}^2}$$

(13) Differential coefficient of a function

To explain the meaning of **'function of a function'**, let us consider a function $(ax + b)^n$. Here$(ax + b)^n$ is a function of $(ax + b)$, whereas $(ax + b)$ is itself a function of 'x'. Thus, $(ax + b)^n$ is a 'function of a function'. Again consider a function log cos x. Here, log (cos x) is a function of 'cos x', whereas cos x is itself a function of x. Hence, log cos x is also a 'function of a function'.

Therefore, in general, if **y is a function of a variable 't' and t is a function of 'x', then we say that y is a 'function of a function of 'x'**. We give below the method to differentiate a function of a function.

Method. The following are the steps to find the differenial coefficient of the function of a function, say $y = f[g(x)]$.

(i) First of all put the inner function $g(x) = t$ and $y = f(t)$.

(ii) Now differentiate y w.r.t. 't' *i.e.*, find $\frac{dy}{dt}$.

(iii) Secondly, differentiate t w.r.t. 'x' *i.e.* find $\frac{dt}{dx}$.

(iv) Multiply $\frac{dy}{dt}$ by $\frac{dt}{dx}$ and find $\frac{dy}{dx}$, *i.e.*,

$$\mathbf{\frac{dy}{dx} = \frac{dy}{dt} \cdot \frac{dt}{dx}} \qquad \ldots (15)$$

(v) Now put the value of $t = g(x)$.

1·8. PARTIAL DIFFERENTIATIONS

We know that the differential coefficient of $f(x)$ with respect to x is $\lim\limits_{\delta x \to 0} \frac{f(x + \delta x) - f(x)}{\delta x}$, provided this limit exists and is expressed as,

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*A function $f(x)$ is said to be continuous at a point $x = a$, if for $\varepsilon > 0$, however small, there exists a positive number δ, depending upon ε, such that

$$|f(x) - f(a)| < \varepsilon, \text{ for all } x \text{ such that } |x - a| < \delta$$

From the above definition of continuity, we can infer that the function $f(x)$ is said to be continuous at a point $x = a$ if and only if $\lim\limits_{x \to 0} f(x) = f(a)$.

$$f'(x) \quad \text{or} \quad \frac{d}{dx}[f(x)]$$

If $u = f(x, y)$ be a continuous function* of two independent variables x and y, then the differential cofficient w.r.t. x (taking y as constant) is called the partial derivative or partial differential coefficient of u w.r.t. x and is represented by different symbols such as

$$\frac{\partial u}{\partial x}, \frac{\partial f}{\partial x}, f_x\,(x, y), f_x.$$

Symbolically, if $u = f\,(x, y)$ then

$$\lim_{\delta x \to 0} \frac{f(x + \delta x, y) - f(x, y)}{\delta x}$$

If it exists then it is called the partial derivative or partial differential coefficient of u w.r.t. x. It is denoted by, $\frac{\partial u}{\partial x}$ or $\frac{\partial f}{\partial x}$ or f_x or u_x

Similarly, by keeping x constant and allowing y alone to vary, we can define the partial derivative or partial differential coefficient of u w.r.t. y. It is represented by any one of the following symbols.

$$\frac{\partial u}{\partial y}, \frac{\partial f}{\partial y}, f_y\,(x, y), f_y$$

Symbolically, $$\frac{\partial u}{\partial y} = \lim_{\partial y \to 0} \frac{f(x, y + \delta y) - f(x, y)}{\delta y}$$

provided this limit exists.

For example, if $$u = ax^3 + 2hx^2y + by^2$$

then $$\frac{\partial u}{\partial x} = 3ax^2 + 4hxy$$

and $$\frac{\partial u}{\partial y} = 2hx^2 + 2by$$

[I] Rules of Partial Differentiation

Rule (1) :

(a) If u is a function of x, y and we are to differentiate partially w.r.t. x, then y is treated as constant.

(b) Similarly, if we are to differentiate u partially w.r.t. y, then x is treated as constant.

(c) If u is a function of x, y, z, and we are to differentiate u w.r.t. x, then y and z are treated as constants.

Rule (2) :

If $z = u \pm v$, where u and v are functions of x and y, then

$$\frac{\partial z}{\partial x} = \frac{\partial u}{\partial x} \pm \frac{\partial v}{\partial x} \quad \text{and} \quad \frac{\partial z}{\partial y} = \frac{\partial u}{\partial y} \pm \frac{\partial v}{\partial y}$$

Rule (3) :

If $z = uv$, where u and v are functions of x and y, then

$$\frac{\partial z}{\partial x} = \frac{\partial}{\partial x}(uv) = u\frac{\partial v}{\partial x} + v\frac{\partial u}{\partial x}$$

and $$\frac{\partial z}{\partial y} = \frac{\partial}{\partial y}(uv) = u\frac{\partial v}{\partial y} + v\frac{\partial u}{\partial y}$$

Rule (4) :

If $z = \frac{u}{v}$, where u and v ae functions of x and y, then

$$\frac{\partial z}{\partial x} = \frac{\partial}{\partial x}\left(\frac{u}{v}\right) = \frac{v\left(\frac{\partial u}{\partial x}\right) - u\left(\frac{\partial v}{\partial x}\right)}{v^2}$$

and $$\frac{\partial z}{\partial y} = \frac{\partial}{\partial y}\left(\frac{u}{v}\right) = \frac{v\left(\frac{\partial u}{\partial y}\right) - u\left(\frac{\partial v}{\partial y}\right)}{v^2}$$

Rule (5) :

If $z = f(u)$, where u is a function of x and y, then

$$\frac{\partial z}{\partial x} = \frac{\partial z}{\partial u} \cdot \frac{\partial u}{\partial x} \text{ and } \frac{\partial z}{\partial y} = \frac{\partial z}{\partial u} \cdot \frac{\partial u}{\partial y}$$

Note :

(i) If z is a function of one variable x, then $\frac{\partial z}{\partial x} = \frac{dz}{dx}$.

(ii) If z is a function of two variables, x_1 and x_2, then we get $\frac{\partial z}{\partial x_1}$ and $\frac{\partial z}{\partial x_2}$.

(iii) If z is a function of n variables, $x_1, x_2, \ldots\ldots\ldots\ldots, x_n$, then we get $\frac{\partial z}{\partial x_1}, \frac{\partial z}{\partial x_2}, \ldots\ldots\ldots, \frac{\partial z}{\partial x_n}$.

[II] Symmetric Function

A function $u = u(x, y)$ is said to be symmetric if on interchanging x and y, the value of u remains unchanged.

[III] Homogeneous Functions

A function $f(x, y)$ is said to be homogeneous function of order n if the degree of each of its terms in x and y is equal to n. Thus,

$$a_0x^n + a_1x^{n-1}y + a_2x^{n-2}y^2 + \ldots\ldots\ldots + a_{n-1}xy^{n-1} + a_ny^n$$

is homogeneous function in x and y of order n.

[IV] The Euler Reciprocal Relations (or Reciprocity Relations)

Suppose $z = f(x, y)$ is a state function of two independent variables x and y. A state function depends on the initial and final states of a system and is independent of the path through which the state is reached (state functions are generally encountered in chemical thermodynamics). The differential of z, called an exact or total differential is given by,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \ldots (1)$$

$$= M(x, y)\,dx + N(x, y)\,dy \quad \ldots (2)$$

where $M(x,y) = \left(\frac{\partial z}{\partial x}\right)_y$ and $N(x,y) = \left(\frac{\partial z}{\partial y}\right)_x$ ... (3)

Since $M(x, y)$ and $N(x, y)$ are supposed to have continuous partial derivatives,

$$\frac{\partial^2 z}{\partial x \,.\, \partial y} = \frac{\partial^2 z}{\partial y \,.\, \partial x} \quad \text{... (4)}$$

Taking mixed second derivatives of equation (3), we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \,.\, \partial x} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \,.\, \partial y} \quad \text{... (5)}$$

From equations (4) and (5), we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \text{... (6)}$$

Equation (6) is known as ***Euler reciprocity relation***. A differential which has the property (6) is also known as an *exact differential.*

[V] The Euler Chain Relation (The Cyclic Rule)

From equation (1), we see that if the change occurs at constant z then $dz = 0$, so,

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \text{... (7)}$$

$$\therefore \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \quad \text{... (8)}$$

or

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \quad \text{... (9)}$$

Equation (9) is known as Euler chain relation (or the cyclic rule). It is applicable only for state functions.

Problem 1. ***Determine the first order partial derivatives of the functions :***

(i) y^x **(ii)** $\log(x^2 + y^2)$

Solution. (i) Let $z = y^x$

Taking logs, $\log z = x \log y$ ... (i)

Differentiating w.r.t. x, $\frac{1}{z}\frac{\partial z}{\partial x} = \log y$

$$\therefore \quad \frac{\partial z}{\partial x} = z \log y = y^x \log y$$

Now differentiate equation (i), w.r.t y, we get

$$\frac{1}{z}\frac{\partial z}{\partial y} = x\left(\frac{1}{y}\right) = \frac{x}{y}$$

or

$$\frac{\partial z}{\partial y} = z\left(\frac{x}{y}\right) = y^x\left(\frac{x}{y}\right) = xy^{x-1}$$

(ii) Suppose $z = \log(x^2 + y^2)$

$$\therefore \quad \frac{\partial z}{\partial x} = \frac{1}{x^2 + y^2}(2x) = \frac{2x}{x^2 + y^2}$$

$$\frac{\partial z}{\partial y} = \frac{1}{x^2 + y^2}(2y) = \frac{2y}{x^2 + y^2}$$

Following are some differentials of different functions :

(1) $\frac{d}{dx}(\sin x) = \cos x$ (2) $\frac{d}{dx}(\cos x) = -\sin x$

(3) $\frac{d}{dx}(\tan x) = \sec^2 x$ (4) $\frac{d}{dx}(\cot x) = \mathrm{cosec}^2 x$

(5) $\frac{d}{dx}(\sec x) = \sec x \tan x$ (6) $\frac{d}{dx}(\mathrm{cosec}\, x) = -\mathrm{cosec}\, x \cot x$

(7) $\frac{d}{dx}(\sin mx) = m \cos mx$ (8) $\frac{d}{dx}(\cos mx) = -m \sin mx$

(9) $\frac{d}{dx}(\tan mx) = m \sec^2 mx$ (10) $\frac{d}{dx}(\sin^{-1} x) = \frac{1}{\sqrt{1 - x^2}}$

(11) $\frac{d}{dx}(\cos^{-1} x) = \frac{-1}{\sqrt{1 - x^2}}$ (12) $\frac{d}{dx}(\tan^{-1} x) = \frac{1}{(1 + x^2)}$

(13) $\frac{d}{dx}(\cot^{-1} x) = \frac{-1}{1 + x^2}$ (14) $\frac{d}{dx}(\sec^{-1} x) = \frac{1}{|x| \sqrt{x^2 - 1}}$

(15) $\frac{d}{dx}(\mathrm{cosec}^{-1} x) = \frac{-1}{|x| \sqrt{x^2 - 1}}$.

EXAMPLES

Ex. 1. ***Find the differential coefficients of the following :***

(i) x^5 *(ii)* x^{-2} *(iii)* $\sqrt{(x)^3}$ *(iv)* $x^{-5/2}$

Solution.

(i) $\frac{d}{dx}(x^5) = 5x^{5-1} = 5x^4$ (ii) $\frac{d}{dx}(x^{-2}) = -2x^{-2-1} = -2x^{-3}$

(iii) $\frac{d}{dx}\sqrt{x^3} = \frac{d}{dx}(x)^{3/2} = \frac{3}{2} x^{\frac{3}{2}-1} = \frac{3}{2} x^{1/2}$ (iv) $\frac{d}{dx}(x^{-5/2}) = \frac{-5}{2} x^{\frac{-7/2}{2}-1} = \frac{-5}{2} x^{-7/2}$

Ex. 2. ***Find the differential coefficients of the following :***

(i) ax^4 *(ii)* $5e^x$ *(iii)* 10^x *(iv)* $7 \log_{10} x$

Solution.

(i) $\frac{d}{dx}(ax^4) = a \frac{d}{dx}(x^4) = 4ax^3$ (ii) $\frac{d}{dx}(5e^x) = 5 \frac{d}{dx}(e^x) = 5e^x$

(iii) $\frac{d}{dx}(10^x) = 10^x \log_e 10$ (iv) $\frac{d}{dx}(7 \log_{10} x) = 7 \frac{d}{dx}(\log_{10} x) = 7 \cdot \frac{1}{x} \log_{10}(e)$

Ex. 3. ***Find the differential coefficients of the following:***

(i) $4x^2 + 6x + 10$ *(ii)* $e^x + \cos x + 6 \log x$

(iii) $\tan x + \sin x$ *(iv)* $a^x + \log x + a^3 e^x$

(v) $x^2 \sin x$ *(vi)* $x^3 \log x$

Solution.

(i) $\frac{d}{dx}(4x^2 + 6x + 10) = \frac{d}{dx}(4x^2) + \frac{d}{dx}(6x) + \frac{d}{dx}(10) = 8x + 6$

(ii) $\frac{d}{dx}(e^x + \cos x + 6 \log x) = \frac{d}{dx}(e^x) + \frac{d}{dx}(\cos x) + \frac{d}{dx}(6 \log x) = e^x - \sin x + (6/x)$

(iii) $\frac{d}{dx}(\tan x + \sin x) = \frac{d}{dx}(\tan x) + \frac{d}{dx}(\sin x) = \sec^2 x + \cos x$

(iv) $\frac{d}{dx}(a^x + \log x + a^3 e^x) = \frac{d}{dx}(a^x) + \frac{d}{dx}(\log x) + \frac{d}{dx}(a^3 e^x) = a^x \log a + \frac{1}{x} + a^3 e^x$

(v) $\frac{d}{dx}(x^2 \sin x) = x^2 \frac{d}{dx}(\sin x) + \frac{d}{dx}(x^2) . \sin x = x^2 . \cos x + 2x \sin x$

(vi) $\frac{d}{dx}(x^3 \log x) = x^3 \frac{d}{dx}(\log x) + \frac{d}{dx}(x^3) . \log x$

$$= x^3 (1/x) + 3x^2 . \log x$$

$$= x^2 + 3x^2 \log x = x^2 (1 + 3\log x)$$

Ex. 4. ***Find the differential coefficients of the following :***

(i) $\frac{\sin x}{x^2}$ *(ii)* $\frac{\log x}{x}$ *(iii)* $\frac{x}{(x+1)^2}$

Solution.

(i) $$\frac{d}{dx}\left(\frac{\sin x}{x^2}\right) = \frac{x^2 \frac{d}{dx}(\sin x) - \sin x . \frac{d}{dx}(x^2)}{(x^2)^2}$$

$$= \frac{x^2 \cos x - \sin x . 2x}{x^4}$$

$$= \frac{x \cos x - 2 \sin x}{x^3}$$

(ii) $$\frac{d}{dx}\left(\frac{\log x}{x}\right) = \frac{x . \frac{d}{dx}(\log x) - \log x . \frac{d}{dx}(x)}{x^2}$$

$$= \frac{x . \frac{1}{x} - \log x . 1}{x^2} = \frac{1 - \log x}{x^2}$$

(iii) $$\frac{d}{dx}\left[\frac{x}{(x+1)^2}\right] = \frac{(x+1)^2 \frac{d}{dx}(x) - x . \frac{d}{dx}(x+1)^2}{(x+1)^4}$$

$$= \frac{(x+1)^2 . 1 - x . 2 . (x+1)}{(x+1)^4}$$

$$= \frac{(x+1)[x + 1 - 2x]}{(x+1)^4} = \frac{(1-x)}{(x+1)^3}$$

Ex. 5. ***Find the differential coefficients of the following :***

(i) **$\sin 5x$** *(ii)* **$\tan^3 x$** *(iii)* **$\log \sin x$**

Solution.

(i) Let $y = \sin 5x \Rightarrow y = \sin t$, where $t = 5x$

$$\therefore \quad \frac{dy}{dt} = \cos t \text{ and } \frac{dt}{dx} = 5$$

$$\therefore \quad \frac{dy}{dx} = \frac{dy}{dt} . \frac{dt}{dx} = \cos t . 5 = 5 \cos 5x$$

(ii) Let $y = \tan^3 x \Rightarrow y = t^3$, where $t = \tan x$

$\therefore \quad \frac{dy}{dt} = 3t^2$ and $\frac{dt}{dx} = \sec^2 x$

$\therefore \quad \frac{dy}{dx} = \frac{dy}{dt} \cdot \frac{dt}{dx} = 3t^2 \cdot \sec^2 x$

or $\quad \frac{dy}{dx} = 3 \tan^2 x \cdot \sec^2 x$

(iii) Let $y = \log \sin x \Rightarrow y = \log t$, where $t = \sin x$

$\therefore \quad \frac{dy}{dt} = \frac{1}{t}$ and $\frac{dt}{dx} = \cos x$

$\therefore \quad \frac{dy}{dx} = \frac{dy}{dt} \cdot \frac{dt}{dx} = \frac{1}{t} \cdot \cos x$

or $\quad \frac{dy}{dx} = \frac{1}{\sin x} \cdot \cos x = \cot x$

Ex. 6. ***Calculate the value of*** $\frac{dy}{dx}$ ***from the following :***

(i) $x = a \cos t, y = a \sin t$ ***(ii)*** $x = at^2, y = 2at$

Solution.

(i) $x = a \cos t, y = a \sin t$

$\therefore \quad \frac{dx}{dt} = -a \sin t, \frac{dy}{dt} = a \cos t$

$\therefore \quad \frac{dy}{dx} = \frac{dy}{dt} \cdot \frac{dt}{dx} = \frac{a \cos t}{-a \sin t} = -\frac{\cos t}{\sin t}$

or $\quad \frac{dy}{dx} = -\cot t$

(ii) $x = at^2, y = 2at$

$\therefore \quad \frac{dx}{dt} = 2at, \frac{dy}{dt} = 2a.1 = 2a$

$\therefore \quad \frac{dy}{dx} = \frac{dy}{dt} \cdot \frac{dt}{dx} = \frac{2a}{2at} = \frac{1}{t}.$

Ex. 7. ***Differentiate the following with respect to x :***

(i) $x^2e^x + \log x$ ***(ii)*** $\sqrt{x^2 + 5x + 7}$

(iii) $\sin^2 x \cos^2 x$ ***(iv)*** $(1 + \sin x)^3$

(v) $(1 - x^2 + x^3)(3x + 6)$ ***(vi)*** $(6x^3 + 5x^2 + 11x + 10)^{11}$

Solution.

(i) $\frac{d}{dx}(x^2e^x + \log x) = \frac{d}{dx}(x^2e^x) + \frac{d}{dx}(\log x)$

$$= \left\{ x^2 \cdot \frac{d}{dx}(e^x) + \frac{d}{dx}(x^2) \cdot e^x \right\} + \frac{1}{x}$$

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

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

(ii) Let $y = \sqrt{x^2 + 5x + 7}$

$\therefore \quad y = \sqrt{t}$ where $t = x^2 + 5x + 7$

$\frac{dy}{dt} = \frac{1}{2} t^{(1/2 - 1)} = \frac{1}{2} t^{-1/2}$ and $\frac{dt}{dx} = 2x + 5$

$\therefore \quad \frac{dy}{dx}=\frac{dy}{dt}\cdot\frac{dt}{dx}=\frac{1}{2}\cdot t^{-1/2}(2x+5)=\frac{1}{2}(x^2+5x+7)^{-1/2}\cdot(2x+5)$

(iii) $\frac{d}{dx}(\sin x\,.\cos^2 x)=\sin^2 x\,.\frac{d}{dx}(\cos^2 x)+\frac{d}{dx}(\sin^2 x)\,.\cos^2 x$

$$=\sin^2 x\,.\,2\cos x\frac{d}{dx}(\cos x)+2\sin x\,.\frac{d}{dx}(\sin x)\cos^2 x$$
$$=2\sin^2 x\,.\cos x\,.(-\sin x)+2\sin x\,.(\cos x)\,.\cos^2 x$$
$$=-2\sin^3 x\cos x+2\sin x\cos^3 x$$
$$=2\sin x\cos x(\cos^2 x-\sin^2 x)$$
$$=\sin 2x\,.\cos 2x.$$

(iv) $\frac{d}{dx}(1+\sin x)^3=3(1+\sin x)^2\,.\cos x$

(v) Let $y=(1-x^2+x^3)(3x+6)$

$\therefore \quad \frac{dy}{dx}=\frac{d}{dx}(1-x^2+x^3)\,.(3x+6)+(1-x^2+x^3)\frac{d}{dx}(3x+6)$

$$=(-2x+3x^2)(3x+6)+(1-x^2+x^3)\,.\,3$$
$$=-6x^2+9x^3-12x+18x^2+3-3x^2+3x^3$$
$$=12x^3+6x^2-10x+3$$

(vi) $\frac{d}{dx}(6x^3+5x^2+11x+10)^{11}=11(6x^3+5x^2+11x+10)^{11-1}\,.(18x^2+10x+11)$

$$=11(6x^3+5x^2+11x+10)(18x^2+10x+11).$$

Ex. 8. ***If*** $y=\tan^{-1}\left(\frac{2x}{1-x^2}\right)$, ***then calculate the value of*** $\frac{dy}{dx}$.

Solution. Let $x=\tan\theta$, then

$$y=\tan^{-1}\left(\frac{2\tan\theta}{1-\tan^2\theta}\right)=\tan^{-1}(\tan 2\theta)=2\theta=2\tan^{-1}x$$

$$\therefore \quad \frac{dy}{dx}=\frac{2}{1+x^2}.$$

Ex. 9. ***If*** $y=\tan^{-1}\left(\frac{\sin x+\cos x}{\cos x-\sin x}\right)$, ***then calculate the value of*** $\frac{dy}{dx}$.

Solution. Let $y=\tan^{-1}\left(\frac{\sin x+\cos x}{\cos x-\sin x}\right)$

Dividing the numerator and denominator by $\cos x$, we get,

$$y=\tan^{-1}\left(\frac{\tan x+1}{1-\tan x}\right)$$
$$=\tan^{-1}\left[\tan\left(x+\frac{\pi}{4}\right)\right]=x+\frac{\pi}{4}$$
$$\therefore \quad \frac{dy}{dx}=1.$$

Ex. 10. ***Calculate the value of*** $\frac{dy}{dx}$ ***if*** $x^y=e^{x-y}$.

Solution. $\quad x^y=e^{x-y}$

Taking logs, $\quad y\log x=(x-y)\log e$

or $\quad y\log x=x-y \qquad (\because \log e=1)$

or $\quad y\log x+y=x$

or $$y\,(1 + \log x) = x$$

or $$y = \frac{x}{1 + \log x}$$

$\therefore$ $$\frac{dy}{dx} = \frac{(1 + \log x).\,1 - x\left(\frac{1}{x}\right)}{(1 + \log x)^2} = \frac{1 + \log x - 1}{(1 + \log x)^2}$$

or $$\frac{dy}{dx} = \frac{\log x}{(1 + \log x)^2}$$

1·9. MAXIMA AND MINIMA

[I] Maxima and Minima of a Function of Single Independent Variable

(1) Maximum value : Suppose $y = f(x)$ is a function of a single independent variable x. Then $f(x)$ is said to have its maximum value at $x = a$, if the function stops to increase and begins to decrease at $x = a$.

(2) Minimum value : A function is said to have a minimum value at $x = a$, if $f(x)$ stops to decrease and begins to increase at $x = a$.

In figure (4), the function has maximum value at $x = a$ and has minimum value at $x = b$. It should be noted that the maximum value of $f(x)$ at a point is not necessarily its greatest value and similarly the minimum value of the function at a point is not necessarily its smallest value.

(1) At least one maxima or one minima lies between two equal values of a function.

(2) Maxima and minima must occur alternately.

(3) A function may have several maxima and minima.

(4) A function $y = f(x)$ is maximum at $x = a$, if $\frac{dy}{dx}$ changes is sign from positive to negative as x passes through a.

(5) A function $y = f(x)$ is minimum at $x = a$, if $\frac{dy}{dx}$ changes its sign from negative to positive as x passes through a.

(6) If the sign of $\frac{dy}{dx}$ does not change, while x passes through a, then $y = f(x)$ is neither maximum nor minimum at $x = a$.

(7) A function $f(x)$ is said to be monotonically increasing if $f'(x) > 0$.

(8) A function $f(x)$ is said to be monotonically decreasing if $f'(x) < 0$.

[II] Rules for Finding Maxima–Minima

To find the maxima and minima of a function $y = f(x)$, the following steps are undertaken.

(1) First find the derivative $\frac{dy}{dx}$ of the given function.

(2) Find the value or values of x for which $\frac{dy}{dx} = 0$. Let $x = a, b$,....... be the values of x at which $\frac{dy}{dx} = 0$.

(3) Now find the second derivative $\frac{d^2y}{dx^2}$.

(4) Put $x = a$ in $\frac{d^2y}{dx^2}$. If a negative value of $\frac{d^2y}{dx^2}$ is obtained, then $y = f(x)$ will have maximum value at $x = a$ and this maximum value is $y = f(a)$. If the value of $\frac{d^2y}{dx^2}$ is positive, then $y = f(x)$ will have minimum value at $x = a$ and this minimum value is $y = f(a)$.

(5) If $\frac{d^2y}{dx^2} = 0$ at $x = a$, then find $\frac{d^3y}{dx^3}$. If $\frac{d^3y}{dx^3}$ is not equal to zero, then function $y = f(x)$ has neither maximum nor minimum value.

Note :

(i) For maximum : $\frac{dy}{dx} = 0$ and $\frac{d^2y}{dx^2} < 0$

(ii) For minimum : $\frac{dy}{dx} = 0$ and $\frac{d^2y}{dx^2} > 0$

Problem 1. ***Determine the interval in which :***

(i) $f(x) = 2x^3 - 15x^2 + 36x + 7$ ***is increasing.***

(ii) $f(x) = x^3 + 3x^2 - 105x + 5$ ***is decreasing.***

Solution. (i) $f'(x) = 6x^2 - 30x + 36 = 6(x - 3)(x - 2)$

Clearly, $f'(x) > 0$ when $x < 2$ and also when $x > 3$. Hence, $f(x)$ is increasing in the interval $]-\infty, 2\,(\cup)\,3, \infty[$.

(ii) $f'(x) = 3x^2 + 6x - 105 = 3(x - 5)(x + 7)$.

Clearly, $f'(x) < 0$, when $-7 < x < 5$. So, $f(x)$ is decreasing in the interval $]-7, 5[$.

Problem 2. ***Determine the interval on which*** $f(x) = x^x$ ***decreases.***

Solution. $f'(x) = x^x(1 + \log x)$

Clearly, $f'(x) < 0$ when $x > 0$ and $(1 + \log x) < 0$, *i.e.*, $x > 0$ and $\log x < -1$, *i.e.*, $x > 0$ and $x < \frac{1}{e}$, as $\log(1/e) = -1$. So , $f(x)$ is decreasing in the interval $]0, 1/e[$.

Problem 3. ***When x is positive, what is the maximum value of*** $(1/x)^x$**?**

Solution. Let $y = (1/x)^x = x^{-x}$

Taking logs, $\log y = -x \log x$

Differentiating, $\frac{1}{y} \cdot \frac{dy}{dx} = -x \cdot \frac{1}{x} - \log x . 1 = -(1 + \log x)$

or $$\frac{dy}{dx} = -x^x(1 + \log x)$$

$$\frac{d^2y}{dx^2} = x^{-x}(1 + \log x)^2 - x^{-x} \cdot \frac{1}{x}$$

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

Now $\frac{dy}{dx} = 0$ means that $1 + \log x = 0$

or $\log x = -1 = \log(1/e)$, so $x = (1/e)$.

$\therefore$ $$\left[\frac{d^2y}{dx^2}\right]_{x = 1/e} = -\left(\frac{1}{e}\right)^{-\frac{1}{e}-1} < 0$$

So, $x = 1/e$ is a point of maxima.

$\therefore$ Maximum value $= e^{1/e}$.

Problem 4. ***Find the maximum and minimum values of $x^3 - 3x^2 - 9$.***

Solution. Suppose $y = x^3 - 3x^2 - 9$ ... (i)

Differentiating equation (i), w.r.t. x,

$$\frac{dy}{dx} = 3x^2 - 6x \qquad \text{... (ii)}$$

For the maximum and minimum, we have,

$$\frac{dy}{dx} = 0$$

$$\Rightarrow \quad 3x^2 - 6x = 0$$

$$\Rightarrow \quad 3x(x-2) = 0$$

$$\Rightarrow \quad x = 0, x = 2$$

Differentiating equation (ii) w.r.t. x,

$$\frac{d^2y}{dx^2} = 6x - 6$$

At $x = 0$, $\quad \left(\frac{d^2y}{dx^2}\right)_{x=0} = 6 \times 0 - 6 = -6 < 0$

$\therefore$ $y = x^3 - 3x^2 - 9$ is maximum at $x = 0$ and its maximum value is obtained by putting $x = 0$ in equation (i).

$$y_{\max} = (0)^3 - 3(0)^2 - 9 = -9$$

At $x = 2$, $\quad \left(\frac{d^2y}{dx^2}\right)_{x=2} = 6 \times 2 - 6 = 12 - 6 = 6 > 0$

$\therefore$ $y = x^3 - 3x^2 - 9$ is minimum at $x = 2$ and its minimum value is obtained by putting $x = 2$ in equation (i),

$$y_{\min} = (2)^3 - 3(2)^2 - 9$$

$$= 8 - 12 - 9 = -13.$$

Problem 5. ***Show that in all the rectangles of the same area, the sum of the sides of the square is the least.***

Solution. Suppose x and y are the length and breadth of a rectangle, then its,

(a) Area $= xy = A$ (given) ... (i)

(b) Perimeter, $P = 2(x + y) = 2\left(x + \frac{A}{x}\right)$ [Using equation (i)]

$\therefore$ P is a function of x, so for maximum and minimum value of P, we must have, $\frac{dP}{dx} = 0$

$$\because \quad P = 2\left(x + \frac{A}{2}\right)$$

$$\therefore \quad \frac{dP}{dx} = 2\left(1 - \frac{A}{x^2}\right)$$

Now $\quad \frac{dP}{dx} = 0 \Rightarrow 2\left(1 - \frac{A}{x^2}\right) \Rightarrow x^2 = A$

Now $\quad \frac{d^2P}{dx^2} = \frac{d}{dx}\left(\frac{dP}{dx}\right) = \frac{d}{dx}\left(2 - \frac{2A}{x^2}\right)$

$$= 0 + \frac{4A}{x^2}$$

$\therefore$ At $x = \sqrt{A}$, $\frac{d^2P}{dx^2} > 0$

Therefore, the perimeter (P) of the rectangle is least when $x = \sqrt{A}$

or $x^2 = A = xy.$

$\therefore$ $x^2 = xy \Rightarrow x\,(x - y) = 0$

$\Rightarrow$ $x = y$ $\qquad$ $(\because\ x \neq 0)$

So, all the rectangles with given area are square if the perimeter of rectangle is least.

Problem 6. ***What is the maximum area of a rectangle of perimeter 176 cm?***

Solution. Suppose x and y are the length and breadth of the rectangle, respectively. Then.

$$2(x + y) = 176 \quad \text{or} \quad x + y = 88$$

Area, $A = xy = x(88 - x)$

$\therefore$ $\frac{dA}{dx} = 88 - 2x$ and $\frac{d^2A}{dx^2} = -2 < 0$

$\frac{dA}{dx} = 0 \Rightarrow x = 44$

$\therefore$ $x = 44$ is a point of maximum.

$\therefore$ Maximum area $= 44\,(88 - 44) = 44 \times 44 = 1936\ \text{cm}^2$.

Problem 7. ***If*** $x > 0$ ***and*** $xy = 1$, ***then find the minimum value of*** $x + y$.

Solution. Let $z = x + y = x + \frac{1}{x}$ $\qquad$ $[\because\ xy = 1]$

$$\frac{dz}{dx} = 1 - \frac{1}{x^2} \quad \text{and} \quad \frac{d^2z}{dx^2} = \frac{2}{x^3}$$

$$\frac{dz}{dx} = 0 \text{ means that } 1 - \frac{1}{x^2} = 0 \quad \text{or} \quad x = \pm 1$$

Thus, $x = 1$, because $x > 0$ (given), so

$$\left(\frac{d^2z}{dx^2}\right)_{x=1} = 2 > 0$$

$\therefore$ $x = 1$ is a point of minimum.

$\therefore$ Minimum value $= 1 + 1 = 2$.

1·10. INTEGRATION

[I] Definition

Antiderivative process of a function is known as ***integration***. In other words, the inverse process of a derivative of a function is known as ***integration.*** Since the derivative of x is 1, so the integral of 1 is x. Similarly, the derivative of $\sin x$ is $\cos x$, so the integral of $\cos x$ is $\sin x$.

Suppose $f(x)$ is the differential coefficient of a function $F(x)$ then the integral of $f(x)$ with respect to x is $F(x)$. We write it as

$$\frac{d}{dx}\,[F(x)] = f(x)$$

$$\therefore \qquad F(x) = \int f(x)\,dx$$

or

$$\int f(x)\,dx = F(x)$$

The function $f(x)$ is called the integrand of $\int f(x)\,dx$. The symbol "$\int$" stands for the word integral. The expression $\int f(x)\,dx$ is read as *'integral of $f(x)$ with respect to x'*. Between the symbol $\int$ and dx, the integrand is inserted.

[II] Constant of Integration

Suppose c is any constant number, then its differential coefficient w.r.t. x is zero, *i.e.*, $\frac{d}{dx}(c) = 0$. Let $f(x)$ be the differential coefficient of a function $F(x)$, then

$$\frac{d}{dx}[F(x)] = f(x)$$

$$\Rightarrow \qquad \frac{d}{dx}[F(x)] + \frac{dc}{dx} = f(x) \qquad \left[\because \frac{dc}{dx} = 0\right]$$

$$\Rightarrow \qquad \frac{d}{dx}[F(x) + c] = f(x)$$

$$\Rightarrow \qquad F(x) + c = \int f(x)\,dx$$

or

$$\int f(x)\,dx = F(x) + c$$

In the above equation c is any arbitrary constant and is known as ***constant of integration.***

[III] Types of Integrals

There are two types of integrals *viz.*, indefinite integrals and definite integrals.

(1) Indefinite integrals : If $f(x)$ is the differential coefficient of a function $F(x)$ and c is constant of integration, then,

$$\frac{d}{dx}[F(x) + c] = f(x)$$

$$\Rightarrow \qquad \int f(x)\,dx = F(x) + c$$

The integral $\int f(x)\,dx$ is known as an indefinite integral.

(2) Definite integrals : If $f(x)$ is the differential coefficient of a function $F(x)$ and c is constant of integration, then

$$\frac{d}{dx}[F(x)+c]=f(x)$$

$$\Rightarrow \qquad \int f(x)\,dx = F(x)+c$$

$$\int_a^b f(x)\,dx = [F(x)+c]_a^b$$

or

$$\int_a^b f(x)\,dx = [\{F(b)+c\}-\{F(a)+c\}]$$

$$= F(b)-F(a) = A \text{ constant number}$$

So, we can say that the integral whose value comes out to be a constant and depends on two real numbers (called limits of integration) is known as definite integral between the limits of integration. Thus, the integral, $\int_a^b f(x)\,dx$ is a definite integral between the numbers a and b and the numbers a and b are known as limits of integration. We infer that a is the lower limit, while b is the upper limit of the integral.

[IV] Theorems of Integration

(1) If the two functions are $f(x)$ and $g(x)$, then

$$\int [f(x) \pm g(x)]\,dx = \int f(x)\,dx \pm \int g(x)\,dx$$

(2) If the function is $f(x)$ and c is a constant, then

$$\int c\,f(x)\,dx = c\int f(x)\,dx$$

[V] Elementary Standard Formulae for Integration

(1) $\int x^n\,dx = \frac{x^{n+1}}{n+1}$ $[n \neq -1]$, if $n = 0$, then $\int dx = x$

(2) $\int k dx = kx$, k = constant

(3) $\int \frac{1}{x}\,dx = \log_e x$

(4) $\int e^x\,dx = e^x$

(5) $\int a^x\,dx = a^x \log_a e$

(6) $\int \sin x\,dx = -\cos x$

(7) $\int \cos x\,dx = \sin x$

(8) $\int \sec^2 x\,dx = \tan x$

(9) $\int \tan x\,dx = \log_e \sec x$

(10) $\int \cot x \, dx = \log_e \sin x$

(11) $\int \sec x \, dx = \log_e \left[\tan \left(\frac{\pi}{4} + \frac{x}{2} \right) \right] = \log_e (\sec x + \tan x)$

(12) $\int \operatorname{cosec} x \, dx = \log_e (\operatorname{cosec} x - \cot x) = \log_e (\tan x/2)$

(13) $\int \frac{dx}{\sqrt{1 - x^2}} = \sin^{-1} x$ (14) $\int \frac{(-1)}{\sqrt{1 - x^2}} dx = \cos^{-1} x$

(15) $\int \frac{dx}{1 + x^2} = \tan^{-1} x$ (16) $\int \frac{(-1) \, dx}{1 + x^2} = \cot^{-1} x$

(17) $\int \frac{dx}{x \sqrt{x^2 - 1}} = \sec^{-1} x$ (18) $\int \frac{(-1) \, dx}{x \sqrt{x^2 - 1}} = \operatorname{cosec}^{-1} x$

Problem 1. ***Evaluate the following integrals :***

(i) $\int x^7 \, dx$ *(ii)* $\int e^x \, dx$ *(iii)* $\int x^{-10/3} \, dx$

Solution. (i) $\int x^7 \, dx = \frac{x^{7+1}}{7+1} = \frac{x^8}{8}$

(ii) $\int e^x \, dx = e^x$

(iii) $\int x^{-10/3} \, dx = \frac{x^{-10/3+1}}{(-10/3)+1} = \frac{x^{-7/3}}{-7/3} = -\frac{3}{7} x^{-7/3} = -\frac{3}{7} \cdot \frac{1}{x^{7/3}}$

Problem 2. ***Find the value of the following integrals :***

(i) $\int (x^3 + 2x + 7) \, dx$ *(ii)* $\int \left(\frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3} + 1 \right) dx$

(iii) $\int (x^3 - 2)^2 \, dx$ *(iv)* $\int \frac{k}{x^3} \, dx$

Solution. (i) $\int (x^3 + 2x + 7) \, dx = \int x^3 \, dx + \int 2x \, dx + \int 7 \, dx$

$$= \frac{x^4}{4} + \frac{2x^2}{2} + 7x$$

$$= \frac{x^4}{4} + x^2 + 7x$$

(ii) $\int \left(\frac{1}{x} + \frac{1}{x^2} + \frac{1}{x^3} + 1 \right) dx = \int \frac{1}{x} dx + \int \frac{1}{x^2} dx + \int \frac{1}{x^3} dx + \int dx$

$$= \int \frac{1}{x}\,dx + \int x^{-2}\,dx + \int x^{-3}\,dx + \int dx$$

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

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

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

(iii) $\int (x^3 - 2)^2\,dx = \int (x^6 + 4 - 4x^3)\,dx$

$$= \int x^6\,dx + \int 4\,dx - \int 4x^3\,dx$$

$$= \frac{x^7}{7} + 4x - \frac{4\,x^{3+1}}{3+1}$$

$$= \frac{x^7}{7} + 4x - \frac{4x^4}{4}$$

$$= \frac{x^7}{7} + 4x - x^4$$

(iv) $\int \frac{k}{x^3}\,dx = \int k\,x^{-3}\,dx$

$$= \frac{k\,.\,x^{-3+1}}{-3+1} = k\,.\,\frac{x^{-2}}{-2}$$

$$= \frac{-kx^{-2}}{2} = -\,k\,.\,\frac{1}{2x^2}$$

Problem 3. ***Evaluate the following integrals :***

(i) $\int \frac{dx}{1 - \sin x}$ *(ii)* $\int \tan^2 x\,dx$

Solution. (i) $\int \frac{dx}{1 - \sin x} = \int \frac{(1 + \sin x)\,dx}{(1 - \sin x)\,(1 + \sin x)}$

$$= \int \frac{(1 + \sin x)\,dx}{1 - \sin^2 x}$$

$$= \int \frac{(1 + \sin x)\,dx}{\cos^2 x}$$

$$= \int \left[\frac{1}{\cos^2 x} + \frac{\sin x}{\cos^2 x}\right] dx$$

$$= \int \sec^2 x\,dx + \int \tan x\,.\,\sec x\,dx$$

$$= \tan x + \sec x$$

(ii) $$\int \tan^2 x\, dx = \int (\sec^2 x - 1)\, dx$$

$$= \int \sec^2 x\, dx - \int dx$$

$$= \tan x - x$$

Problem 4. ***Find the values of the following integrals :***

(i) $\displaystyle\int \frac{x^4}{x^2+1}\, dx$ *(ii)* $\displaystyle\int \frac{(x+a)^3}{2\sqrt{x}}\, dx.$

Solution. (i) $$\int \frac{x^4}{x^2+1}\, dx = \int \frac{x^4 - 1 + 1}{x^2+1}\, dx$$

$$= \int \frac{x^4-1}{x^2+1}\, dx + \int \frac{1}{x^2+1}\, dx$$

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

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

$$= \int x^2\, dx - \int dx + \int \frac{dx}{x^2+1}$$

$$= \frac{x^3}{3} - x + \tan^{-1} x$$

(ii) $$\int \frac{(x+a)^3\, dx}{2\sqrt{x}} = \frac{1}{2}\int \frac{(x^3 + 3x^2 a + 3xa^2 + a^3)}{\sqrt{x}}\, dx$$ [On expanding $(x+a)^3$]

$$= \frac{1}{2}\int \frac{x^3}{\sqrt{x}}\, dx + \frac{1}{2}\int \frac{3x^2 a}{\sqrt{x}}\, dx + \frac{1}{2}\int \frac{3xa^2}{\sqrt{x}}\, dx + \frac{1}{2}\int \frac{a^3}{\sqrt{x}}\, dx$$

$$= \frac{1}{2}\int x^{(3-1/2)}\, dx + \frac{3a}{2}\int x^{3/2}\, dx + \frac{3a^2}{2}\int x^{1/2}\, dx + \frac{a^3}{2}\int x^{-1/2}\, dx$$

$$= \frac{1}{2}\int x^{5/2}\, dx + \frac{3a}{2}\int x^{3/2}\, dx + \frac{3a^2}{2}\int x^{1/2}\, dx + \frac{a^3}{2}\int x^{-1/2}\, dx$$

$$= \frac{1}{2}\cdot\frac{x^{5/2+1}}{5/2+1} + \frac{3a}{2}\cdot\frac{x^{3/2+1}}{3/2+1} + \frac{3a^2}{2}\cdot\frac{x^{1/2+1}}{1/2+1} + \frac{a^3}{2}\cdot\frac{x^{-1/2+1}}{-1/2+1}$$

$$= \frac{1}{2}\cdot\frac{x^{7/2}}{7/2} + \frac{3a}{2}\cdot\frac{x^{5/2}}{5/2} + \frac{3a^2}{2}\cdot\frac{x^{3/2}}{3/2} + \frac{a^3}{2}\cdot\frac{x^{1/2}}{1/2}$$

$$= \frac{1}{7}x^{7/2} + \frac{3a}{5}\, x^{5/2} + a^2 x^{3/2} + a^3 x^{1/2}$$

[VI] Methods of Integration

Integration can be carried out by the following methods :

(1) Integration by substitution : In case the integral is not easy to integrate using the formula directly, we can use *substitution method.* In this method, we substitute the new variable t, u or v etc in place of x by using some suitable relation betwen x and the new variable. So, the integral is changed into new variable which is directly solved by using the standard formulae. After integration, we use the back substitution from new variable to the original variable x.

Problem 5. ***Evaluate the following integrals by substitution method :***

(i) $\int (ax+b)^7\,dx$ *(ii)* $\int e^{10x}\,dx$

(ii) $\int \sqrt{ax+b}\,dx$ *(iv)* $\int \cos(ax+b)\,dx$

Solution. (i) In $\int (ax+b)^7\,dx$, put $ax+b=t$, so that

$$adx = dt$$

or $$dx = \frac{dt}{a}$$

$$\therefore \quad \int (ax+b)^7\,dx = \int t^7 \frac{dt}{a} = \frac{1}{a}\int t^7\,dt$$

$$= \frac{1}{a}\left(\frac{t^8}{8}\right)$$

$$= \frac{1}{8a}(ax+b)^8$$

(ii) In $\int e^{10x}\,dx$, put $10x=t$, so that $dx = \frac{dt}{10}$

$$\therefore \quad \int e^{10x}\,dx = \int e^t \frac{dt}{10} = \frac{1}{10}\int e^t\,dt$$

$$= \frac{1}{10}e^t = \frac{1}{10}e^{10x}$$

(iii) In $\int \sqrt{ax+b}\,dx$, put $ax+b=t$

$$\therefore \quad a\,dx = dt \quad \text{or} \quad dx = \frac{dt}{a}$$

$$\therefore \quad \int \sqrt{ax+b}\,dx = \int \sqrt{t}\,.\,\frac{dt}{a} = \frac{1}{a}\int t^{1/2}\,dt$$

$$= \frac{1}{a}\cdot\frac{t^{1/2+1}}{1/2+1} = \frac{1}{a}\cdot\frac{t^{3/2}}{(3/2)}$$

$$= \frac{2}{3a}\,.\,(ax+b)^{3/2}$$

(iv) In $\int \cos(ax+b)\,dx$, put $ax+b=t$

$\therefore \quad a\,dx = dt \quad \text{or} \quad dx = \frac{dt}{a}$

$$\therefore \quad \int \cos(ax+b)\,dx = \int \cos t \,.\, \frac{dt}{a} = \frac{1}{a}\int \cos t\,dt$$

$$= \frac{1}{a}\sin t = \frac{1}{a}\sin(ax+b)$$

Problem 6. ***Evaluate the following integrals :***

(i) $\int \frac{e^x}{e^x+1}\,dx$ *(ii)* $\int \frac{\log x}{x}\,dx$

(iii) $\int x \sin x^2\,dx$ *(iv)* $\int \frac{x^5}{1+x^{12}}\,dx$

(v) $\int \frac{e^x}{1+e^{2x}}\,dx$ *(vi)* $\int \frac{dx}{x\sqrt{x^4-1}}$

Solution. (i) In $\int \frac{e^x}{e^x+1}\,dx$, put $e^x + 1 = t$

$\therefore \quad e^x\,dx = dt$

$$\therefore \quad \int \frac{e^x\,dx}{e^x+1} = \int \frac{dt}{t} = \log_e t$$

$$= \log_e(e^x+1)$$

(ii) In $\int \frac{\log x}{x}\,dx$, put $\log x = t$

$\therefore \quad \frac{1}{x}\,dx = dt$

$$\therefore \quad \int \frac{\log x}{x}\,dx = \int t\,dt = \frac{t^2}{2}$$

$$= \frac{(\log x)^2}{2}$$

(iii) In $\int x \sin x^2\,dx$, put $x^2 = t$

$\therefore \quad 2x\,dx = dt \quad \text{or} \quad x\,dx = \frac{dt}{2}$

$$\therefore \quad \int x\sin x^2\,dx = \int \sin t\left(\frac{dt}{2}\right) = \frac{1}{2}\int \sin t\,dt$$

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

(iv) In $\int \frac{x^5}{1+x^{12}}\,dx$, put $x^6 = t$

$\therefore \quad 6x^5\,dx = dt \quad \text{or} \quad x^5\,dx = \frac{dt}{6}$

$$\therefore \quad \int \frac{x^5}{1+x^{12}}\,dx = \frac{1}{6}\int \frac{dt}{1+t^2} = \frac{1}{6}\tan^{-1} t$$

$$= \frac{1}{6}\tan^{-1} x^6.$$

(v) In $\int \frac{e^x}{1+e^{2x}}\,dx$, put $e^x = t$

$$\therefore \quad e^x\,dx = dt$$

$$\therefore \quad \int \frac{e^x}{1+x^{2x}}\,dx = \int \frac{dt}{1+t^2} = \tan^{-1} t$$

$$= \tan^{-1} e^x.$$

(vi) In $\int \frac{dx}{x\sqrt{x^4-1}}$, put $x^2 = t$

$$\therefore \quad 2x\,dx = dt \qquad \text{or} \qquad x\,dx = \frac{dt}{2}$$

$$\therefore \quad \int \frac{dx}{x\sqrt{x^4-1}} = \int \frac{x\,dx}{x^2\sqrt{x^4-1}} = \frac{1}{2}\int \frac{dt}{t\sqrt{t^2-1}}$$

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

Problem 7. ***Evaluate the following integrals :***

(i) $\int \frac{2x+3}{x^2+3x+2}\,dx$ ***(ii)*** $\int \frac{6x^2+7}{2x^3+7x}\,dx$

(iii) $\int \frac{1}{x\log x}\,dx$ ***(iv)*** $\int \frac{e^x - e^{-x}}{e^x + e^{-x}}\,dx$

Solution. (i) Put $x^2 + 3x + 2 = t$

$$\therefore \quad (2x+3)\,dx = dt$$

$$\therefore \quad \int \frac{2x+3}{x^2+3x+2}\,dx = \int \frac{dt}{t} = \log_e t$$

$$= \log_e (x^2 + 3x + 2)$$

(ii) Put $2x^3 + 7x = t$

$$\therefore \quad (6x^2+7)\,dx = dt$$

$$\therefore \quad \int \frac{6x^2+7}{2x^3+7x}\,dx = \int \frac{dt}{t} = \log_e t$$

$$= \log_e (2x^3 + 7x)$$

(iii) Put $\log x = t$ or $\frac{1}{x}\,dx = dt$

$$\therefore \quad \int \frac{1}{x\log x}\,dx = \int \frac{dt}{t} = \log_e t$$

$$= \log_e (\log x)$$

(iv) Put $e^x + e^{-x} = t$

$\therefore$ $(e^x - e^{-x})\, dx = dt$

$\therefore$ $$\int \frac{e^x - e^{-x}}{e^x + e^{-x}}\, dx = \int \frac{dt}{t} = \log_e t = \log_e (e^x + e^{-x})$$

---

(2) Integration by parts : If $f(x)$ and $g(x)$ are two functions, then we have

$$\int f(x)\, g(x)\, dx = f(x) \int g(x)\, dx - \int \left\{ \frac{d}{dx} f(x) \cdot \int g(x)\, dx \right\} dx$$

Problem 8. ***Evaluate the following integrals :***

(i) $\int \log x\, dx$ *(ii)* $\int x e^x\, dx$

(iii) $\int x \log x\, dx$ *(iv)* $\int x^2 e^x\, dx$

(v) $\int x \sin x\, dx$ *(vi)* $\int \sin^{-1} x\, dx$

Solution. (i) $$\int \log x\, dx = \int 1 \cdot \log x\, dx$$

$$= \log x \int dx - \int \left\{ \frac{d}{dx} (\log x) \int dx \right\} dx$$

$$= x \log x - \int \frac{1}{x} \cdot x\, dx$$

$$= x \log x - \int dx$$

$$= x \log x - x = x (\log x - 1)$$

(ii) $$\int x e^x\, dx = x \int e^x\, dx - \int \left\{ \frac{d}{dx} (x) \cdot \int e^x\, dx \right\} dx$$

$$= x e^x - \int 1 \cdot e^x\, dx$$

$$= x e^x - \int e^x\, dx = x e^x - e^x$$

$$= e^x (x - 1)$$

(iii) $$\int x \log x\, dx = \log x \int x\, dx - \int \left\{ \frac{d}{dx} (\log x) \cdot \int x\, dx \right\} dx$$

$$= \frac{x^2}{2} \log x - \int \frac{1}{x} \cdot \frac{x^2}{2}\, dx$$

$$= \frac{x^2}{2} \log x - \frac{1}{2} \int x \, dx$$

$$= \frac{x^2}{2} \log x - \frac{1}{2} \frac{x^2}{2}$$

$$= \frac{x^2}{2} \left(\log x - \frac{1}{2} \right)$$

$$= \frac{x^2}{4} (2 \log x - 1)$$

(iv) $$\int x^2 e^x \, dx = x^2 \int e^x \, dx - \int \left\{ \frac{d}{dx} (x^2) \int e^x \, dx \right\} dx$$

$$= x^2 e^x - \int 2x \, . \, e^x \, dx$$

$$= x^2 e^x - 2 \left[x \int e^x \, dx - \int \left\{ \frac{d}{dx} (x) \int e^x \, dx \right\} dx \right]$$

$$= x^2 e^x - 2 \left[x e^x - \int 1 \, . \, e^x \, dx \right]$$

$$= x^2 e^x - 2 \, (x e^x - e^x)$$

$$= x^2 e^x - 2x e^x + 2e^x$$

$$= e^x \, (x^2 - 2x + 2)$$

(v) $$\int x \sin x \, dx = x \int \sin x \, dx - \int \left\{ \frac{d}{dx} (x) \int \sin x \, dx \right\} dx$$

$$= x \, (- \cos x) - \int 1 \, . \, (- \cos x) \, dx$$

$$= - x \cos x + \int \cos x \, dx$$

$$= - x \cos x + \sin x$$

(vi) $$\int \sin^{-1} x \, dx = \int 1 \, . \, \sin^{-1} x \, dx$$

$$= \sin^{-1} x \int dx - \int \left\{ \frac{d}{dx} (\sin^{-1} x) \int dx \right\} dx$$

$$= x \sin^{-1} x - \int \frac{1}{\sqrt{1 - x^2}} \, . \, x \, dx$$

Put $1 - x^2 = t$

or $\quad - 2x \, dx = dt$

∴ $\quad x \, dx = - \frac{dt}{2}$

$$\therefore \quad \int \frac{1}{\sqrt{1-x^2}}\,dx = -\frac{1}{2}\int \frac{dt}{\sqrt{t}} = -\frac{1}{2}\int t^{-1/2}\,dt = -\frac{1}{2}\cdot\frac{t^{-1/2+1}}{-1/2+1}$$

$$= -\frac{1}{2}\,2\sqrt{t} = -\sqrt{t} = -\sqrt{1-x^2}$$

$$\therefore \quad \int \sin^{-1} x\,dx = x\sin^{-1} x - (-\sqrt{1-x^2})$$

$$= x\sin^{-1} x + \sqrt{1-x^2}$$

Problem 9. ***Evaluate the following integrals :***

(i) $\int e^x \sin x\,dx$ *(ii)* $\int \frac{e^x(1+x\log x)}{x}\,dx$

Solution. (i) Let $I = \int e^x \sin x\,dx$

$$= \sin x \int e^x\,dx - \int\left\{\frac{d}{dx}(\sin x)\int e^x\,dx\right\}dx$$

$$= e^x \sin x - \int \cos x \,.\, e^x\,dx$$

$$= e^x \sin x - \left[\cos x \int e^x\,dx - \int \frac{d}{dx}(\cos x)\int e^x\,dx\right]dx$$

$$= e^x \sin x - \left[e^x \cos x - \int -\sin x \,.\, e^x\,dx\right]$$

$$= e^x \sin x - \left[e^x \cos x + \int \sin x\, e^x\,dx\right]$$

$$\therefore \quad I = e^x \sin x - e^x \cos x - \int (\sin x)\, e^x\,dx$$

or $$I = e^x \sin x - e^x \cos x - I$$

or $$2I = e^x \sin x - e^x \cos x$$

$$\therefore \quad I = \frac{1}{2}e^x(\sin x - \cos x)$$

(ii) $$\int \frac{e^x(1+x\log x)}{x}\,dx = \int e^x\left[\frac{1}{x} + \log x\right]dx$$

$$= \int e^x \,.\, \frac{1}{x}\,dx + \int e^x \log x\,dx$$

$$= e^x \int \frac{1}{x}\,dx - \int\left\{\frac{d}{dx}(e^x)\int \frac{1}{x}\,dx\right\}dx + \int e^x \log x\,dx$$

$$= e^x \log x - \int e^x \log x\,dx + \int e^x \log x\,dx$$

$$= e^x \log x$$

(3) Integration using partial fractions : If we have to integrate any rational function, we first split it into partial fractions. Some partial fractions for the given function are as follows :

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

(b) $\frac{f(x)}{(x-a)(x-b)(x-c)} = \frac{A}{(x-a)} + \frac{B}{(x-b)} + \frac{C}{(x-c)}$

(c) $\frac{f(x)}{(x-a)^2(x-b)} = \frac{A}{x-a} + \frac{B}{(x-a)^2} + \frac{C}{x-b}$

Problem 10. ***Evaluate the following integrals :***

(i) $\int \frac{dx}{x^2 - 3x + 2}$ *(ii)* $\int \frac{dx}{(x-a)(x-b)}$

(iii) $\int \frac{dx}{(x-3)(x+5)}$ *(iv)* $\int \frac{x^2\,dx}{(x-1)^2(x+2)}$

Solution. (i) $\int \frac{dx}{x^2 - 3x + 2} = \int \frac{dx}{(x-1)(x-2)}$

Let $\frac{1}{(x-1)(x-2)} = \frac{A}{(x-1)} + \frac{B}{(x-2)}$

or $\frac{1}{(x-1)(x-2)} = \frac{A(x-2) + B(x-1)}{(x-1)(x-2)}$

or $1 = A(x-2) + B(x-1)$ ... (1)

Put $x = 1$ in equation (1), we get

$1 = A(1-2) = -A$

Now put $x = 2$ in equation (1), we get

$1 = B.1$ or $B = 1$

$\therefore$ $\frac{1}{(x-1)(x-2)} = \frac{1}{[(-1)-(-2)]}\left[\frac{1}{(x-1)} - \frac{1}{(x-2)}\right]$

or $\int \frac{dx}{(x-1)(x-2)} = \int \frac{dx}{(x-1)} - \int \frac{dx}{(x-2)}$

$= \log_e (x-1) - \log_e (x-2)$

$= \log_e \frac{(x-1)}{(x-2)}.$

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

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

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

Put $x = a$ in equation (1), we get,

$1 = A(a-b)$

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

Now put $x = b$ in equation (1), we get,

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

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

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

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

$$= \frac{1}{(a-b)}[\log_e (x-a) - \log_e (x-b)]$$

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

(iii) Let $$\frac{x}{(x-3)(x+5)} = \frac{A}{(x-3)} + \frac{B}{(x+5)}$$

or $$x = A(x+5) + B(x-3) \qquad \ldots (1)$$

Putting $x = -5$ and 3 in equation (1), we can find

$$A = \frac{3}{8}, B = \frac{5}{8}$$

$\therefore$ $$\frac{x}{(x-3)(x+5)} = \frac{3}{8(x-3)} + \frac{5}{8(x+5)}$$

$\therefore$ $$\int \frac{x\,dx}{(x-3)(x+5)} = \frac{3}{8}\int \frac{dx}{(x-3)} + \frac{5}{8}\int \frac{dx}{(x+5)}$$

$$= \frac{3}{8}\log_e (x-3) + \frac{5}{8}\log_e (x+5)$$

(iv) Let $$\frac{x^2}{(x-1)^2(x+2)} = \frac{A}{(x-1)} + \frac{B}{(x-1)^2} + \frac{C}{(x+2)}$$

or $$x^2 = A(x-1)(x+2) + B(x+2) + C(x-1)^2 \qquad \ldots (1)$$

Putting $x = 1, -2$ in equation (1), we get,

$$B = \frac{1}{3}, \quad C = \frac{4}{9}$$

Conparing the coefficients of x^2 on both sides of equation (1), we get

$$1 = A + C$$

or $$A = 1 - C = 1 - \frac{4}{9} = \frac{5}{9}$$

$\therefore$ $$\frac{x^2}{(x-1)^2(x+2)} = \frac{5}{9(x-1)} + \frac{1}{3(x-1)^2} + \frac{4}{9(x+2)}$$

$\therefore$ $$\int \frac{x^2}{(x-1)^2(x+2)}dx = \frac{5}{9}\int \frac{dx}{(x-1)} + \frac{1}{3}\int \frac{dx}{(x-1)^2} + \frac{4}{9}\int \frac{dx}{(x+2)}$$

$$= \frac{5}{9}\log_e (x-1) + \frac{1}{3(x-1)} + \frac{4}{9}\log_e (x+2)$$

1.11. PERMUTATION AND COMBINATION

[I] Introduction

Consider three objects A, B, C. From these, selecting two objects at a time, we can form three groups, *viz.*, AB, BC, AC.

On the other hand, we can formthe following six arrangements of these three objects taking two at a time.

AB, BA, BC, CB, AC, CA.

Obviously, AB and BA differ in way of writing them otherwise both involves the same pair of objects. Thus, when we talk of "arrangements" we also distinguish between their ways of writing.

[II] Permutations

The different arrangements of given things made by selecting few or all of the given objects, are called permutations. The total number of permutations of n objects made by selecting r at a time, is denoted by ${}^nP_r$. Thus, from the above example ${}^3P_2 = 6$.

[III] The Fundamental Principle of Counting

If an event occurs in p ways and if after the occurrence of this event in any one of the p ways, another event occurs in q ways, then the number of different ways in which both events can occur, is $p \times q$.

[IV] Determination of Number of Permutations of *n*-Distinguishable Objects Taken *r* at a Time

To find the number of permutations of n dissimilar objects taken r at a time, without repeating the objects. In this problem, we are to find the number of arrangements in which the groups of r objects out of n given objects can be arranged. This amounts to finding the number of ways in which r empty places can be filled by the given n objects.

The first place can be filled in n ways as any one of the n given objects can be put. After filling the first place in any one of the n ways, the second place can be filled by any one of the remaining $(n - 1)^*$ objects in $(n - 1)$ ways, *i.e.*, corresponding to each of the n ways of filling the first place, there are $(n - 1)$ ways of filling the second place. Hence, the two places can be filled in $n \times (n - 1)$ ways. Now, when the first two places have been filled in any one of the $n \times (n - 1)$ ways, we are left with $(n - 2)$ objects to fill up the third place. Therefore, the third place can be filled in $(n - 2)$ ways. Hence, the first three places can be filled in $n\,(n - 1)\,(n - 2)$ different ways.

Continuing in this way, we find that the r places can be filled in

$$[n \times (n-1) \times (n-2) \times (n-3) \times \ldots \text{ upto } r \text{ factor}] \text{ ways,}$$

i.e., in $$(n-1) \times (n-2) \times (n-3) \times \ldots \times [n-(r-1)] \text{ ways}$$

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*We assumed that the objects cannot be repeated, *i.e.*, in one arrangement one particular objects cannot be used more than once. Therefore, the objects which is placed at the first place cannot be placed on any other place.

or in $n(n-1)(n-2)\ldots(n-r+1)$ ways.

Thus, $${}^nP_r = n(n-1)(n-2)(n-3)\ldots(n-r+1) \qquad \ldots (1)$$

where ${}^nP_r$ denotes the number of permutations of n different objects taking r at a time.

[V] Factorial Notation

The product of first n natural numbers is denoted by symbl $n\,!$ and is read as *factorial n*. Thus

$$n\,! = 1\,.\,2\,.\,3\,.\,4\ldots(n-2)\,.\,(n-1)\,.\,n.$$

It is customary to write it is

$$n\,! = n(n-1)(n-2)(n-3)\ldots3\,.\,2\,.\,1 \qquad \ldots (2)$$

For instance, $3\,! = 3\,.\,2\,.\,1 = 6$,

$5\,! = 5\,.\,4\,.\,3\,.\,2\,.\,1 = 120$, and so on.

According to the above definition, we observe that

$$4\,! = 4\,.\,3\,.\,2\,.\,1 = 4\,.\,3\,! = 4\,.\,3\,.\,2\,!$$
$$5\,! = 5\,.\,4\,.\,3\,.\,2\,.\,1 = 5\,.\,4\,.\,3\,! = 5\,.\,4\,.\,3\,.\,2\,!$$

....

....

$$r\,! = r\,.\,(r-1)\,! = r\,.\,(r-1)\,.\,(r-2)\,!$$
$$= r\,.\,(r-1)\,.\,(r-2)\,.\,(r-3)\,!$$
$$\therefore\ n\,! = n\,(n-1)\,! \qquad \ldots (3)$$
$$= n\,(n-1)\,.\,(n-2)\,! = n\,.\,(n-1)\,.\,(n-2)\,.\,(n-3)\,!$$

[VI] Formula for the Value of ${}^nP_r$.

From equation (1), we have

$${}^nP_r = n(n-1)(n-2)(n-3)\ldots(n-r+1)$$
$$\frac{[n(n-1)\,.\,(n-2)(n-3)\ldots(n-r+1)]\,[(n-r)\ldots3\,.\,2\,.\,1]}{[(n-r)(n-r-1)\ldots3\,.\,2\,.\,1]}$$

[Multiplying above and below by $(n-r)\,.\,(n-r-1)\,.\,3\,.\,2\,.\,1$]

$$= \frac{n\,.\,(n-1)\,.\,(n-2)\,.\,(n-3)\ldots3\,.\,2\,.\,1}{(n-r)\,.\,(n-r-1)\ldots3\,.\,2\,.\,1} = \frac{n!}{(n-r)\,!}$$

$$\therefore \qquad {}^nP_r = \frac{n\,!}{(n-r)\,!} \qquad \ldots (4)$$

[VII] Important Formulae for Finding the Number of Permutations

(i) Number of permutations of n distinct objects taken r at a time $= {}^nP_r$.

(ii) If $n = p + q + r + t$ where p are of one type, q are of second type, r of third type and t are of different types. Then the total number of permutations $= \frac{n!}{p!\,q!\,r!}$.

(iii) The number of permutations of n distinct objects taken r at a time when each object may be repeated once, twice, . . . up to r times $= n^r$.

(iv) The number of permutations of n distinct objects taken r at a time when a particular object is always taken from $r = r \times {}^{n-1}P_{r-1}$.

[VIII] Cyclic or Circular Permutation

The number of ways to arrange all or some objects out of given objects in a circle or around a round table, are known as circular permutations.

[IX] Important Formulae Related to Circular Permutation

(i) The number of circular permutations of n distinct objects taken r at a time when the clockwise and anticlockwise arrangements are distinguishable $= \dfrac{{}^nP_r}{r}$.

(ii) In the above case when clockwise and anticlockwise arrangements are indistinguishable $= \dfrac{1}{2} \cdot \dfrac{{}^nP_r}{r}$.

(iii) The number of circular permutations of n distinct objects taken all at a time when the clockwise and anticlockwise arrangements are distinguishable $= (n-1)!$.

(iv) The number of circular permutations of n distinct objects taken all at a time when the clockwise and anticlockwise arrangements are indistinguishable $= \dfrac{(n-1)!}{2}$.

Note :

(1) The number of permutations of n persons on a round table $= (n-1)!$.

(2) The number of permutations of n flowers to make a garland $= \dfrac{1}{2}[(n-1)!]$.

Problem 1. ***To prove that*** **$0! = 1$.**

Solution. The number of permutations of n different objects taking all of them at a time, is

$$^nP_n = (n-1)(n-2) \ldots (n-n+1)$$

[By putting $r = n$ in equation (1)]

$$= n(n-1)(n-2) \ldots 1 = n!$$

$$^nP_n = n!. \quad \ldots (5)$$

Also by the formula (4), $^nP_n = \dfrac{n!}{(n-n)!} = \dfrac{n!}{0!}$. ... (6)

∴ From equations (5) and (6) we get

$$n! = \frac{n!}{0!} \text{ or } \mathbf{0! = 1}. \quad \ldots (7)$$

Problem 2. ***Find the value of*** **$^6P_3$.**

Solution. $^6P_3 = \dfrac{6!}{(6-3)!} = \dfrac{6!}{3!} = \dfrac{6 \cdot 5 \cdot 4 \cdot 3!}{3!} = 6 \cdot 5 \cdot 4 = 120.$

Problem 3. ***Prove that*** $^{2n}P_n = 2^n\,[1\,.\,3\,.\,5\,\ldots\,(2n-1)]$.

Solution.

$$^{2n}P_n = \frac{2n\,!}{(2n-n)\,!} = \frac{2n!}{n\,!}$$

$$= \frac{2n\,.\,(2n-1)\,.\,(2n-2)\,\ldots\,5\,.\,4\,.\,3\,.\,2\,.\,1}{n!}$$

$$= \frac{[2n\,.\,(2n-2)\,\ldots\,4\,.\,2]\,[(2n-1)\,\ldots\,5\,.\,3\,.\,1]}{n!}$$

$$= \frac{2^n\,[\,n\,.\,(n-1)\,\ldots\,2\,.\,1]\,[(2n-1)\,\ldots\,5\,.\,3\,.\,1]}{n!}$$

$$= 2^n\,.\,\frac{n!\,[(2n-1)\,\ldots\,5\,.\,3\,.\,1]}{n!}$$

$$= 2^n\,.\,[1\,.\,3\,.\,5\,\ldots\,(2n-1)].$$

Problem 4. ***If*** $^{2n+1}P_{n-1} : {}^{2n-1}P_n = 3 : 5$, ***find the value of n.***

Solution. $^{2n+1}P_{n-1} : {}^{2n-1}P_n = 3 : 5$

$$\frac{^{2n+1}P_{n-1}}{^{2n-1}P_n} = \frac{3}{5}$$

or $$\frac{\dfrac{(2n+1)}{(2n+1-n+1)\,!}}{\dfrac{(2n-1)\,!}{(2n-1-n)\,!}} = \frac{3}{5} \quad \text{or} \quad \frac{\dfrac{(2n+1)\,!}{(n+2)\,!}}{\dfrac{(2n-1)\,!}{(n-1)\,!}} = \frac{3}{5}$$

or $$\frac{(2n+1)\,!}{(n+2)\,!}\cdot\frac{(n-1)\,!}{(2n-1)\,!} = \frac{3}{5}$$

or $$\frac{(2n+1)\,.\,2n\,(2n-1)\,!}{(n+2)\,.\,(n+1)\,.\,n\,(n-1)!}\cdot\frac{(n-1)!}{(2n-1)\,!} = \frac{3}{5}$$

or $$\frac{(2n+1)\,.\,2n}{(n+2)\,.\,(n+1)\,.\,n} = \frac{3}{5} \quad \text{or} \quad \frac{4n+2}{n^2+3n+2} = \frac{3}{5}$$

or $$20n + 10 = 3n^2 + 9n + 6$$

or $$3n^2 - 11n - 4 = 0 \quad \text{or} \quad (3n+1)\,(n-4) = 0.$$

$\therefore$ $n = 4$ or $n = -\frac{1}{3}$ which is impossible.

Hence, $n = 4$.

Problem 5. ***Prove that*** $^nP_r = n \times {}^{n-1}P_{r-1}$.

Solution. R.H.S. $= n \times {}^{n-1}P_{r-1} = \dfrac{n\,(n-1)\,!}{[n-1-(r-1)]\,!}$

$$= \frac{n\,!}{(n-1-r+1)\,!} = \frac{n\,!}{(n-r)\,!} = {}^nP_r = \text{L.H.S.}$$

Problem 6. ***Three persons enter into a car of five seats. In how many ways can they occupy their seats?***

Solution. First person can sit in five ways as all the five seats are lying vacant at the time of his entrance. The second person can sit on any one of the remaining four seats (one is already filled by first person). So, the second person can sit in 4 different ways. Similarly, third person can sit in 3 different ways on any one of the three vacant seats (two already filled). Hence, all the three can sit in 5 × 4 × 3 = 60 different ways.

Problem 7. ***(i) How many words can be formed with the letters of the word "DELHI"?***

(ii) How may of these will begin with D?

(iii) How many of these will end at D?

(iv) How many of these will begin with D or L?

(v) How many of these will begin with D and end at L?

(vi) How many of these will begin with D or end at L?

(vii) How many of the vowels "E, I" occupy the even number of places?

(viii) How many of these will end at vowel only?

(ix) In how many of these vowels come together?

(x) How many of these will begin and end at vowel?

(xi) How many of these will begin and end with D or L?

Solution. (i) There are five letters "D, E, L, H, I" in the word DELHI. These five letters can be rearranged among themselves in 5 ! = 120 ways, (or say ${}^5P_5$, *i.e.*, the number of permutations of these five letters taking all the five at a time). Hence, we can form 120 different words.

(ii) All the arrangements in which D is in the beginning can be obtained by fixing 'D' at the first place and then rearranging the remaining four letters. Remaining four letters can be arranged in 4 ! ways. Hence, in 4 ! = 24 arrangements the words will begin with D.

Alternatively. First place can be filled by D in 1 way only, the second place in 4 ways as any of the letters L, H, E, I can be put there; 3rd place can be filled in 3 ways, 4th place in 2 ways and 5th place in one way only. Hence, all the five can be filled in $1 \times 4 \times 3 \times 2 \times 1 = 4\,! = 24$ ways.

(iii) The problem is similar to problem (ii) except that now we fix the letter D on the last place. Hence, the remaining four letters can be arranged in 4 ! ways. Hence, the required number of words, ending at D, is 4 ! = 24.

(iv) As above there will be 4 ! arrangements starting with D, and also 4 ! arrangements will begin with L. Hence, the total number of arrangements beginning with D or L are 4 ! + 4 ! = 48.

Alternatively. First place can be filled in two ways as any of the letters D or L can be put there. Then second place can be filled in 4 ways as any one of the remaining four letters can be put there. The third place can be filled in three ways, fourth place in two ways and fifth place can be filled in one way only. Hence, all the five places can be filled in $2 \times 4 \times 3 \times 2 \times 1 = 48$ ways.

(v) In this we fix D at the beginning and L at the end. The remaining three letters E, H, I can be rearranged in 3 ! ways. Hence, 3 ! = 6 arrangements will begin with D and end at L.

(vi) The arrangements which begin with D are 4 ! and which end at L are also 4 !. Hence total number of arrangements which begin with D or end at L are 4 ! + 4 ! = 48.

(vii) There are only two even places namely 2nd, 4th. E and I can be rearranged on these places in 2 ! ways. Further, remaining three letters D, L, H can be put on 2st, 3rd and 5th places in 3 ! ways. Hence, the total number of arrangements in which E, I occur at even places only, is 2 ! × 3! = 12.

(viii) The arrangements ending at E or I give the arrangements ending at vowels. Such arrangements are 4 ! + 4 ! = 48. Proceed as in (iv).

(ix) We consider the two vowels forming as one letter say (E I). Thus there are four letters D, L, H, (E I). These can be rearranged in 4 ! ways. Further, two vowels E, I can be rearranged among themselves in 2 ! ways. Hence, total number of arrangements in which vowels come together is 2 ! × 4 ! = 48.

(x) We want to put E or I in the beginning and at the end. For the 3 ! arrangements will begin with E and end at I. Again 3 ! arrangements will begin with I and end at E. Hence, the number of required ways are 3 ! + 3 ! = 12.

(xi) As above the required number of ways is 12 (only letters E and I are replaced by D and L).

Problem 8. ***How many words can be formed with the letters of the word "MEERUT"? In how many of these words vowels occupy only even places?***

Solution: (i) There are 6 letters in the word "MEERUT", and the letter *E* is repeated 2 times in this word. Therefore, the total number of words that can be formed with the letters of the word "MEERUT"

$$= \frac{6!}{2!} = \frac{6 \times 5 \times 4 \times 3 \times (2!)}{2!}$$

$$= 6 \times 5 \times 4 \times 3 = 360$$

(ii) There are three even places in the word "MEERUT", namely, second, fourth and sixth places, respectively. At these places the vowels E, E and U are to be arranged. So, the number of ways to arrange E, E and U at these three places

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

Now at the odd places, the letters M, R, T are to be arranged; so the number of ways to arrange M, R, T at three odd places

$$= 3! = 6$$

Thus, the total number of words in which the vowels occupy even places = 3 × 6 = 18.

Problem 9. ***How many seven digited telephone numbers are possible if only odd digits may be used?***

Solution: There are 10 digits namely 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9. Out of these digits odd digits are 1, 3, 5, 7 and 9. Thus, there are 5 odd digits. Now seven digited telephone numbers are to be formed using 1, 3, 5, 7 and 9, so there will be a repetition of 1, 3, 5, 7 and 9. Also each place of a seven digited number can be filled by any five digits 1, 3, 5, 7 and 9. Thus, the total number of seven digited telephone numbers are

$$= 5 \times 5 \times 5 \times 5 \times 5 \times 5 \times 5$$

$$= 5^7$$

$$= 78125.$$

Problem 10. ***How many permutations can be made out of the letters of the word "BUSINESS". How many of these will begin with B and end with N?***

Solution: (i) There are 8 letters in the word "BUSINESS", and the letter S is repeated 3 times and others are different. Then the total number of words formed by the letters of the word "BUSINESS" are

$$= \frac{8!}{3!}$$

$$= 8 \times 7 \times 6 \times 5 \times 4 = 6720$$

(ii) If each word begins with letter B and ends with N, then except these two letters, the remaining letters are 6 and out of 6 the letter S is repeated 3 times.

Now in this case, the total words formed by the letters of word "BUSINESS" which begin with B and end with N are

$$= \frac{6!}{3!} = 6 \times 5 \times 4 = 120$$

[X] Combination

Combination is the number of selections or groups which can be made by taking some or all distinguishable objects or things.

(i) If A, B, C are three distinct objects, then the number of selections or groups which can be made by taking letters A, B, C two at a time are three, namely,

AB, BC, CA

From this it appears that in forming combinations we are only concerned with the number of objects each selection contains.

(ii) If there are four distinct letters, namely, A, B, C and D, then the number of groups which can be made by taking letters A, B, C, D two at a time are six, namely,

AB, BC, CD, CA, BD, DA

[XI] Combinations of *n* Distinguishable Objects Taken *r* at a Time

Let ${}^nC_r$ be the required number of combinations. Each of these combinations consists of a group of n distinct objects which can be arranged in r ways. Therefore, the number of arrangements of n objects taken r at a time $= {}^nC_r \times r!$.

The number of arrangements of n distinct objects taken r at a time $= {}^nP_r$

$$\therefore \qquad {}^nC_r \times r! = {}^nP_r = \frac{n!}{(n-r)!}$$

$$\Rightarrow \qquad {}^nC_r = \frac{n!}{r!\,(n-r)!}$$

Note :

(1) The number of combinations of n distinct objects taken r at a time is equal to the number of permutations of n distinct objects taken $(n-r)$ at a time, *i.e.*,

$${}^nC_r = {}^nC_{n-r}$$

(2) If ${}^nC_x = {}^nC_y$, either $x = y$ or $x + y = n$.

[XII] Important Formulae for Finding the Number of Combinations

(1) The number of combinations of n distinct objects taken r at a time subjected to the condition that p number of particular objects are always selected

$$= {}^{n-p}C_{r-p}$$

(2) The number of combinations of n objects taken r at a time when p particular objects are always discarded

$$= {}^{n-p}C_r$$

(3) The total number of combinations in which it is possible to make a selection by taking some or all of n objects $= 2^n - 1$.

(4) The number of ways in which $n = p + q + r$ objects can be divided into three groups containing p, q, r objects, respectively

$$= \frac{(p+q+r)\,!}{p\,!\,q\,!\,r\,!}$$

(5) If $p = q = r$, and the groups are equal, then in this case the number of different ways of sub-division is

$$\frac{(3p)!}{p!\,p!\,p!\,3!} = \frac{(3p)!}{[(p)^3!]\,3!}$$

(6) If $p = q = r$ and the groups are distinct, then the number of different ways of sub-division is

$$\frac{(3p)!}{p!\,p!\,p!}$$

Problem 11. ***Prove that*** $^nC_r = {}^nC_{n-r}$.

Solution. R.H.S. $= {}^nC_{n-r} = \dfrac{n\,!}{(n-r)\,!\,[n-(n-r)]\,!}$

$$= \frac{n\,!}{(n-r)\,!\,(n-n+r)\,!}$$

$$= \frac{n\,!}{(n-r)\,!\,r\,!}$$

$$= {}^nC_r = \text{L.H.S.}$$

Problem 12. ***Find the value of the following :***

(i) $^{24}C_4$ ***(ii)*** $^{20}C_{15}$

Solution. (i) $^{24}C_4 = \dfrac{24\,!}{4\,!\,(24-4)\,!}$ $\left[\because \; {}^nC_r = \dfrac{n\,!}{r\,!\,(n-r)\,!}\right]$

$$= \frac{24\,!}{4\,!\,20\,!}$$

$$= \frac{24 \times 23 \times 22 \times 21 \times (20!)}{4 \times 3 \times 2 \times 1 \times (20!)}$$

$$= \frac{24 \times 23 \times 22 \times 21}{4 \times 3 \times 2 \times 1}$$

$$= 6 \times 23 \times 11 \times 7$$

$$= 10626$$

(ii) $^{20}C_{15} = \dfrac{20!}{15!\,(20-15)!}$

$$= \frac{20!}{15!\,5!}$$

$$= \frac{20 \times 19 \times 18 \times 17 \times 16 \times 15!}{(15!) \times 5 \times 4 \times 3 \times 2 \times 1}$$

$$= \frac{20 \times 19 \times 18 \times 17 \times 16}{5 \times 4 \times 3 \times 2 \times 1}$$

$$= 4 \times 19 \times 6 \times 17 \times 2$$

$$= 15504$$

Problem 13. ***Find the value of r if*** $^{20}C_{r-1} = {}^{20}C_{r+1}$.

Solution. Since, we know that if $^nC_x = {}^nC_y$, then either $x = y$ or $x + y = n$

Here, $^{20}C_{r-1} = {}^{20}C_{r+1}$ and $r - 1 \neq r + 1$

So, $r + 1 + r - 1 = 20$ $(\because x + y = n)$

$\Rightarrow$ $2r = 20$

$\Rightarrow$ $r = 10$

Problem 14. ***In how many ways 11 players out of 16 cricket players can be selected?***

Solution. The number of ways to select 11 players out of 16 cricket players

$$= {}^{16}C_{11}$$

$$= \frac{16!}{11!\,(16-11)!}$$

$$= \frac{16!}{11!\,5!} = \frac{16 \times 15 \times 14 \times 13 \times 12 \times 11\,!}{11\,! \times 5\,!}$$

$$= \frac{16 \times 15 \times 14 \times 13 \times 12}{5 \times 4 \times 3 \times 2 \times 1}$$

$$= 2 \times 14 \times 13 \times 12$$

$$= 4368$$

Problem 15. ***In how many ways can a cricket eleven be chosen out of 15 players? How many of them will always (i) include a particular player? (ii) exclude a particular player?***

Solution. Number of ways of selecting cricket eleven

= Number of ways of selecting 11 players out of 15

$$= {}^{15}C_{11} = \frac{15!}{11!\,4!} = \frac{15\,.\,14\,.\,13\,.\,12\,.\,11!}{11!\,4.\,3.\,1} = 1365.$$

(i) Now since a player is to be included always, we are to select remaining 10 players out of the rest 14 players. This can be done in ${}^{14}C_{10} = 1001$ ways.

(ii) Again since a player is never to be included, *i.e.*, always excluded, we are selecting 11 players out of 14 only. This can be done in ${}^{10}C_{11} = 364$ ways.

Problem 16. ***Of 10 electric bulbs, three are faulty but it is not known, which one are faulty. In how many ways three bulbs can be selected? How many of these selections will include at least one faulty bulb?***

Solution. The three bulbs can be selected in ${}^{10}C_3$ ways = 120 ways.

Further, number of ways containing one faulty bulb

= Number of ways of selecting 2 clear bulbs × number of ways of selecting 1 faulty bulb

$= {}^{7}C_2 \times {}^{3}C_1$ [Note that 7 bulbs are clear and 3 faulty]

= 63.

Similarly, number of selections containing 2 faulty and 1 clear bulb

$$= {}^{7}C_1 \times {}^{3}C_2 = 7 \times 3 = 21.$$

Number of selections containing all the 3 faulty bulbs $= {}^{3}C_3 = 1$.

∴ Total number of selections including at least one faulty bulb

$$= 63 + 21 + 1 = 85.$$

Problem 17. ***How many triangles can be made by joining 12 points in a plane, given that 7 are in one line?***

Solution. The triangles can be formed by joining any three points. But 7 points are in one line. Hence, with three points out of these 7 points in one line, we cannot form a triangle. Hence, the required number of triangles is ${}^{12}C_3 - {}^{7}C_3 = 185$.

Alternative. Triangles can be formed in the following ways :

(i) Three points are taken from the five non-collinear points. Number of ways is ${}^{5}C_3 = 10$.

(ii) One point is taken from 5 non-collinear and 2 out of 7 collinear points. This can be done in ${}^{5}C_1 \times {}^{7}C_2$ ways = 105 ways.

(iii) Two points are taken from 5 non-collinear and 1 from 7 collinear points. This can be done in ${}^5C_2 \times {}^7C_1$ ways = 70 ways.

Therefore, the required number of triangles $= 10 + 105 + 70 = 185$. (Note that possibilities (i), (ii) are (iii) are mutually exclusive.)

Problem 18. ***Find the number of diagonals that can be drawn by joining anglar points of a sixteen sided figure?***

Solution. In a sixteen sided figure there will be 16 angular points (vertices).

Total number of lines which can be drawn by joining any two angular points $= {}^{16}C_2 = 120$.

But out of these lines, 16 will be sides. Hence, the required number of diagonals $= 120 - 16 = 104$.

Problem 19. ***There are six points on the circumference of a circle. How many straight lines can be drawn through these points?***

Solution : Here no three points lie on a line and through any two points, a straight line can be drawn. Therefore, the total number of lines that can be drawn from 6 points

$$= {}^6C_2$$

$$= \frac{6!}{2!\,4!} = \frac{6 \times 5}{2 \times 1} = 15$$

Problem 20. ***In how many ways can 12 things be divided equally among 4 persons?***

Solution: 12 things are divided equally among 4 persons, so each person gets three things. Therefore, the total number of ways

$$= \frac{12!}{3!\,3!\,3!\,3!}$$

$$= \frac{12 \times 11 \times 10 \times 9 \times 8 \times 7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1}{6 \times 6 \times 6 \times 6}$$

$$= \frac{479001600}{6 \times 6 \times 6 \times 6}$$

$$= 369600$$

Problem 21. ***A person has 6 friends. In how many ways can he invite one or more of them to dinner?***

Solution: Since the person has to select some or all of his friends, and, therefore, the number of ways is $2^6 - 1 = 64 - 1 = 63$.

Alternative: The guests may be invited, singly, in twos, threes, . . . etc., therefore, the number of selections

$$= {}^6C_1 + {}^6C_2 + {}^6C_3 + {}^6C_4 + {}^6C_5 + {}^6C_6$$

$$= 6 + 15 + 20 + 15 + 6 + 1$$

$$= 63$$

Problem 22. ***From 12 books in how many ways can a selection of 5 be made (i) when one specified book is always included, (ii) when one specified book is always excluded?***

Solution: (i) 5 books are to be selected out of 12 books with the condition that one specified book is always included. Then the number of ways

$$= {}^{12-1}C_{5-1}$$

$$= {}^{11}C_4$$

$$\frac{11!}{4!\,(11-4)!}$$
$$=\frac{11!}{4!\,(7!)}=\frac{11\times 10\times 9\times 8}{4\times 3\times 2\times 1}$$
$$=330$$

(ii) In this case, one specified book is always excluded. So, 5 books are to be selected out of 12 − 1 = 11 books. Then the total number of ways

$$={}^{11}C_5$$
$$=\frac{11!}{5!\,(11-5)!}$$
$$=\frac{11!}{5!\,6!}=\frac{11\times 10\times 9\times 8\times 7}{5\times 4\times 3\times 2\times 1}=462$$

Problem 23. ***Out of 6 teachers and 4 students, a committee of 5 is to be formed. How many such committees can be formed including (i) at least one student (ii) 3 teachers and 2 students?***

Solution: (i) In this case we have to select at least one student; this means that from one to all students are to be selected. So, there can be the following formations, of a committee of 5 persons :

(a) 1 student and 4 teachers
(b) 2 students and 3 teachers
(c) 3 students and 2 teachers
(d) 4 students and 1 teacher

Total ways in case (a) $={}^4C_1\times{}^6C_4=\frac{4!}{1!\,3!}\times\frac{6!}{4!\,2!}$

$$=4\times 15=60$$

Total ways in case (b) $={}^4C_2\times{}^6C_3$

$$=\frac{4!}{2!\,2!}\times\frac{6!}{3!\,3!}=6\times 20=120$$

Total ways in case (c) $={}^4C_3\times{}^6C_2$

$$=\frac{4!}{3!\,1!}\times\frac{6!}{2!\,4!}=60$$

Total ways in case (d) $={}^4C_4\times{}^6C_1$

$$=1\times 6=6$$

Hence, the total ways = 60 + 120 + 60 + 6 = 246.

(ii) In this case the committee has 3 teachers and 2 students. So the total ways to form this committee

$$={}^6C_3\times{}^4C_2$$
$$=\frac{6!}{3!\,3!}\times\frac{4!}{2!\,2!}$$
$$=20\times 6=120.$$

1·12. PROBABILITY

[I] Introduction

In our daily life, we generally come across with the following statements :

(i) Most probably Sanjay will stand first in his class.

(ii) It is quite probable that Sanjay may stand first in his class.

(iii) It is least expected that Sanjay may stand first in his class.

(iv) It is impossible that Sanjay will stand first in his class.

In all these above statements we have tried to express the chances of Sanjay for standing first in his class qualitatively. This is an event which may and may not happen. But we are predicting the result of the event with some *uncertainty*. This uncertainty associated with the event may be lesser or greater, *i.e.*, it may vary. In mathematics we measure this uncertainty in terms of number *quantitatively which* we call *probability or chance.* With the help of probability we can predict the outcome of any random experiment by associating some probability to that outcome.

[II] Definitions Used in Probability

(1) Random experiments. Suppose we throw a coin. It is an experiment. We cannot say with surety what will come upon the coin. It is a random experiment as its result cannot be predicted in advance with surty. Similarly, "throwing of a 6 faced cubical die (*pasaa*)", "drawing one or two cards from a pack of 52 cards are all random experiments.

(2) Elementary events. Every outcome (called a sample point) of a random experiment is called an *elementary event.* For instance, if we throw a cubical die marked numbers 1, 2, 3, 4, 5, 6 on its six faces, then there are six possible outcomes, *viz.*,

Number 1 may come on the upper face.
Number 2 may come on the upper face.
Number 3 may come on the upper face.
Number 4 may come on the upper face.
Number 5 may come on the upper face.
Number 6 may come on the upper face.

Every above outcome (sample point) is an elementary event, *e.g.*, if 6 appears on the upper face we say that event of getting 6 has occurred. We may denote these events by $e_1, e_2, e_3, e_4, e_5,$ and e_6. Thus, in this experiment there are 6 total outcomes.

Similarly, in the experiment of throwing one coin, there two possible outcomes denoted by H or T showing that *"head is appearing on the coin"* or *"tail is appearing on the coin"*.

Similarly, of the random experiment of throwing of 2 coins, the total outcomes are four, denoted by HH, HT, TH, TT and of the experiment of throwing one coin and one die together there are 12 outcomes (using fundamental principle of counting, ways are 2 × 6), denoted by H1, H2, H3, H4, H5, H6, T1, T2, T3, T4, T5, T6. Thus, in this experiment the total ways are 12.

(3) Events. Recall that every outcome (sample point) of a random experiment is an *elementary event.* (This is a smallest event). Now consider a situation which is favoured by more than one outcome. For example, consider *"getting an even number* in the throw of a single cubical dic", then 3 outcomes e_2, e_4, e_6 give this result. This is called an event as it is favoured by 3 outcomes. Thus, its favourable ways are 3.

Similarly, in the throw of a pair of coins; the event of "getting at least one H" is favoured by 3 outcomes HH, HT, TH.

In the throw of 3 coins, there are eight possible outcomes say

HHH (all 3 heads)
HHT, HTH, THH (exactly 2H, one T)
HTT, THT, TTH (exactly 1H, 2T)
TTT (all the 3 tails)

Out of these, event *"getting at least one* H" is favoured by first 7 ways and not favoured by one way only (last outcome TTT).

Similarly, in the *"throw of a pair of cubical dice"*, there are 6 × 6 = 36 ways of ending the experiment as follows :

(1, 1),	(1, 2),	(1, 3),	(1, 4),	(1, 5),	(1, 6)
(2, 1),	– –,	– –,	– –,	– –,	(2, 6)
(3, 1),	– –,	– –,	– –,	– –,	(3, 6)
(4, 1),	– –,	– –,	– –,	– –,	(4, 6)
(5, 1),	– –,	– –,	– –,	– –,	(5, 6)
(6, 1),	(6, 2),	(6, 3),	(6, 4),	(6, 5),	(6, 6)

In the pair (i, j), first number denotes the number coming up on the first dic and second on the second dic.

We may also denote these outcomes by e_{ij}, where $i = 1, 2, ..., 6, j = 1, 2, ..., 6$.

Out of these 36 outcomes, only 6 are the favourable outcomes to the event of *getting the sum* 7, namely,

(1, 6), (2, 5), (3, 4), (4, 3), (5, 2), (6, 1),

or say, $e_{11}, e_{25}, e_{34}, e_{43}, e_{52}, e_{61}$.

Thus, favourable ways of getting the sum 7 is 6 and 30 are unfavourable ways *i.e.*, in 30 ways this event does not occur.

[III] Definition of Probability

If an event E can happen in m ways and fails (cannot happen) in n ways, all the ways are equally likely to occur, then the probability of happening of the event E, denoted by $P(E)$, is given by

$$P(E) = \frac{m}{m+n} \qquad \text{... (1)}$$

Note that $0 \le P(E) \le 1$.

If we denote the event of *"not happening of event E"* by symbol E or by E', then according to the above definition

$$P(\bar{E}) = P(E') = \frac{n}{m+n} \qquad \text{... (2)}$$

From equation (1) and (2), we get

$$P(E) + P(\bar{E}) = 1$$

or $$P(E) = 1 - P(\bar{E})$$

and $$P(\bar{E}) = 1 - P(E)$$

In equation (1) note that $(m + n)$ are the total number of ways (outcomes) in which a trial or an experiment may end. Out of these $(m + n)$ ways in m ways, event E happens or say m ways are favourable to the event E. Therefore, the probability of event E is also given by

$$P(E) = \frac{\text{Favourable number of ways to event } E}{\text{Total number of ways of the experiment}}$$

[IV] Types of Events

(1) Exhaustive event. *An event which is favoured by every outcome of a random experiment,* is called an **exhaustive event**. It is generally denoted by symbol "*S*".

Its probability $= P(S) = \frac{m+n}{m+n} = 1$

This is also called *sure event*. Whenever the experiment is performed this event will always happen.

(2) Impossible event. *An event which never happens, i.e.,* no *outcome favours this event, is called* **a null event**. It is denoted by ϕ. Its probability $= P(\phi) = \frac{0}{m+n} = 0.$

(3) Complementary event. The event of *"not happening the event E"* is called *complementary event of E*, denoted by E^c or E or $\bar{E}$. Its probability can be found by subtracting the $P(E)$ from 1. (See formula (2)).

(4) Compound events. The events which are made up by the combination of two or more events are called **compound events**. It is explained follows :

If A and B are any two events of the same random experiment, *then the event of the happening of any of these (clearly speaking happening of at least one out of these events A, B)* is a compound event, denoted by (A + B) (modern symbol $A \cup B$ and is called *addition or union of events*).

For example, suppose we throw a single dice, and "A is the event of getting an even number on the dice" and B is the event of "getting a number less than 3, then A + B or $A \cup B$ is the event of getting an even number or a number less than 3. Note that A is favoured by four outcomes namely e_1, e_2, e_4, e_6 by the 3 outcomes e_2, e_4, e_6 while B is favoured by two outcomes e_1, e_2. Thus A + B is favoured by four outcomes e_1, e_2, e_4, e_6. Therefore,

$$P(A + B) = \frac{4}{6} = \frac{2}{3}.$$

Similarly, the event of *happening of both the events* A, B *simultaneously is a compound event* denoted by AB (or $A \cap B$) and is called *multiplication (or intersection) of events*. (This is also a compound event).

In the above example AB will be favoured by only one outcome e_2 because when e_2 will happen, number 2 will come up on the die and so A will happen as this number is an even number and B will also happen as this number is less that 3 also. Therefore,

$$P(A \cap B) \text{ or Probability } (AB) = \frac{1}{6}$$

(5) Mutually exclusive events or disjoint events. *Two events A, B are said to be mutually exclusive or disjoint events if A happens, then B cannot happen and if B happens then A cannot happen. Thus, out of A, B only one can happen at a time, i.e., both cannot happen simultaneously. Thus, in this case*

$$P(AB) = 0.$$

In general, n events $E_1, E_2, \ldots\ldots, E_n$ are said to be *mutually exclusive if happening of any one of these stops the happening of all other events.*

For example, from a pack of playing cards, if '*R*' is the event drawing a red card and *B* is the event of drawing a black card. Then in experiment of drawing a card, both '*R*' and '*B*' cannot happen simultaneously or say when '*R*' happens, then '*B*' cannot happen and vice versa. So these are mutually exclusive events.

(6) Independent events. *Two events A, B are said to be independent if happening of one event does not affect the happening of the other, i.e.,* when A happens, 'B' may or may not occur. The occurrence of B is not linked with the happening of A *i.e.* B is independent of A.

For example, if we throw a coin and a dice simultaneously, then the "result of coin" is independent of "result of dice". So 'H' and 'e_5' are two independent events.

Students must note that in mutually exclusive events, happening of A will make the probability of happening of B zero, *i.e.*, happening of A very much affects the prob. of happening of B. So, in case of mutually exclusive events, the events cannot be independent also.

[V] Addition Theorem of Probability

(1) If A and B are any two events of the same random experiment, then probability of happening of atleast one event out of these is given by

$$P((\mathrm{A}+\mathrm{B}) = P(\mathrm{A} \cap \mathrm{B}) = P(\mathrm{A}) + P(\mathrm{B}) - P(\mathrm{AB})$$

(2) *If the events are mutually exclusive then both cannot happen simultaneously* and hence $P(\mathrm{AB}) = 0$.

Therefore probability of happening of any one out of A, B will become

$$P(A+B) = P(A) + P(B) \qquad \ldots (3)$$

i.e., probability of happening of any one out of disjoint events *A*, *B* can be obtained by adding the probabilities of their happening separately.

(3) In general, if $E_1, E_2, \ldots, E_n$ are n pairwise mutually exclusive events, *i.e.*, $P(E_i E_j) = 0$ for all $i \neq j$, then

$$P(E_1 + E_2 + \ldots + E_n) = P(E_1) + P(E_2) + \ldots + P(E_n) \qquad \ldots (4)$$

For example, if S_6, S_7 and S_8 are the events of getting the sum 6, 7, 8 in the throw of a pair of dice, then these events are mutually exclusive. Also,

$$P(S_6) = \frac{5}{36}, P(S_7) = \frac{6}{36} \text{ and } P(S_8) = \frac{5}{36}.$$

Then probability of getting a sum 6, 7 or 8 is given by

$$P(S_6 + S_7 + S_8) = \frac{5}{36} + \frac{6}{36} + \frac{5}{36} = \frac{16}{36} = \frac{4}{9}$$

In an another example, suppose '*K*', '*Q*', '*J*' are the events of getting "a king" "a queen" or "a jack", in the draw of a single card from a well shuffled pack of 52 cards, then these three events are mutually exclusive.

Now the prob. of getting a picture card is given by

$$P(K+Q+J)=P(K)+P(Q)+P(J)$$

$$=\frac{4}{52}+\frac{4}{52}+\frac{4}{52}=\frac{12}{52}=\frac{4}{13}$$

[VI] Multiplication Theorem of Probability

(1) If A and B are two independent events, then probability of simultaneous happening of both the events is given by

$$P(\mathrm{AB})=P(\mathrm{A}).P(\mathrm{B}) \qquad \ldots (5)$$

= Product of the probabilities of happening of A and B separately.

(2) In general, if $E_1, E_2, \ldots, E_n$ are n independent events, then probability of happening of all the events simultaneously is given by

$$P(E_1 E_2 \ldots E_n), = P(E_1).P(E_2)\ldots P(E_n) \qquad \ldots (6)$$

= Product of probabilities of happening of each event separately.

(3) If A and B are any two events (not necessarily independent), then probability of their simultaneous happening is given by

$$P\,(\mathrm{AB})=P(\mathrm{A}).P(\mathrm{B/A})$$

or

$$=P(\mathrm{B}).\mathrm{P(A/B)} \qquad \ldots (7)$$

where B/A is conditional event of happening of B after the happening of event A and P(B/A) is the conditional probability of happening of B after the happening of A.

Similarly, P(A/B) is the conditional probability of happening of A when B has already occurred.

Particularly if A, B are independent events, then P(B/A) = P(B) as happening of A will not affect the event B. Then result (7) will become $P(\mathrm{AB})=P(\mathrm{A}).P(\mathrm{B})$ which is the same as given in relation (5).

(4) An important result. If $p_1, p_2, \ldots, p_n$ are the probabilities of happening of n independent events $E_1, E_2, \ldots, E_n$, then the probability of occurrence of at least one of them is given by

$$P(E_1+E_2+\ldots+E_n)=1-P\ (\text{none of } E_1, E_2, \ldots, E_n \text{ occurs})$$

$$=1-P(\bar{E}_1, \bar{E}_2\ldots\bar{E}_n)$$

$$=1-P(\bar{E}_1).P(\bar{E}_2)\ldots P(\bar{E}_n)$$

$$=1-(1-p_1).(1-p_2)\ldots(1-p_n) \qquad \ldots (8)$$

This is called as *"negative or indirect approach"* for determining the probability and is particularly useful in many problems.

(5) Odds in favour and odds against an event. *If an event E can happen in m ways and fails (does not happen) in n ways, then we say that the odds in favour of E are m to n (m : n).*

The same thing is sometimes also expressed by saying that the odds against E are n to $m(n : m)$.

Problem 1. ***Find the chance of throwing more than 4 in one throw of one cubic dice marked 1 to 6 on its six faces.***

Solution. Here are 6 equally likely cases of which only 2 are favourable because we want 5 or 6 on the upper face of the cubical dice. Hence, the required probability of throwing more than 4 in one throw with one dice

$$= \frac{2}{6} = \frac{1}{3}.$$

Problem 2. ***In a single throw with two dices, what is the probability of throwing 9?***

Solution. The number of the first die may appear in 6 ways. Similarly on the second dice also the number may appear in 6 ways. Hence, the two dices may appear in 6 × 6 ways namely.

$$\begin{array}{cccccc} (1, 1), & (1, 2), & (1, 3), & (1, 4), & (1, 5), & (1, 6), \\ (2, 1), & (2, 2), & (2, 3), & (2, 4), & (2, 5), & (2, 6), \\ (3, 1), & (3, 2), & (3, 3), & (3, 4), & (3, 5), & (3, 6), \\ (4, 1), & (4, 2), & (4, 3), & (4, 4), & (4, 5), & (4, 6), \\ (5, 1), & (5, 2), & (5, 3), & (5, 4), & (5, 5), & (5, 6), \\ (6, 1), & (6, 2), & (6, 3), & (6, 4), & (6, 5), & (6, 6). \end{array}$$

Out of these 36 ways, those which give desired sum of 9 are (3, 6), (4, 5), (5, 4) and (6, 3), *i.e.*, only 4 favourable ways.

$\therefore$ The probability of throwing 9 = 4/36 = 1/9.

Problem 3. ***Find the probability of throwing more than 16 in a single throw with three dices.***

Solution. The total number of equally likely ways is 6 × 6 × 6 or 216. Now we want more than 16 in the throw which means we must get 17 or 18. But 17 can be obtained only in the following cases :

(6, 6, 5); (6, 5, 6); (5, 6, 6), which are 3 in number.

Similarly, 18 can be got only in one following case:

(6,6,6)

So, the total number of cases in which either 17 or 18 is obtained = 3 + 1 = 4.

$$\Rightarrow \quad \text{The required probability} = \frac{4}{216} = \frac{1}{54}.$$

Problem 4. ***A bag contains 5 white, 8 black and 3 red balls. If three balls are drawn at random from the bag, then find the probability of the event***

(i) that all the balls may be white,

(ii) that one ball may be black and the other two white.

Solution. Total number of balls = 5 + 8 + 3 = 16.

Total number of ways of drawing three balls from the 16 balls in the bag

$$= {}^{16}C_3 = \frac{16!}{3!\,13!} = \frac{16\,.\,15\,.\,14}{3\,.\,2\,.\,1} = 560$$

(i) Total number of ways of drawing three white balls out of 5

$$= {}^{5}C_3 = 10.$$

$\therefore$ The probability of drawing 3 white balls together

$$= \frac{10}{560} = \frac{1}{56}.$$

(ii) Total number of ways ofdrawing two white balls out of 5 and one black ball out of 8

$$= {}^{5}C_2 \times {}^{8}C_1 = 80.$$

So, number of ways of drawing three balls of which one is black and the other two white

$$=\frac{80}{560}=\frac{1}{7}.$$

Problem 5. ***Three cards are drawn from a pack of 52 cards. Find the probability that :***

(i) all the three will be kings,

(ii) the cards are a king, a queen and a jack.

Solution. (i) Total number of ways of drawing 3 cards from a pack of 52 cards $= {}^{52}C_3 = \frac{52!}{3!\,49!}\,\frac{52\times 51\times 50}{3\times 2\times 1} = 22100$. Number of kings in the packet is 4, so the favourable number of ways of drawing three kings

$$= {}^4C_3 = \frac{4!}{3!\,1!} = 4.$$

So, the required probability $= \frac{4}{22100} = \frac{1}{5525}$.

(ii) The favourable ways are ${}^4C_1 \times {}^4C_1 \times {}^4C_1 = 4\times 4\times 4 = 64$.

$\therefore$ Required probability $= \frac{64}{22100} = \frac{16}{5525}$.

Problem 6. ***Two cards are drawn from a pack of 52. Find the probability that one may be queen and the other a king.***

Solution. Total number of ways of drawing 2 cards out of pack of 52.

$$= {}^{52}C_2 = \frac{52!}{2!\,50!}\,\frac{52\times 51\times 50!}{2\times 1\times 50!} = 1326$$

Now, number of favourable ways of drawing 2 cards together, of which one is a queen and the other a king

$$= {}^4C_1 \times {}^4C_1 = 4\times 4 = 16.$$

$\therefore$ the required probability $= \frac{16}{1326} = \frac{8}{663}$.

Problem 7. ***Two cards are drawn from a full pack of 52 cards. What is the chance that (i) both are aces of different colours (ii) one is red and other is black?***

Solution. Total number of ways of drawing two cards from 52 cards

$$= {}^{52}C_2 = \frac{52!}{2!\,(52-2)!} = \frac{52\times 51\times 50!}{2\times 1\times 50!} = 26\times 51.$$

(i) Now there are 2 black and 2 red aces. So, two aces can be drawn in

$$= {}^2C_1 \times {}^2C_1 \text{ ways} = 2\times 2 \text{ ways} = 4 \text{ ways}.$$

$\Rightarrow$ Required probability $= \frac{6}{26\times 51} = \frac{2}{663}$.

(ii) There are 26 red and 26 black cards. So, one red and one black card can be drawn in ${}^{26}C_1 \times {}^{26}C_1$ ways $= 26\times 26$ ways.

$\Rightarrow$ Required probability $= \frac{26\times 26}{26\times 51} = \frac{26}{51}$.

Problem 8. ***A number is chosen from the integers from 1 to 50. What is the probability that this number chosen is (i) a multiple of 7? (ii) a doublet?***

Solution. One number can be chosen in 50 ways.

(i) But out of 1 to 50 numbers, numbers multiple of 7 are only 7, 14, 21, 28, 35, 42, 49, *i.e.*, only 7 numbers. Hence, favourable number of ways are only 7.

$\Rightarrow$ Required probability $= \frac{7}{50}$.

(ii) In this case, we want a number of the form 11, 22, 33, 44 (only four numbers).

$\Rightarrow$ Required probability $= \frac{4}{50} = \frac{2}{25}$.

Problem 9. ***A pair of dice is thrown. What is the probability of getting a total of 7?***

Solution. Total number of possible outcomes $= 6 \times 6 = 36$

Let E be the event of getting a total of 7, then

$$E = [(1, 6), (2, 5), (3, 4), (4, 3), (5, 2), (6, 1)]$$

$$P(\text{a total of } 7) = \frac{n(E)}{n(S)} = \frac{6}{36} = \frac{1}{6}.$$

Problem 10. ***Find the probability that a leap year selected at random will contain 53 Sundays.***

Solution. A leap year contains 366 days, *i.e.*, 52 weeks and 2 days. The different possibilities for the ramaining two days are:

(1) Monday and Tuesday (2) Tuesday and Wednesday (3) Wednesday and Thursday (4) Thursday and Friday (5) Friday and Saturday (6) Saturday and Sunday (7) Sunday and Monday.

So, we see that the last two cases are favourable to the happening of 53 Sundays, out of a total of seven equally likely cases. So, the required probability $= \frac{2}{7}$.

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. Differentiate $\log \sin e^{2x}$ with respect to x.
2. Differentiate the following w.r.t. x.

   (i) $xy + x^2 + y^2 = a$ (ii) $\log xy = x^2 + y^2$
3. Evaluate the following integrals :

   (i) $\int 2x^3\,dx$ (ii) $\int \frac{1}{t\sqrt{t^2-1}}\,dt$

   (iii) $\int \frac{dx}{1-\sin x}$ (iv) $\int \left(\sqrt{x} - \frac{1}{\sqrt{x}} + \frac{1}{x} + \frac{1}{x^2}\right) dx$

   (v) $\int_0^1 \frac{1-x}{1+x}\,dx$ (vi) $\int e^x x^2\,dx$
4. If $x^y = e^{x-y}$, then prove that :
   $$\frac{dy}{dx} = \frac{\log x}{(\log_e x)^2}.$$
5. Find the first partial derivative of $\log(x^2 + y^2)$.
6. Find the maximum value of $(x-1)(x-2)(x-3)$.
7. Show that $x^3 - 3x^2 + 3x + 7$ has neither a maximum nor a minimum at $x = 1$.
8. Divide a number into two such parts that the square of one part multiplied by the cube of the other shall give the greatest possible product.
9. Show that the maximum rectangle inscribed in a circle is a square.

10. Find the value of the following :

(i) ${}^{25}C_5$ (ii) ${}^{20}C_{15}$ (iii) ${}^{n}C_{n}$

11. In how many ways can 5 things be divided between 2 persons?

12. In how may ways 11 players out of 13 cricket players can be selected?

13. In an examination paper, 10 questions are set, out of which 5 have to be attempted. In how many ways, can the choice be made?

14. How many words can be formed with the letters of the word BHARAT? How many of them will begin with B?

15. In how many ways can 7 persons be seated (i) in a row (ii) in a circle ?

16. How many different words can be formed by the letters of the word INDIA?

17. How many five digit numbers can be formed from the digits 0, 1, 2, 3, 4 if (i) the digits are not repeated and (ii) the digits are repeated?

18. A coin is tossed 6 times in succession. What is the probability of getting at least one head?

19. Find the probability of drawing a king, a queen and an ace in this order from a pack of 52 cards in three consecutive draws, the cards drawn not being replaced.

20. A person can kill a bird once in three shots. On this basis, he fired three shots. Find the probability that the bird is not killed.

[II] Multiple Choice Questions

1. If ${}^{n}C_{10} = {}^{n}C_{15}$, then value of n is,

(a) 5 (b) 15 (c) 20 (d) 25

2. Value of ${}^{n}C_r + {}^{n}C_{r-1}$ is :

(a) ${}^{n}C_r$ (c) ${}^{n+1}C_r$ (c) ${}^{n+1}C_{r-1}$ (d) ${}^{n}C_{r+1}$

3. Values of ${}^{8}C_3$ and ${}^{9}P_2$ are respectively:

(a) 28, 72 (b) 56, 72 (c) 56, 36 (d) 28, 36

4. If ${}^{n}C_x = {}^{n}C_y$ and $x \neq y$, then $x + y$ is given by

(a) 0 (b) $-n$ (c) n (d) $2n$

5. The value of $\int_1^3 \frac{dx}{x}$ is :

(a) log 3 (b) log 2 (c) $\log_e x$ (d) $\log_{10} x$

6. The value of $\int \frac{dx}{ax+b}$ is :

(a) $\log(ax+b)$ (b) $\log \frac{1}{ax+b}$

(c) $\frac{1}{b}\log(ax+b)$ (d) $\frac{1}{a}\log(ax+b)$

7. The probability of throwing more than 4 by one dice is :

(a) $\frac{1}{2}$ (b) $\frac{1}{3}$ (c) $\frac{2}{3}$ (d) None of the above

8. The probability of selecting a girl from a class consisting of 5 boys and 7 girls is :

(a) $\frac{1}{2}$ (b) $\frac{1}{6}$ (c) $\frac{5}{7}$ (d) $\frac{7}{12}$

9.

A coin is tossed until a tail appears at most five times. Given that the tail does not appear on the first two tosses, the probability that the coin will be tossed 5 times is :

(a) $\frac{1}{8}$ (b) $\frac{5}{38}$ (c) $\frac{4}{27}$ (d) $\frac{9}{80}$

10. Value of $\frac{d}{dx}x^{7/2}$ is :

(a) $\frac{7}{2}x^{9/2}$ (b) $\frac{7}{2}x^{5/2}$ (c) $\frac{7}{2}x^{7/2}$ (d) $\frac{7}{2}\log x^{7/2}$

11. The value of $\frac{x^{3/4}}{x^{2/3}}$ is :

(a) $x^{17/12}$ (b) $x^{9/8}$ (c) $x^{1/2}$ (d) $x^{1/12}$

12. $\log_x(x^2)$ is equal to :

(a) $2x$ (b) 2 (c) x (d) None of these

13. The slope of straight line $2x + 3y = 4$ is :

(a) $-\frac{2}{3}$ (b) $\frac{2}{3}$ (c) $\frac{3}{2}$ (d) $-\frac{3}{2}$

14. An equation of a straight line $y = 2x$ means that :

(a) Line passes through the origin

(b) Line does not pass through the origin

(c) The slope of line is $\frac{1}{2}$

(d) Every statement is wrong

15. If $f(x) = x^2 + 2x + 3$, the value of $f(-1)$ is :

(a) 0 (b) 2 (c) 6 (d) 1

16. The value of $\int dx$ will be :

(a) 1 (b) 0 (c) x (d) $\frac{1}{x}$

17. The number of three digit numbers which can be formed by using numbers 0, 1, 2, 3, 4, while repetition of number is not allowed is :

(a) 12 (b) 24 (c) 36 (d) 48

18. The value of $\frac{12!}{3! \times 8!}$ is :

(a) 2900 (b) $\frac{1}{2}$ (c) 1980 (d) 198

19. Two coins are tossed simultaneously. The probability of tail in both cases is :

(a) $\frac{1}{2}$ (b) $\frac{1}{4}$ (c) $\frac{1}{8}$ (d) 1

20. The value of $\int \frac{x^4}{x^5 + 4}dx$ is :

(a) $\log(x^5 + 4)$ (b) $\log\frac{x^5}{(x^6 + 4)}$ (c) $\frac{x^5}{x^6 + 4}$ (d) $\frac{1}{5}\log(x^5 + 4)$

[III] Fill in the Blanks

1. Differential coefficient of a constant function 'c' is ....

2. If $x = at^2$ and $y = 2at$, then $\frac{dy}{dx} =$ ....

3. The value of $\frac{d}{dx}[f_1(x) \cdot f_2(x)]$ is ....

4. The value of $\int x \log x \, dx$ is ....

5. The value of $\int (ax + b)^{n-1} \, dx$ is ....

6. The value of $\int_0^1 (x + 1)^3 \, dx$ is ....

7. The value of 0! is ....

8. The number of arrangements of n distinct objects taken r at a time t is ....

9. The value of ${}^6P_3$ is ....

10. The value of $r! \times {}^nP_r$ is ....

[IV] True or False

State whether the following statements are true (T) or false (F) ?

1. The number of arrangements of n distinct objects taken all at a time is $(n - 1)!$.

2. $(n - 1)! \times {}^nP_r = n!$

3. If ${}^{2n}P_3 = {}^{2 \times n}P_4$, then $n = 7$.

4. The value of ${}^7C_0$ is 7.

5. $\int_1^2 x^3 \, dx = 3\frac{3}{4}$.

6. The value of $\int \cot x \, dx$ is $\log \sin x$.

7. The value of probability varies from – 1 to 1.

8. The value of $\frac{d}{dx} e^{-\tan x}$ is $e^{\tan^{-1} x}$.

9. The value of $\log \frac{x}{y}$ is $\log (x - y)$.

10. For a straight line $2y = 3x - 3$, the intercept on Y-axis is – 3.

ANSWERS

[I] Essay Type or Long answer Type Questions

1. $2e^{2x} \sin e^{2x}$

2. (i) $-\frac{y + 2x}{x + 2y}$ (ii) $\frac{y(2x^2 - 1)}{x(1 - 2y^2)}$

3. (i) $\frac{1}{2}x^4$ (ii) $\sec^{-1} t$ (iii) $\tan x + \sec x$ (iv) $\frac{2}{3}x\sqrt{x} - 2\sqrt{x} + \log x - \frac{1}{x}$

(v) $2 \log (1 + x) - 2x$ (vi) $e^x (x^2 - 2x + 2)$

5. $\frac{2x}{x^2 + y^2}, \frac{2y}{x^2 + y^2}$

6. Maximum value $= \frac{2}{3\sqrt{3}}$ at $x = 2 - \frac{1}{\sqrt{3}}$

8. $\frac{2a}{5}, \frac{3a}{5}$

10. (i) 53130 (ii) 15504 (iii) 1

11. 32

12. 78

13. $^{10}C_5$

14. (6!/2!), (5!/2!)

15. (i) 7! (ii) 6!

16. 5!/2!

17. (i) 96 (ii) 2500

18. 63/64

19. $\frac{8}{16575}$ 20. $\frac{8}{27}$

[II] Multiple Choice Questions

1. (d) **2.** (b) **3.** (b) **4.** (c) **5.** (a)

6. (d) **7.** (b) **8.** (d) **9.** (d) **10.** (b)

11. (d) **12.** (b) **13.** (a) **14.** (a) **15.** (b)

16. (c) **17.** (d) **18.** (c) **19.** (b) **20.** (d).

[III] Fill in the Blanks

1. 0 **2.** $\frac{1}{t}$ **3.** $f(x) f'_2(x) + f_2(x) . f'(x)$ **4.** $\frac{x^2}{4} (2 \log x - 1)$

5. $\frac{1}{an} (ax + b)^n$ **6.** $\frac{15}{4}$ **7.** 1 **8.** ^nP_r

9. 120 **10.** ^nC_r

[IV] True or False

1. (F) **2.** (T) **3.** (F) **4.** (F) **5.** (T)

6. (T) **7.** (F) **8.** (F) **9.** (F) **10.** (T)

Chapter 2

COMPUTERS – FUNDAMENTALS AND WORKING

2·1. NEED FOR COMPUTER LEARNING

With the change of time, the requirements of man have also changed. The slow movements have been changed to faster ones. At present, the time demands faster working speed. The industrial revolution has made the emphasis to shift from physical labour to mental labour. Complete business structure depends on the mobility of information round the entire globe. With the speedy change in working system and dependency on the stored information, man had no option but to opt for computerisation. In this fast working system, the man has understood the importance of computer literacy, which has been accepted as a part of life.

[I] Systems of Numeration

There are diferent systems of counting the numbers. It has been observed that some systems are very efficient in handling the large numbers, whereas others are slower. Some systems used fingers, symbols and group of numbers for counting. When man faced difficulty in dealing with large numbers, he found the need to develop the system of numeration. Each civilization used different systems of numeration which are as follows :

(1) Babylonian system of numeration. In this system, Babylonian civilization had its calender having total twelve months. At that time, the year was called as *lunar year*, which is now known as *solar year*. The Babylonian system used total 60 digits, so it was known as having a base of 60.

As in present system, we use total 10 numbers starting from 0 to 9 and refer to this system having its base as 10. The Babylonion system of numeration is also known as sexagesimal system. The symbols used in this system is of triangle shape.

(2) Roman system of numeration. Before using Roman system for counting the numbers, man discovered Greek system of counting for counting purpose. Greek system is used only in few places of its origin during some special occasions like religious ceremonies. Some decimal equivalent values of Roman numbers are given below :

Roman number	I	II	III	IV	V	VI	VII	VIII	IX	X
Decimal number	1	2	3	4	5	6	7	8	9	10

The Roman system uses total 7 symbols to represent its digits. These symbols are I, V, X, L, C, D and M, where M = 1000, D = 500, C = 100, L = 50, X = 10, V = 5, I = 1. This system is still in use.

(3) Base of 10 system of numeration. This is the present system of numeration used in a major part of the globe. This number system uses total 10 digits which are 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9. As it uses total 10 digits, so it is known as base of 10 system. The number 0 (zero) was invented by a mathematician from Hindu race. The decimal numeration system is the outcome of base of 10 system. This system is known as *decimal system*, because it uses total 10 digits and the meaning of word *'deci'* is ten.

[II] Calculating Machines

As already discussed, when man started counting large numbers he found it difficult to arrange them and also to remember. For this purpose, it needed the help of some calculating machine. We will name a few devices used for calculating purpose in olden days.

(1) Abacus and Napier's bones. An Egyptian scientist developed abacus (abacus = calculating board). This board is fitted with beads in iron bars. These beads can slide horizontally on the iron bars. It counts the numbers with the help of these beads. Abacus is still in use at many places.

An English mathematician John Napier (1617) built a mechanical device for multiplying the numbers. He named this device as *'Napier's Bones'*. This machine consists of several vertical rods, which were divided into different portions. Each rod was marked with the numbers from 0 to 9 in a particular pattern. Rotating these rods performed the calculations.

(2) Slide rule. This machine was developed in seventeenth century by an English mathematician. It was considered a very successful machine at that time because it could perform functions like addition, subtraction, multiplication and division.

(3) Pascal's wheel calculator. A French philosopher and mathematician Blaise Pascal (1642) discovered a mechanical machine for adding and subtracting the numbers. This machine used wheels, gears and cylinders, for performing the operation. The places of digits like one's place, ten's place, hundred's place and so on were represented with different wheels. So, this machine was also referred to as *wheel calculator*.

(4) Babbage's analytical engine. An English scientist Charles Babbage (1823) developed a calculating machine for the purpose of making simple calculations. This machine was purely mechanical in its operation. It could not prove to be successful and was replaced by some other advanced machines.

(5) Mechanical and calculating calculators. The mechanical calculators were first introduced in the beginning of nineteenth century. It was a discovery with lots of efforts and amendments. These were built to perform only few mathematical calculations. These were kept in use till the mid of twentieth century.

After some more advancement, the rotating parts of these mechanical calculators were replaced with the parts moving with the help of electric motors. The electrical calculators were very bulky in the beginning of their use because of heavy electronic parts used to assemble them. With the invention of small electronic switches like transistors, the size and weight of these calculators were reduced. Their calculating efficiency also increased with the use of transistors. The speed became comparatively faster than those calculators which were used in the beginning. The speeds were then measured in microseconds and the computer–the hand held calculator–cost a few hundred dollars. This was done in 1950s and 1960s, when computers were built using transistors. In the mid 1960s, the integrated circuit (IC) was developed. This involved placing a number of electronic components, *e.g.*, transistors, diodes etc with interconnected wiring on a silicon chip. A typical chip size is roughly 0.25 cm^2 (0.5 cm × 0.5 cm). This increased the speed to tens of millions of operations per second.

[III] What is a Computer ?

A computer is just like a fast calculator. However, calculator and computer cannot have the same definition because of some basic differences. These differences are :

(1) A calculator has small size of its working memory, whereas the computers generally are made with large size of working and storage memory.

(2) Calculators do not have the capability to perform the logical functions, whereas a computer can perform the logical functions. The logical function means the ability to decide and select one choice out of given alternatives. This also includes the comparison of data.

(3) Computers can choose, copy, move, compare and perform non-arithmetic operations on many alphabetic, numeric and other symbols we use to represent the things.

(4) Computer is a fast and accurate electronic machine which manipulates the data for processing.

[IV] Classification of Computers

The computers have been classified into four categories. The classification is based on several facts like their size, data handling capacity, working speed etc.

(1) Micro-computers. These computers are of small size. These computers use small microprocessor as main controlling device. Some chips support the microprocessor which work as main memory and other supporting device. Small circuits are used for input and output devices. The cost of these computers is less.

(2) Mini-computers. Mini-computers are superior to micro-computers. We can say that the improved version of micro-computer is said to be a mini-computer. The memory size of mini-computer is slightly larger than mini-computer. Now, the mini-computers have been improved to control the network of computers.

(3) Mainframe computers. These computers are used to control the work environment, where more than one user shares the processor. The processing speed of these computers is normally high. The fixed memory and removeable memory are used in such computers. The size of such computers is large.

(4) Super-computers. These are generally known as fifth generation computers. These computers use more than one processor. These processors work parallel and this system of working is known as parallel processing system. The speed of these computers is very fast and they can process millions of instructions per second.

[V] Generations of Computer

There has been an improvement in the operation of computers with the change of time and technology. Different generations of computers are mentioned below.

(1) **First generation computers.** These computers had the following features:

   (a) These computers were named as 'Electronic Numerical Integrator and Calculator' (ENIAC). These computers used vacuum tubes as electronic switches.

(b) The size of computers was large.
(c) A large space was required to instal the computer.
(d) These computers required high voltage for operation.
(e) As the operating voltage was high, the heat generated by the computers was also high.
(f) Efficiency was low.
(g) Speed was very slow.

(2) Second generation computers. These computers had the following features :
(a) Transistors were used as electronic switches.
(b) The life of transistor is much more than that of a vacuum tube.
(c) The operation of these computers was stable because of the use of transistors.
(d) These computers used independent CPU and memory.
(e) Programming languages were developed for use on these computers.

(3) Third generation computers. These computers were developed around 1964 and had the following features :
(a) These computers used integrated circuits as switching devices.
(b) Integrated circuits consisted of many electronic components like transistors, resistors and capacitors.
(c) These computers had higher speed.
(d) The accuracy and efficiency were better.
(e) Many high level languages were developed and used on these computers.
(f) Input and output devices were also developed and used with these computers.

(4) Fourth generation computers. These computers were invented and put in operation in 1975. The present day computers belong to this category. These computers had the following features :
(a) The integrated circuits were converted to 'Large Scale Integration' (LSI) and 'Very Large Scale Integration' (VLSI). The term LSI is used to describe the technology to squeeze hundreds of thousands of components into a single chip. VLSI refers to the technology now used to compress the components even further:
(b) With the above advancement, computer speed is now measured in *nanoseconds* and the latest unit of measure is *picosecond.*
(c) The size of these computers was very small and could be accommodated on a working table.
(d) These computers used magnetic memory as well as semiconductor memory.
(e) These computers can control multi-user environment also.

(5) Fifth generation computers. The computers of 1990 are said to belong to this type. The features of such computers are as follows :

(a) These are the fastest out of all computers developed so far.

(b) These computers use more than one CPU, so parallel processing is possible with such computers.

(c) These computers are very efficient to handle high graphics data.

[VI] Capabilities of Computer

We understand the computer only as a calculating machine. The computer is much more than a calculator. It can manipulate the text. It can transfer the text from one location of document to another location by cutting and pasting it. Computers can be used for drawing the pictures and figures. It is also used for accessing the *Internet* and handling the *e-Mail.*

The computer performs only one task at a time. The speed of performing the task is very fast. The working speed of computer is measured in parts of second and it performs millions of operations per second. The result produced by the computer is accurate. A computer can perform all the tasks which a human being can do. The computer works with the help of instructions given by the user through a program. A computer performs the task automatically in sequence as per the given instructions. It does not suffer from human traits and tiredness. It can work for hours without any effect on its speed and accuracy.

[VII] Algorithms

We should mention the role of algorithms and flow-charts in solving a problem on the computer. *The detailed and precise step-by-step method is called an* ***algorithm***. So, an algorithm is a finite sequence of instructions (to solve a problem) and it should have the following characteristics :

(1) It should begin instructions to accept *inputs*. These inputs are processed by the subsequent instructions in the algorithm.

(2) The processing rules mentioned in the algorithm must be precise and unambiguous.

(3) The total time to carry out all the steps in the algorithm must be finite.

(4) Each instruction must be capable of being carried out in a definite time.

(5) The algorithm must produce one or more *outputs*, *i.e.*, the result of processing the inputs.

After the algorithm is obtained, it is then to be represented in a pictorial form called a *flow-chart.* The flow-chart is an aid in formulating and understanding algorithm. Next step is to mention the flow-chart in a more concise and precise language, known as programming language.

2·2. DIFFERENT COMPONENTS OF A COMPUTER

The important components of a computer system are :

(1) The input unit. (2) The central processing unit (CPU), and (3) The output unit.

The schematic block diagram of a computer is shown in figure (1).

[I] The Input Unit

This unit is employed to read the external data and instructions from the user. An input device converts data and instructions into binary form so that it can be accepted by the computer. The input devices are: keyboard, mouse, scanner, digitizer, magnetic floppy, disc reader, magnetic ink character reader (MICR), optical mark reader (OMR), optical character reader, light pen etc.

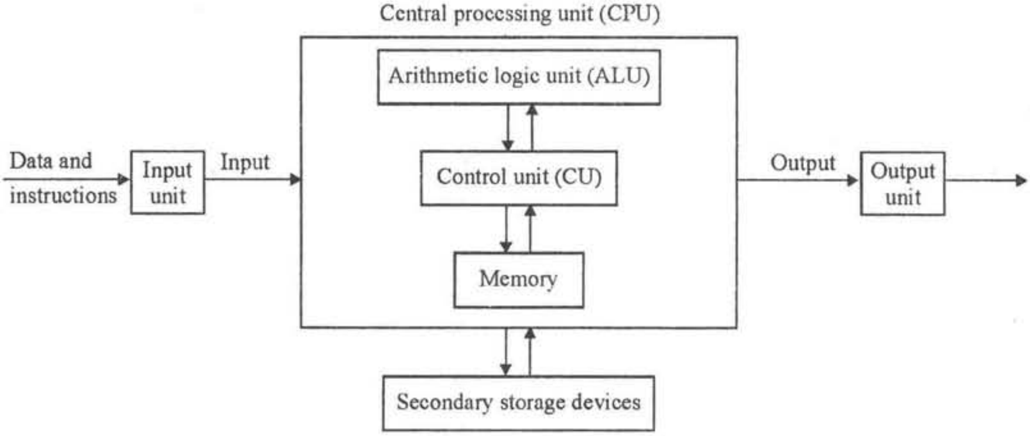


Fig. 1. Block diagram of a computer.

(1) Keyboard. The keyboard is the main method to feed the input to the computer. It is generally used to type the programs, feed the input and give the commands for computer peripherals. The keyboard has many keys used to generate the characters. Modern computer contains upto 110 keys. The position of these keys is almost similar to that of a typewriter. There are some special keys which are called the *operational keys*. The keyboard is connected to the main board through a cable to feed the information to the processer (Fig. 2). The key pressed is converted into a unique binary code and supplied to CPU.

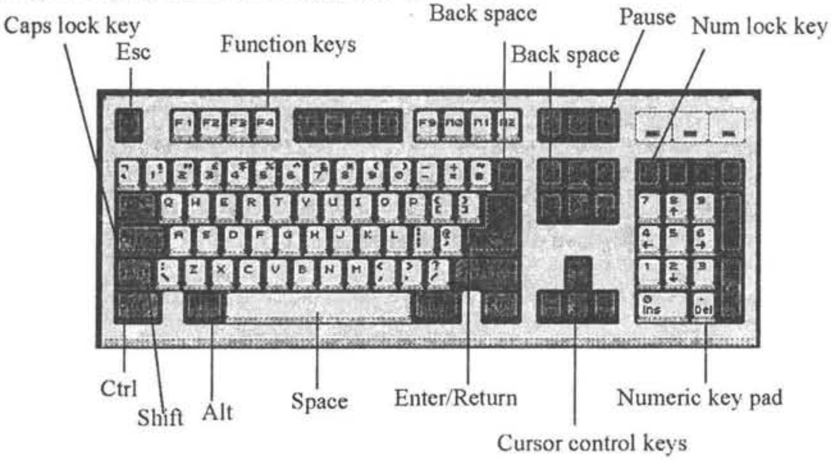


Fig. 2. Keyboard

(2) Mouse. There is no restriction of having more than one input devices attached to the computer. Now a days, almost all the computers have mouse connected to them along with the keyboard. The mouse is generally used to select the graphical input and feed it to computer. Mouse cannot be used to write the characters into computer's memory, because it does not have the keys to represent characters. But it is more fast and suitable for inputting data through graphical user interface system. The mouse has a free rotating ball at its base, which can rotate in any direction and its corresponding arrow (called cursor) moves on the screen. Mouse has generally two or three buttons having different functions. The pulses transmitted by the mouse determine the distance covered. The mouse is used to draw sketches, distance covered. The mouse is used to draw sketches, diagrams etc., on the CTR screen. It is also used for selecting one option from the number of options available.

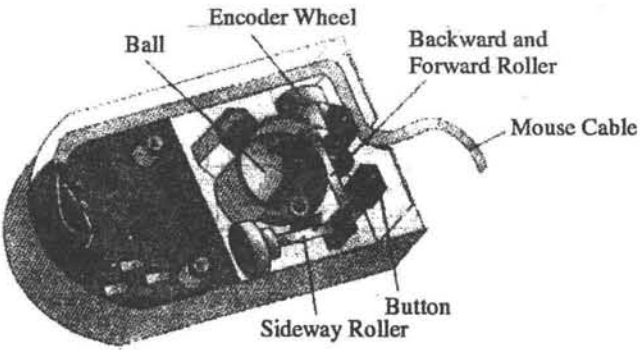


Fig. 3. Mouse

(3) Scanner. A scanner is a device which recognises the graphics or characters. It is similar to a xerox machine which can scan the entire input that is provided to it. The scanned image can be edited, manipulated, combined and printed. The resolution of scanners is usually 1200 DPI, 4800 DPI, 9600 DPI (DPI = dots per inch). A scanner can scan both monochrome and coloured images.

(4) Digitizer. A digitizer is an input device that converts the graphics and pictorial data to the binary or digital form, which can be directly fed and stored inside the computer. The function of a digitizer is that it stores the coordinates of the image and sends them to the computer. The coordinates transferred are then displayed on the screen. Thus, the graphical image can be transferred to the system.

(5) Light pen. A light pen [Fig. (4)] consists of light sensing element such as a photo-diode or photo-transistor set at the end of a pen or a stylus like holder. On the contrary, a cable is attached through which the signal is transmitted. The tip of the pen is positioned by hand to a desired screen location and the screen is then touched with the tip of the pen. The pen can be activated by depressing it. A signal is sent to the system showing the position of the pen. So, a graphic element can be identified. The pen is useful for drawing graphics.

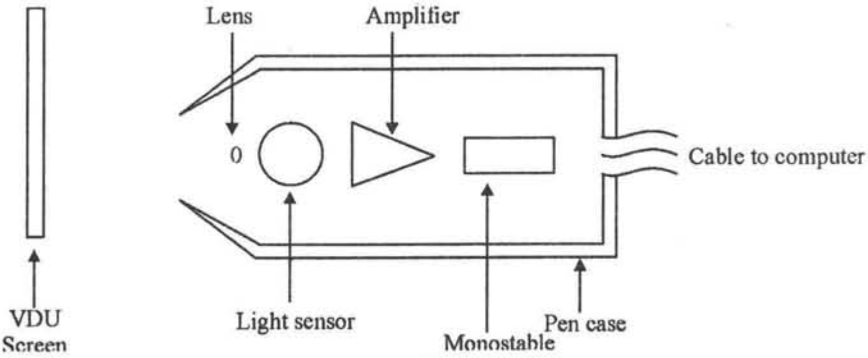


Fig. 4. Light pen

(6) Magnetic ink character recognition (MICR). This method of input is used to read the important documents (like bank cheques) written with special ink. The cheque number and other bank information are written on the cheque using magnetic sensitive ink. The numbers written at the base of the cheque are called *magnetic ink characters*. The recognition of these numbers is done through a magnetic scanner.

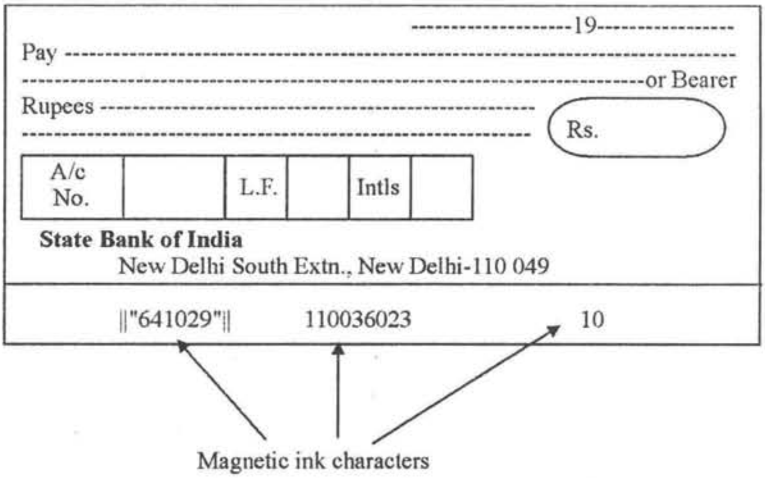


Fig. 5. Magnetic ink character recognition

(7) Optical mark reader (OMR). In this method, special pre-printed forms are designed with boxes which can be marked with a black pen or a dark pencil. Each box is annotated clearly so that the user can clearly understand what response he is making. Such a document is read by a document reader which transcribes the marks into electrical pulses which are transmitted to the computer.

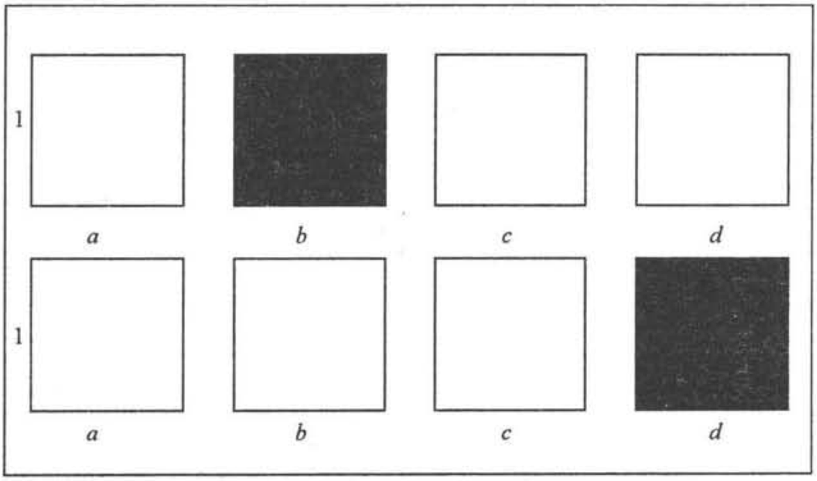


Fig. 6. Optical mark reader

(8) Optical character recognition (OCR). In many advanced countries, the prices of many items are printed on them using bar codes style. The bar codes are printed as vertical lines where number of lines, width between the two lines and thickness of the lines specifies its meaning. The bar coding is an example of *Optical Character Recognition*'. OCR reader reads the character as collection of small spots.

After scanning the group of tiny spots, the shape formed by these spots is compared with the shape stored in the computer. If this shape matches with any shape stored in computer, the computer will treat the scanned shape same as its match stored in computer. The computer rejects the unmatched shapes. The speed of OCR is not very fast, because focus is put more on accuracy than on speed. If the speed of scanner is made very fast, the chances of creating errors may also increase.

Fig. 7

[II] Central Processing Unit (CPU)

The central processing unit or CPU is the main part of the computer, which is used to execute and process the data. CPU can very well be said the brain of computer. It is the combination of following basic parts in computer :

(a) Control unit

(b) Arithmetic and logic unit

(c) Master clock

(d) Memory

All the parts except main memory are installed together on a single semi-conductor chip. This chip is generally referred to as a *'microprocessor'*. The microprocessor sends the information to output devices after processing them.

(1) Control unit. The processing operations are controlled by the *'Control Unit'*. It is just like human mind which instructs and controls the human body. The computer program is written in the form of instructions and executed one instruction at a time in sequence. The control unit passes these instructions to other parts of the computer one by one and maintains the record of their execution. Let us consider the following example to understand the operation of control unit.

```
20    IFK    = 30    then go to 50
30    NUM    = NUM + 5
```

The above statements are taken from BASIC language where the statement number 20 performs a conditional operation in which the value of variable K is compared with 30. If the value of K is 30 then control unit executes the statement number 20. If the value of K is not 30 then control unit will execute statement number 30.

(2) Arithmetic logic unit (ALU). This unit carries out arithmetic and logic operations. In the statement number 20 above, the logical statement K = 30 is sent to the logic unit where the value of K is compared with 30. If the result of this comparison is not true then statement number 30 is executed and value of NUM is sent to arithmetic unit to add 5 to its existing value.

(3) Master clock. The CPU consists of master clock which decides the processing speed of CPU. The processing speed and computer speed refer to the same term. The speed of the clock decides the number of operations processed per second. The clock speed is measured in terms of mega hertz.

1000 Hertz = 1 kilo hertz ; 1000 kilo hertz or 10^6 hertz = 1 mega hertz

1000 mega hertz or 10^9 hertz = 1 giga hertz

The performance of different versions of computer machines depend on the clock speed of the microprocessor.

(4) Computer memory. There are two types of memory used in computer, viz.,

1. The memory, which stores the data permanently and remains as attached memory. This memory is known as *secondary memory*.
2. The memory, which stores the data only in the presence of electricity. This memory is known as *primary memory*. It is non-detachable memory. We shall discuss primary memory which are of the following types :

(i) Read only memory (ROM). 'Read only memory' is like a book. The book can only be used for reading purpose but not for writing purpose. Similarly, ROM also can only be read. The contents of ROM cannot be changed by normal programming technique. ROM is of different types :

(a) Programme read only memory (PROM). This is a type of Read Only Memory, which can be re-progammed only once. The re-programming is done through some special programming technique.

(b) Erasable programmable read only memory (EPROM). These are types of 'Read Only Memory' which can be programmed again and again. Exposing the memory chip to ultra-violet rays can erase the stored data. The chip is reprogrammed by using micro-programming technique.

(c) Random access memory (RAM). Random Access Memory is used in computer as working platform. The processing, data manipulation or calculations are performed in RAM. It works as blackboard of any class room where information can be written or cleared any number of times. The files which are used by the user, are opened in RAM. Whatever matter we type through keyboard is placed in RAM. When we save the contents in a file, it gets stored on secondary storage device (mentioned below).

(5) Units to measure the memory. The computer memory is measured in terms of *bytes*. A computer stores the information in the form of 0 and 1 digits. The 0 and 1 are the digits of binary number system. These 0 and 1 are called *binary digits* or *bits*. Each character is stored in computer memory in a group of 8 bits. A group of 8 bits makes one byte or character. So, the measuring unit of computer memory is *byte*. The different measurement values of computer memory are given below.

8 Bits = 1 Byte

1000 Bytes = 1 Kilobyte = 10^3 Bytes

1000 Kilobytes = 1 Megabyte = 10^6 Bytes
1000 Megabytes = 1 Gigabyte = 10^9 Bytes
1000 Gigabyte = 1 Tetrabyte = 10^{12} Bytes

(6) Sccondary storage devices. The storage capacity of the main memory or primary memory is limited. Sometimes, we have to store millions or billions of data and the primary memory of the computer cannot store all the data. We, then need additional memory *called secondary or auxilliary memory storage*. The chief advantage of secondary memory storage is that the cost involved per bit of storage is appreciably less. The speed of the secondary memory storage device is, however, less than that of the primary memory storage device. Data can be stored in the secondary storage devices in the binary form and can be retrieved whenever required. The secondary storage devices are the floppy disc, the hard disc, optical disc and magnetic tape.

(a) Floppy disc. A floppy disc is a cheap and faster device used for input, output and storage purposes. This is made of flexible plastic and coated by magnetic oxide for recording the data. It is very thin and stored in a plastic jacket. The life of a floppy disc is not more because the friction of head wears out the tracks. The latest flopy discs are available in size of 3.5 inches diameter. The storage capacity of these discs is 1.44 megabytes which means that total 1.44×10^6 characters can be stored in one floppy. The contents of a 400 page of a book can be stored on a floppy disc. Data recorded on a floppy disc are read and stored in computer's memory by a device known as floppy reader. A floppy disc is put in a slot of the floppy input unit. The disc is rotated at about 360 rpm. A reading head is positioned touching a track. A voltage is induced in a coil wound on the head when a magnetised spot moves below the head. The polarity of the induced voltage depends on the direction of magnetisation of the spot under the head. The polarity of the voltage when a 1 is read is opposite to that when a 0 is read. The voltage sensed by the head coil is amplified and changed into the appropriate signal and then stored in the computer's memory.

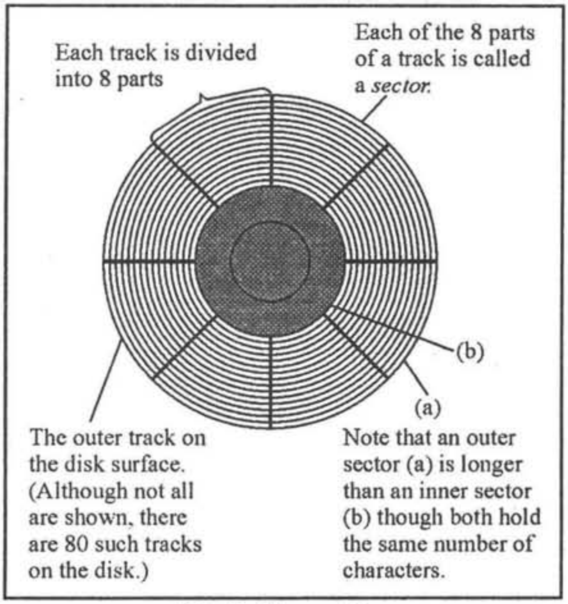


Fig. 8. Floppy disc

***(b) Hard disc*.** A hard disc is also used as input, output and storage device. Hard disc is a circular plate like gramophone record. These plates are coated with

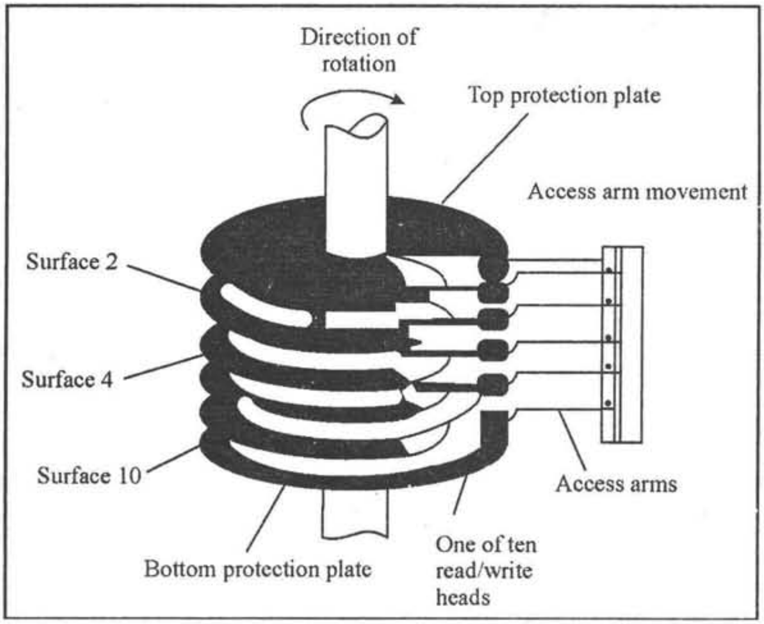


Fig. 9. Hard disc

magnetic agent for data recording purpose. The entire recording area is divided into tracks and sectors. Just by knowing the track and sector number, the information is searched from the disc. There could also be set of plates in a hard disc. These plates are generally called *platter*. These platters can generally be recorded on both the sides. These platters are housed in a single pack and form an assembly known as *hard disc*. Each surface is attached with read/write head. The complete pack of these platters rotates at a very high speed. The read/write head is so arranged that it does not touch the surface of the disc and also can move forward and back to read from the different tracks. In some cases, each track has independent head to read/write the data. When the number of heads increases, the time to search the data also decreases, making the operation faster. Such types of drives are costly because of the inclusion of the cost of multiple read/write heads. The tracks and sectors are numbered. When a particular track of a particular sector is required for read/write operation, the head moves to desired track and read/write operation occurs when required sector reaches under the head.

(c) Magnetic tape. The magnetic tape drive is used to read the information recorded on the magnetic tape. The tape is polished and coated with some magnetic material on its surface, which is used for data recording. The width of the tape is fixed but the length may vary as per the requirement. The tape is mounted on a wheel which drives the tape with the help of a drive. To make the tape writable, a ring is placed on the tape which allows the computer to record the information on the tape. This ring is normally used as a safety device to avoid accidental writing on the tape. The point from where the writing on the tape starts is known as *'beginning of tape'* (BOT) and the point beyond which the tape can not be used for writing is known as *'end of the tape'* (EOT). The reading and writing on the tape is done through read/write head.

(d) CD-ROM. This is the latest development used for storing the data. CD-ROM is a compact disc which stores the data only for reading purpose. Now the CDs are available which can be re-written. The capacity of these discs is approximately 640 megabytes. CD-ROM is used with special drives, which rotate the disc and extract the data.

[III] The Output Unit

The computer output unit consists of the following devices :

(1) Monitor or video display unit (VDU). The visual display unit or monitor is the most commonly used output device. It looks like a television screen. The monitors are used for quick display of information. Immediately after pressing the key on keyboard, the character appears on the screen. The monitor does not produce any hard copy of the matter displayed on the screen. The display is generated in the form of dots and these dots form the shape of the character. Normally, the screens are designed to display 25 lines and each line has 80 characters. When used in graphics mode, the screen is considered to be composed of a number of dots arranged in rows and columns. Each dot is called a *picture element* or *pixel*. By tightening or darkening selected pixels, an image can be displayed on the screen. The term resolution is used to describe the number of pixels per unit area of the screen, *e.g.,* the number of pixels per square centimeter. If there are few pixels per cm^2, we have low resolution display. If there are many pixels per cm^2, we have a high resolution display. The greater the resolution, the greater the detail which can be displayed.

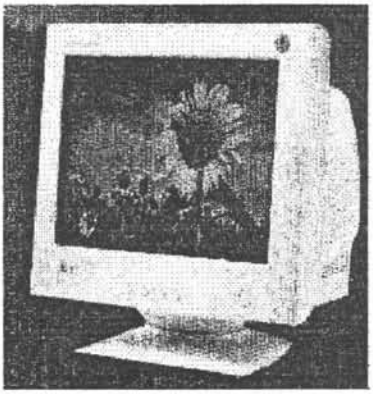


Fig. 10. Monitor of a Computer

(2) Printers. Various types of printers are used as output device just like monitors. Printers are also very commonly used for outputting the information. Printers produce the hard copy of the information displayed on the screen. Printers are of sevral categories, *viz.,* line printers, serial character printers and laser printers etc.

(a) Line printers. These printers are normally used with high processing computers. These computers use more than one terminal. In these types of printers, the characters are engraved on a drum. The drum rotates with the help of electrical motor to print the characters. The printing speed of these printers is very fast varying from 500 to 2000 lines per minute. There are normally 132 characters that can be printed in one line.

(b) Serial printers. These printers print one word at a time, with the print head moving across a line. They are similar to typewriters. These printers are normally slow (30 to 300 characters per second) The characters which are to be printed are sent one character at a time from the memory to the printer. The

Character code is decoded by the printer electronics and activates the appropriate pins in the point head. Character printers are less expensive than line printers. Character printers cannot be used continuously for more than an hour or so and are thus known as *high duty printers.*

(*c*) ***Dot matrix printers.*** These are the most commonly used printers. This is character printer and works on the principle of impact category of printers. The printer head has tiny hammers arranged in the order of rows and columns. Each hammer is of the size of a small pin and attached to a coil. A common dot matrix printer normally has 7 rows having 9 pins in each row. The characters generated by CPU are shaped with the help of these tiny hammers. The printing speed of these printers is about 100 characters per second.

(*d*) ***Laser printers.*** These printers are latest development in the field of IT industry. These are used to take the hard copy of the output. Hard copy means the printed copy of output. These printers work on combined principle of laser and photo copying machine. These printers print the output one page at a time. As they print page by page so the printing speed is very fast. The cost of these printers is very high.

(*e*) ***Inkjet printers.*** These three colour printers are classified in the category of character printers and work on electrostatic principle. The producetion of carbon copies of printed matter is not possible by these printers, because these do not work on impact principle. The ink used for printing purpose is made to pass through a small jet and injected between the electrostatically charged plates which throw the ink on the paper as per the shape of the character. The extra ink is collected back.

Inkjet printers have an advantage over laser printers; they produce colours. However, everything considered, the printing cost per page on inkjets are about ten times greater than on laser printers. In inkjet technology, the problem is that there is a tendency for the ink to smudge immediately after printing. However, with the development of new ink compositions, this problem has been overcome to a certain extent.

(*f*) ***Plotter.*** These are special types of printers used to print graphs and designs. The pens are generally used to plot the shapes and graphs. Fcr printing the shapes, the coordinates are fed to plotting pens through controlling programs. The plotting pens follow the coordinates and draw the shape.

(3) Computer output on microfilm (COM) and microfilche. In this method, the output from the computer, instead of being printed on a line printer is displayed on a high resolution cathode ray tube (CRT). This is photographed on a 35 mm film and a camera is controlled to film successive output pages on the screen of the CRT. A special microfilm reader is employed to read the output. In some systems, the microfilm is changed to a microfilche form. This form is a 4″ × 6″ sheet of film that can hold 98 frames of 8″ × 11″ page images reduced to 24 times. A microfilche is easier to read with a microfilche reader than it is to read a microfilm.

(4) Audio response unit (ARU). An ARU converts data which is output by the computer into sound. The sound can be spoken language, musical notes or simply beeps. Clearly the output is soft copy. When it is used to produce speech, an ARU is known as a speech synthesizer. It is a useful form of output when communication with a computer is made using telephone lines. A user dials the computer and makes an enquiry, the computer output is passed through the speech synthesizer which is situated near the computer, the output is changed to spoken reply which is sent to the user over the telephone line.

2·3. HARDWARE AND SOFTWARE

The physical part of the computer is known as hardware like monitor power supply, cabinet, interface cards etc. So, hardware refers to the components which we can see and touch. The term software refers to computer programs used in the computer system. Software is generally classified into the following types :

(1) Application programs. These are written to solve end-user problems which include educational programs, library control programs, payroll programs, accounting programs, administrative programs, graphic programs etc.

(2) System programs. These programs do not solve end-user problems. They make the users to have an efficient use of the computing facilities for solving their problems. Several system programs are provided by the manufacturer, as to write them a programmer needs detailed knowledge of the hardware of a given computer. The most important system program is the operating system. The operating system consists of a number of programs designed to ensure the smooth working of the computer system.

(3) Utility programs. These programs are also known as disc management programs and perform routine functions and operations which a user may wish to perform. The user may wish to transfer the data from one medium to another, *e.g.*, from tape to disc or vice versa, or from floppy disc to hard disc.

(4) Assembler. An assembler is the software which converts assembly language to machine language.

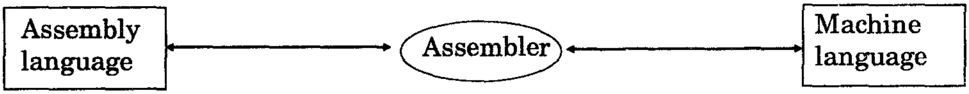


Fig. 11. Role of assembler in computer.

(5) Compiler. A compiler is a software which converts high level language to machine language. The high level language refers to any computer language in which the instructions and data are written using English language. The machine language is the form of 0 and 1, which can directly be understood by the computer.

Fig. 12. Role of compiler in computer.

2·4. THE BINARY NUMBER SYSTEM

[I] Decimal Number system

Man has developed different number systems when he felt the need of counting. The base 10 counting system was considered very helpful and also to develop the machines for the calculation purpose. Base 10 number system involves total 10 digits starting from 0 to 9. These numbers are known as ***digits***. With the combination of these digits we can form any large number. Each digit has its place value. Let us understand the place value of the numbers with the help of examples. Suppose we take the number as 943.

9	4	3
Hundred's place	Ten's place	One's place

Each digit is placed at different position carrying a different place value.

	9		4		3		
	$9 \times 100 = 900$	+	$4 \times 10 = 40$	+	$3 \times 1 = 3$	=	943
or	9×10^2	+	4×10^1	+	$3 \times 10^{\circ}$	=	943

When we add all place values together, we get total value of the number as a whole, which is 943 in our example.

(1) Integers. The integers may be positive or negative. The positive integers can be expressed by multiplying it by its place value. As shown above the place value of different digits of any number will be different.

The place value of unit place in positive integer will be $10^0 = 1$, ten's place will be $10^1 = 10$, hundred's place will be $10^2 = 100$, and so on. When we work on negative integers, we do not find much difference in their handling and calculation except putting negative sign before the number, which shows that the number is negative.

(2) Fractional numbers. The fractional numbers are the numbers, which have decimal value also as a part of the number. For example, the number 21.73 is a fractional number which has .73 as fractional part. These numbers are referred to as ***fractional decimal numbers***. To calculate the place values of each digit in fractional decimal numbers, the place value of the digits at left side of decimal point will increase ten times with the change of place of digit. In case of digits at right side of decimal point, the value of each digit keeps decreasing by ten times as the place of digit moves to right. For example,

	8	4	7	6	3	2
or	8×10^2	4×10^1	7×10^0	6×10^{-1}	3×10^{-2}	2×10^{-3}
or	800 +	40 +	7	. 6 × 0.1	+ 3 × 0.01	+ 2 × 0.001
or	800 +	40 +	7	. 6	+ .03	+ 0.002
or	847.632					

[II] Decimal Arithmetic

The arithmetic broadly means the manipulation and calculation of numbers, which is also applicable to fractional decimal numbers as in integer numbers. Some arithmetic operations are mentioned below for fractional decimal numbers.

(1) Addition. Let us understand the addition of decimal numbers with the help of examples. If the total of two or more fractional decimal numbers contain any integer parts, the integer part will be added with the integer portion of the total of the numbers, *e.g.*,

$$\begin{array}{r} 256.632 \\ 36.35 \\ +\ 786.258 \\ \hline 1079.240 \\ \hline \end{array}$$

The integer and decimal parts of the numbers can be added separately and the result of both additions can then be added together.

$$\begin{array}{r} 256 \\ 36 \\ +\ \ 786 \\ \hline 1078 \\ \hline \end{array} \qquad\qquad \begin{array}{r} .632 \\ .35 \\ +\ \ .258 \\ \hline 1.240 \\ \hline \end{array}$$

Adding 1078 and 1.240, as follows

$$\begin{array}{lr} & 1078 \\ \\ + & 1.240 \\ \hline & 1079.240 \\ \hline \end{array}$$

(2) Subtraction. Subtraction of fractional numbers is done normally as in integers by arranging the decimal point of all the numbers and their place positions, *e.g.*,

$$\begin{array}{lr} & 9328.2746 \\ - & 46.3543 \\ \hline & 9381.9203 \\ \hline \end{array}$$

(3) Multiplication. The multiplication procedure of fractional numbers is also like multiplying two integers numbers. The only difference here is to account the number of decimal places by counting the number of digits at right side of decimal point in both numbers (multiplier and to be multiplied) *e.g.*,

$$\begin{array}{lr} & 242.376 \\ \times & 25.36 \\ \hline & 1454\ 256 \\ & 7271\ 28 \\ & 121188\ 0 \\ & 484752 \\ \hline & 6146.65\ 536 \\ \hline \end{array}$$

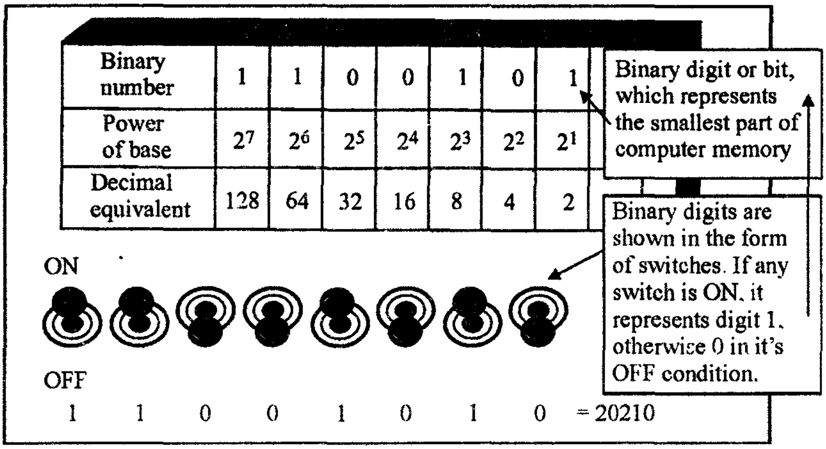
[III] Binary System

A computer interprets information composed of only zeros and ones. So, instructions and data processed by a computer must be in the form of zeros and ones. In other words, the data are stored and processed as strings of two symbols or ***two state devices***. A switch is for example, a two state device, it can be either ON or OFF. As decimal system uses total ten digits to make any number, similarly the binary system uses only two digits (0 and 1) to represent any large number. Each character in computer is represented by a number of decimal system and further converted into 0 and 1 (binary number). Since only two digits 0 and 1 are used in the system, it is called, binary number system. The each digit of this number system is called ***binary digit*** or ***bit.*** This system of numbers can also be said as ***base 2 number system.*** In this system also each digit has its place value as in decimal number system. The digit written at extreme left is called ***'Most Significant Bit'*** (MSB) and the digit written at extreme right is called ***'Least Significant Bit'*** (LSB). Note the place of LSB and MSB in the example given below.

1 1 0 1 0 0 1 0 1

Most Significant Bit Least Significant Bit

(1) Bit. As it has already been stated above that each digit of binary number system is known as *'Binary Digit'*. To make its name short, the B has been taken from Binary and IT is derived from Digit, thus making its name as BIT. A bit represents the smallest part of memory locations in computer, which store either 0 or 1. Refer figure 13 for bit.



Binary number	1	1	0	0	1	0	1
Power of base	2^7	2^6	2^5	2^4	2^3	2^2	2^1
Decimal equivalent	128	64	32	16	8	4	2

Binary digit or bit, which represents the smallest part of computer memory

Binary digits are shown in the form of switches. If any switch is ON, it represents digit 1, otherwise 0 in it's OFF condition.

Fig. 13. Binary digits

(2) Nibble. The combination of 4 adjacent bits is known as *nibble.*

(3) Byte. The combination of 8 bits is called *byte.* The byte represents one character in computer memory. It is now clear that to store one character in computer memory we need at least the space of 1 byte or 8 bits. Now the question arises here that why should there be only 8 bits to represent one character in computer memory? The answer to this question is that the computer works with the help of only 256 characters generated by its keyboard. These characters are A to Z, a to z, 0 to 9 and some special characters such as punctuation marks, arithmetic operator symbols, colon, semicolon, question mark, = ,>, <, etc. Every character is represented by a numeral code. These numeral codes are converted into binary numbers and stored in computer memory. The codes starting from 0 to 255 are represented by a group of binary digits. Now we have to find out the total number of digits required in a group to represent 256 combinations using only two digits, *i.e.*, 0 and 1. We find that 8 is the number which can make 256 combinations using two digits.

$$2^8 \quad \text{or} \quad 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 \times 2 = 256$$

Group of binary numbers using 8 bits	Decimal equivalent
0 0 0 0 0 0 0 0	0
0 0 0 0 0 0 0 1	1
0 0 0 0 0 0 1 0	2
0 0 0 0 0 0 1 1	3
0 0 0 0 0 1 0 0	4
0 0 0 0 0 1 0 1	5
0 0 0 0 0 1 1 0	6
0 0 0 0 0 1 1 1	7
0 0 0 0 1 0 0 0	8
0 0 0 0 1 0 0 1	9
0 0 0 0 1 0 1 0	10
0 0 0 0 1 0 1 1	11
0 0 0 0 1 1 0 0	12
. . . .	. .
. . . .	. .
1 1 1 1 1 1 1 0	255
1 1 1 1 1 1 1 1	256

(4) **Word length.** Let us first consider that what do we understand by the term 'word' in computer. As discussed earlier the data in computer is stored in a group of 8 bits. The group of these 8 bits is called ***computer word***. The omputer processes one word at a time. *The number of bits, which form one word in computer and processed in one operation, is called* ***word length***. Many computers can process more than 8 bits also, *e.g.*, 16 bits or 32 bits in one operation. So, the word length in such case is known to be 16 or 32 bits. The computer of 32-bit word length is generally referred to as 32-bit machine and 16-bit word length computer is referred to as 16-bit machine.

This term can be understood with the help of an example. Suppose you have 256 students in your class and they have to move from classroom to playground. The movement of students can be one by one or in group as per their roll numbers. Suppose the college principal decides that whenever there is a class movement, it has to be in the group of 8 or 16. So, this then becomes a convential method of movement. Here the size of group will broadly represent as word length in computer. The movement of students can be referred to as 8 students group, 16 students group or 32 students group. Similarly, in computer also the movement of 8 bits group is called 8 bit word length, 16 bits movement is called 16 bit word length and so on.

1	0	1	1	0	1	0	1

8 Bits word length

0	0	1	1	0	1	0	0	0	1	1	1	0	0	0	1

16 Bits word length

[IV] Conversion of Numbers

We know that computer understands only binary numbers, so the methods of converting the numbers from one system to another, has been explained below :

(1) Decimal to binary conversion. The base of binary number system is 2 because it uses only two digits to represent the number. The base of decimal number system is 10 because total 10 digits are used to represent the decimal numbers. Each decimal number is converted to binary before it is stored in computer memory. For converting the decimal number to binary, we divide the decimal number by 2 (because the base of binary system is 2) unless we get remainder less than 2. This can be understood by the following problem.

Problem 1. ***Convert decimal number 42 to binary.***

Solution. After dividing the number by 2, the remainder is noted in each step. The last remainder will make most significant digit and first remainder as least significant digit.

2	7	4	2	
2	3	7	1	0
2	1	8	5	1
2		9	2	1
2		4	1	0
2		2	0	1
2		1	0	0
2		5		0
2		2		1
		1		0

Remainders

(LSB)

(MSB)

The binary number will be as :

(0 1 0 0 1 0 1 1 $0)_2 = (742)_{10}$

(2) Binary to decimal conversion. As the numerals are converted to binary system for storing into computer memory, these numbers are converted back into decimal form for output purpose in the same way. The conversion of these numbers is done automatic by the electronic parts fitted in computer. For converting, binary numbers into decimal, following steps are to be followed.

(a) Find the least significant digit and most significant digit in the number.

(b) Mark the place position of each digit starting from LSB to MSB. The first position will be zero position.

(c) Find the place value of each digit with the help of the following formula, Digit × Base number $^{\text{place position of digit.}}$

It is important to note that the base value in binary system is 2.

(d) Add all the place values to get the equivalent decimal number.

This can be understood by the following problem.

Problem 2. ***Convert a binary number (1 0 1 1 0 1)$_2$ to its decimal equivalent.***

Solution.

	Binary digit	Place position	Place value		
MSB	1	5	1×2^5	=	3 2
	0	4	0×2^4	=	0
	1	3	1×2^3	=	8
	1	2	1×2^2	=	4
	0	1	0×2^1	=	0
LSB	1	0	0×2^0	=	0

The equivalent decimal number will be :

32 + 0 + 8 + 4 + 0 + 1 = 45

(3) Decimal to octal conversion. Like binary number system, octal system is also used for coding of decimal numbers. As its name clarifies, octal means 8, so total 8 digits are used in octal system. These digits are 0 to 7. The highest number that can be derived from the group of octal digits without any conversion is equivalent to $(777)_8$ of octal number system. For converting decimal number to binary number, we divide the decimal number by the base value of binary number system (which is 2). Similarly, in octal system also we divide the decimal number by base value of octal system which is 8. This can be understood by the following problem.

Problem 3. ***Convert a decimal number*** $(3\ 4\ 8\ 9\ 2)_{10}$ ***to its octal equivalent.***

Solution.

8	3	4	8	9	2		
8		4	3	6	1	4	(LSB)
8		5	4	5		1	↑
8			6	8		1	
8				8		4	
				1		0	
						1	(MSB)

Thus, the octal equivalent of $(3\,4\,8\,9\,2)_{10}$ decimal number is $(1\,0\,4\,1\,1\,4)_8$. Just like binary conversion here also we keep dividing the number by 8 unless we get remainder less than 8.

---

(4) Octal to decimal conversion. We know that only 8 digits (0 to 7) are used in octal system. It is clear now that digits used in octal system cannot be more than 7. For converting an octal number to decimal, same steps are applicable as from binary system to decimal.

(a) Find the most significant and least significant digits.

(b) Mark the place position of each digit considering LSB at zero place and MSB at highest place.

(c) Find the place value of each digit by applying the following formula,

Digit × Base number $^{\text{Place position of digit}}$

(d) Add all the place values to get the decimal equivalent number.

This can be understood by the following problem.

Problem 4. ***Convert*** $(6\ 5\ 3\ 4\ 2)_8$ ***octal number to its equivalent decimal number.***

Solution.	Octal digit	Place position	Place value
(MSB)	6	4	$6 \times 8^4 = 24576$
│	5	2	$5 \times 8^3 = 2560$
│	3	2	$3 \times 8^2 = 192$
↓	4	1	$4 \times 8^1 = 32$
(LSB)	2	0	$2 \times 8^0 = 2$

∴ Decimal equivalent number is :

$24576 + 2560 + 192 + 32 + 2 = 27362$

So, $(6\ 5\ 3\ 4\ 2)_8 = (2\,7\,3\,6\,2)_{10}$

---

(5) Decimal to hexadecimal conversion. An in binary number system only two digits (0 and 1) are used and in octal system 8 digits (0 to 7) are used to represent the numbers, similarly in hexadecimal number system total 16 digits are used to store and represent the numbers. The digits are 0 to 9 and A to F, where A is used for 10, B for 11, C for 12, D for 13, E for 14 and F for 15. The reason for using these alphabets in place of numbers is that each digit should be represented by single entity. If we write 10 (*i.e.*. one zero) to represent eleventh digit making it a combination of two digits *i.e.*,. 1 and 0, which have already been used for representing the digits 1 (one) and 0 (zero) independently, it will create confusion to recognise among the numbers 0, 1 and 10. So, to avoid this confusion, alphabets from A to F are used to represent numbers from 10 to 15.

As shown above, total 16 digits are used in hexadecimal system. While converting decimal number to hexadecimal number, we divide decimal number by 16 unless we get remainder less than 16 because the base of hexadecimal system is 16. This can be understood by the following problem.

Problem 5. ***Convert*** **$(1\,8\,6\,2\,7\,5\,2)_{10}$** ***decimal number to hexadecimal.***

Solution.

16	1	8	6	2	7	5	2		
16		1	1	6	4	2	2	0	(LSB)
16				7	2	7	0	2	
16					4	5	4	6	
16						2	8	6	
						1		C for 12	
								1	(MSB)

So, $(1\ 8\ 6\ 2\ 7\ 5\ 2)_{10} = (1\ C\ 6\ 6\ 2\ 0)_{16}$

---

(6) Hexadecimal to decimal conversion. The system of number conversion from hexadecimal to decimal system is same as from binary to decimal and octal to decimal. The difference is only of their base value because binary number system has its base value as 2, octal has 8 and hexadecimal has 16. This can be understood by the following Problem.

Problem 6. ***Convert*** **$(5\ 7\ A\ C\ 2)_{16}$** ***hexadecimal number to decimal number.***

Solution.	Hexadecimal digit	Place position	Place value		
MSB	5	4	5×16^4	=	327680
	7	3	7×16^3	=	28672
	A	2	$A \times 16^2$	=	2560
	C	1	$C \times 16^1$	=	192
LSB	2	0	2×16^0	=	2

The decimal equivalent number will be :

$327680 + 28672 + 2560 + 192 + 2 = 359106$

or $(5\ 7\ A\ C\ 2)_{16} = (3\ 5\ 9\ 1\ 0\ 6)_{10}$

---

(7) Hexadecimal to binary conversion. The conversion of hexadecimal to binary number is very simple just by converting each digit of hexadecimal to its binary equivalent. To make it simpler, let us know the binary equivalent of each decimal number from 0 to 15 as shown in table-1.

Table-1. Relationship between the four number systems

Decimal	Binary	Octal	Hexadecimal
0	0 0 0 0 0	0	0
1	0 0 0 0 1	1	1
2	0 0 0 1 0	2	2
3	0 0 0 1 1	3	3
4	0 0 1 0 0	4	4
5	0 0 1 0 1	5	5
6	0 0 1 1 0	6	6
7	0 0 1 1 1	7	7
8	0 1 0 0 0	10	8
9	0 1 0 0 1	11	9
10	0 1 0 1 0	12	A
11	0 1 0 1 1	13	B
12	0 1 1 0 0	14	C
13	0 1 1 0 1	15	D
14	0 1 1 1 0	16	E
15	0 1 1 1 1	17	F

This can be understood by the following problem.

Problem7. ***Convert*** **$(7\ 3\ 0\ A\ D\ E)_{16}$** ***hexadecimal number into its binary equivalent.***

Solution. 7 3 0 A D E

0111 0011 0000 1010 1101 1110

The equivalent binary number will be :

$(0111\ \ 0011\ \ 0000\ \ 1010\ \ 1101\ \ 1110)_2 = (730ADE)_{16}$

Table-2. Hexadecimal numbers and their equivalent binary and decimal numbers

Decimal	Binary	Hexadecimal	Octal	Binary	Hexadecimal
0	0 0 0 0	0	17	1 0 0 0 1	11
1	0 0 0 1	1	18	1 0 0 1 0	12
2	0 0 1 0	2	19	1 0 0 1 1	13
3	0 0 1 1	3	20	1 0 1 0 0	14
4	0 1 0 0	4	21	1 0 1 0 1	15
5	0 1 0 1	5	22	1 0 1 1 0	16
6	0 1 1 0	6	23	1 0 1 1 1	17
7	0 1 1 1	7	24	1 1 0 0 0	18
8	1 0 0 0	8	25	1 1 0 0 1	19
9	1 0 0 1	9	26	1 1 0 1 0	1A
10	1 0 1 0	A	27	1 1 0 1 1	1B
11	1 0 1 1	B	28	1 1 1 0 0	1C
12	1 1 0 0	C	29	1 1 1 0 1	1D
13	1 1 0 1	D	30	1 1 1 1 0	1E
14	1 1 1 0	E	31	1 1 1 1 1	1F
15	1 1 1 1	F	32	1 0 0 0 0 0	20
16	1 0 0 0 0	10			

(8) Binary to hexadecimal conversion. We know that the hexadecimal numbers are represented in a group of 4 bits because the largest digit of hexadecimal system is F, which is equivalent to decimal number 15 and binary number 1111. As the largest digit in hexadecimal system is represented by group of four bits, so each hexadecimal digit will be represented by a group of four bits.

To convert a number from binary to hexadecimal, we have to make the group of each four digits starting from LSB (Least Significant Bit) to MSB (Most Significant Bit). Add the zeros to left side of MSB if required to make the combination of four bits. Now write the hexadecimal equivalent of each group of four bits starting from MSB to LSB. This can be understood by the following problem.

Problem 8. ***Convert*** **$(1001\ 10100111100101)_2$** ***to its equivalent hexadecimal number.***

Solution. Let us make the group of each four bits starting from LSB to MSB.

$\underline{0010}\quad \underline{0110}\quad \underline{1001}\quad \underline{1110}\quad \underline{0101}$

(These two zeroes have been added to make
the MSB as a combination of four bits)

While making the group of each four bits we find that only two bits *i.e.*, 1 and 0 (one and zero) are left in group of MSB, so we have added two zeroes at the left most side to make the combination of four bits which in our problem now shows 0010.

Now we write the hexadecimal equivalent of each group of four bits.

$$\begin{array}{ccccc} \underline{0010} & \underline{0110} & \underline{1001} & \underline{1110} & \underline{0101} \\ 2 & 6 & 9 & E & 5 \end{array}$$

So, the hexadecimal equivalent number will be $(2\ 6\ 9\ E\ 5)_{16}$.

[V] Binary Addition

When we add two decimal numbers and get the result more than its base value then LSB of result is written as answer and MSB is added with next digit. For example, when we have to add 17 and 15, after adding 7 and 5 you get result as 12. In number 12, 1 is MSB and 2 is LSB. Thus, 2 will be written as the value under 7 and 5, and 1 will be carried forward to add with next higher digit. Let's understand this statement with the help of the following example :

$$\begin{array}{rcccc} & 1 & 5 & 2 & 8 \\ + & 4 & 8 & 2 & 7 \\ \hline & 6 & 3 & 5 & 5 \\ \hline \end{array}$$

In the above example, when we add 8 and 7 we get the result as 15. We can also say that the result after adding both the values at unit place is 15. As stated above that if the result is more than or equals the base value (10), the right most digit will be written as a result of addition and rest of the digits will be carried forward. In our example, we get the result as 15 after adding digits at unit place. So, 5 is placed as result and 1 is carried forward to add with next digit, *i.e.*, 2 + 2 + 1 (1 is carried forward from previous step). This system will be followed till we add MSB.

Similarly, the binary addition is also based on the same formula. The result of adding two different digits is shown below:

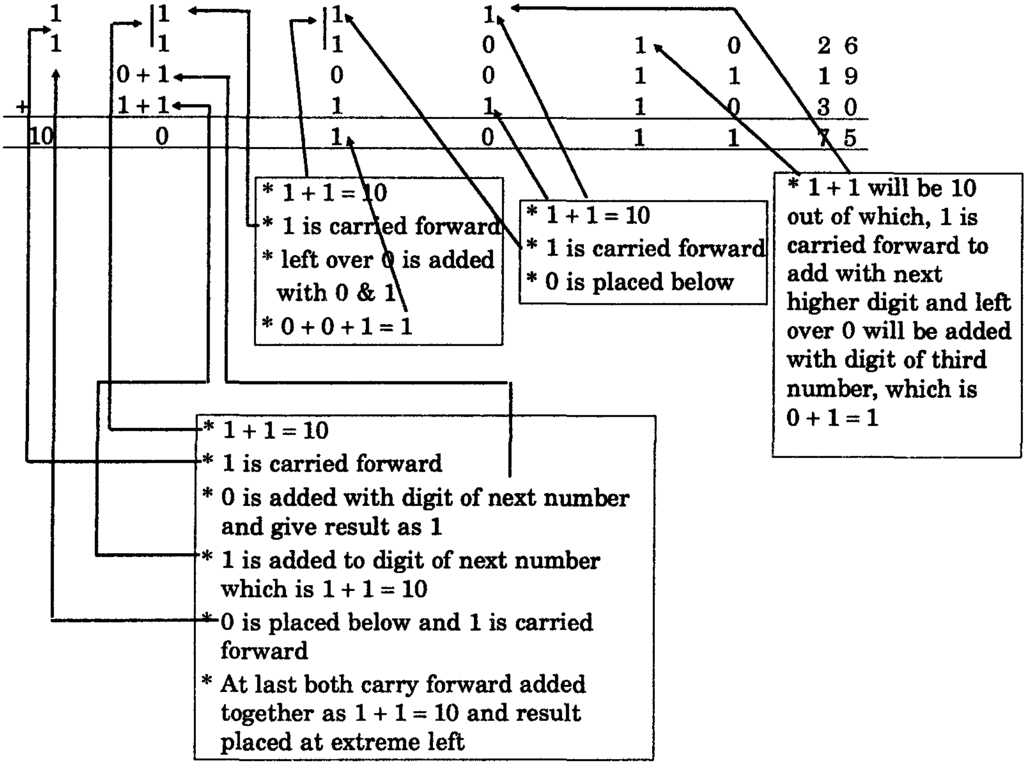
0 + 0 = 0
0 + 1 = 1
1 + 0 = 1
1 + 1 = 10

We get the result of 1 + 1, as 2. But binary system does not include 2 in its digits. So the number 2 is converted into binary system as 10 (one zero). The 0 (zero) will be placed as addition result of 1 + 1 and 1 will be carried forward for adding with next digit. Let us understand it with the help of the following example :

$$\begin{array}{rcccccc} & 1 & & & 1 & & \\ & & 1 & 0 & 1 & 1 & 0 \\ + & & 1 & 0 & 0 & 1 & 1 \\ \hline & 1 & 0 & 1 & 0 & 0 & 1 \\ \hline \end{array}$$

The addition result of these numbers is 10. Zero is placed below and 1 is carried forward to be added to next digits *i.e.*, 1 + 0.

Consider the following



* 1 + 1 = 10
* 1 is carried forward
* left over 0 is added with 0 & 1
* 0 + 0 + 1 = 1

* 1 + 1 = 10
* 1 is carried forward
* 0 is placed below

* 1 + 1 will be 10 out of which, 1 is carried forward to add with next higher digit and left over 0 will be added with digit of third number, which is 0 + 1 = 1

* 1 + 1 = 10
* 1 is carried forward
* 0 is added with digit of next number and give result as 1
* 1 is added to digit of next number which is 1 + 1 = 10
* 0 is placed below and 1 is carried forward
* At last both carry forward added together as 1 + 1 = 10 and result placed at extreme left

Table-3. Binary addition table

Number		Result	
A	**B**	**Sum**	**Carry**
0	0	0	0
0	1	1	0
1	0	1	0
1	1	0	1

[VI] Binary Subtraction

Binary subtraction is also the same as decimal subtraction. In decimal subtraction, we borrow the value from next higher digit when the value of subtrahend is higher than that of minuend. The rules of binary subtraction are as follows :

$1 - 0 = 1$
$1 - 1 = 0$
$0 - 0 = 0$
$0 - 1 = 1$ (Borrow 1)

Example :

$$\begin{array}{r} 1\quad 0\quad 1\quad 1\quad 0 \\ -\;\; 0\quad 1\quad 0\quad 1\quad 1 \\ \hline 0\quad 1\quad 0\quad 1\quad 1 \end{array}$$

* 1 cannot be subtracted from 0
* Borrow 1 from next digit making it 0
* 0 Becomes now 10 and 10 − 1 = 1

In the above example, we start subtraction from LSB to MSB. While subtracting the LSB digits, we have to subtract 1 from 0. As 1 cannot be subtracted from 0 so we borrow 1 from next higher digit which makes this digit as 10 (one zero) and leave zero at the place it is borrowed from. This process will be followed at the steps when subtracted number is of higher value than the number it is to be subtracted from. Consider another example as follows .

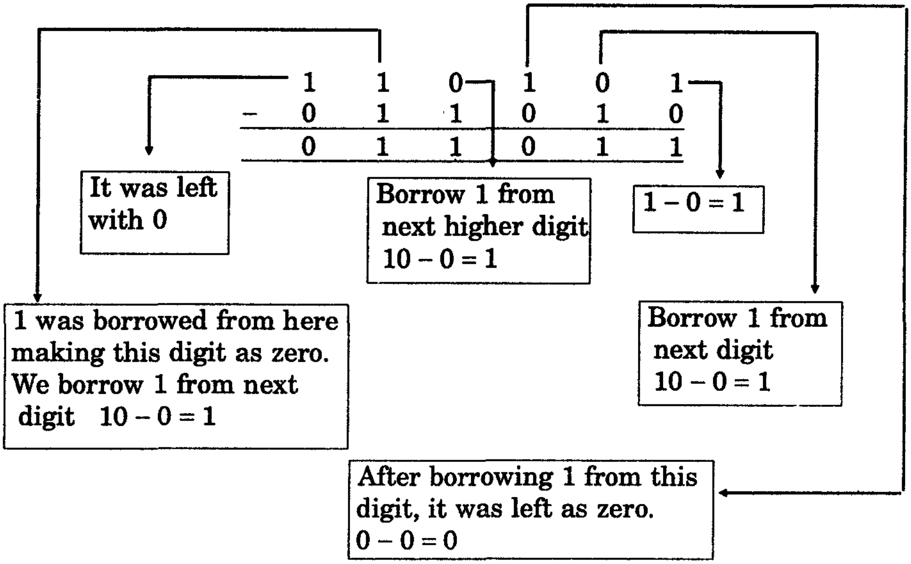


Table-4. Binary subtraction table

Number		Result	
A	**B**	**Sum**	**Carry**
0	0	0	0
0	1	1	1
1	0	1	0
1	1	0	0

[VII] Binary Multiplication

The multiplication rules of binary system are the same as followed in decimal system.

$$0 \times 0 = 0$$
$$0 \times 1 = 0$$
$$1 \times 0 = 0$$
$$1 \times 1 = 1$$

Consider the following example :

$$\begin{array}{ccccc}
 & & 1 & 1 & 0 \\
 & \times & 1 & 0 & 1 \\
\hline
 & & 1 & 1 & 0 \\
 & 0 & 0 & 0 & \\
1 & 1 & 0 & & \\
\hline
1 & 1 & 1 & 1 & 0 \\
\hline
\end{array}
\qquad\qquad
\begin{array}{cccccccc}
 & & & & 1 & 1 & 0 & 1 \\
 & & \times & & 1 & 0 & 1 & 0 \\
\hline
 & & & & 0 & 0 & 0 & 0 \\
 & & & 1 & 1 & 0 & 1 & \\
 & & 0 & 0 & 0 & 0 & & \\
 & 1 & 1 & 0 & 1 & & & \\
\hline
1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
\hline
\end{array}$$

Table-5. Binary multiplication table

A	B	Output
0	0	0
0	1	0
1	0	0
1	1	1

[VIII] Binary One's and Two's Complements

The complement system is used for subtracting the binary numbers by adding them. The number which is to be subtracted is called subtrahend and the number from which is to be subtracted is called minuend. For example, if 42 is to be subtracted from 82 then 82 will be minuend and 42 will be as subtrahend. Following steps are to be carried out for subtracting binary numbers with the help of one's complement.

(a) Minuend and subtrahend should have the same number of digits.

(b) In case of difference in number of digits of both numbers, it should be added with zeros before MSB, to make number of digits equal.

(c) Reverse the subtrahend number, which means that the zeros are to be replaced with 1 and all ones to be replaced with zeroes and add both the numbers.

(d) If we get any carry digit after adding MSB, the carry should be added to the result of addition.

(e) If we get carry after addition of MSB, then the result of subtraction will be positive, otherwise it will be negative.

(f) In case of negative result, it should again be reversed which means that zeros are to be converted to ones and ones to zeros.

[A] Let's now understand the ones complement subtraction step by step.

Example 1.

(1) Step 1. Take two binary numbers, one as minuend and the other subtrahend.

$$\begin{array}{ccccccc}
 & 1 & 1 & 0 & 0 & 1 & 0 \longrightarrow \quad \text{Minuend} \\
- & 0 & 1 & 0 & 1 & 1 & 0 \longrightarrow \quad \text{Subtrahend} \\
\hline
\end{array}$$

(2) Step 2. Subtrahend has one digit less than the minuend, so add the zero at blank place to make the number of digits equal in both the numbers.

$$\begin{array}{rcccccc} & 1 & 1 & 0 & 0 & 1 & 0 \\ - & 0 & 1 & 0 & 1 & 1 & 0 \\ \hline & \uparrow & & & & & \end{array}$$

Place zero at the position of MSB to make number of digits equal in both the numbers.

(3) Step 3. Reverse the digits of subtrahend as zero to one and one to zero and add both the numbers

$$\begin{array}{rcccccc} & 1 & 1 & 0 & 0 & 1 & 0 \\ + & 1 & 0 & 1 & 0 & 0 & 1 \\ \hline & 0 & 1 & 1 & 0 & 1 & 1 \\ + & & & & & & 1 \\ \hline & 0 & 1 & 1 & 1 & 0 & 0 \end{array}$$

→ Carry generated after adding MSB digits of both the numbers.

(4) Step 4. As the result of addition generated carry, so this indicates the result of subtraction is positive and the answer is :

1 1 1 0 0

Let us take another example, which does not generate the carry and gives us the final answer as negative.

Example 2.

(1) Step 1. Take two binary numbers as minuend and subtrahend.

$$\begin{array}{rccccccc} & & & & 1 & 0 & 1 & 1 \\ - & 1 & 0 & 1 & 0 & 0 & 1 & 0 \\ \hline \end{array}$$

1 0 1 1 →Minuend

1 0 1 0 0 1 0 →Subtrahend

(2) Step 2. Minuend has 3 digits lesser than the subtrahend. Let us fill the blank spaces with zeros in minuend.

$$\begin{array}{rccccccc} & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ - & 1 & 0 & 1 & 0 & 0 & 1 & 0 \\ \hline \end{array}$$

0 0 0 1 0 1 1 →Added zeros at blank spaces

(3) Step 3. Reverse the digits of subtrahend as zero to one and one to zero. Now add both the numbers.

$$\begin{array}{rccccccc} & 0 & 0 & 0 & 1 & 0 & 1 & 1 \\ + & 0 & 1 & 0 & 1 & 1 & 0 & 1 \\ & & 1 & 1 & 1 & 0 & 0 & 0 \\ \hline \end{array}$$

1 1 1 0 0 0 →This addition does not generate the carry.

(4) Step 4. As the above addition does not generate any carry so it indicates that the result is negative. So, to get the correct result we have to reverse the digits of answer as zero to one and one to zero and the answer will be :

– 0 0 0 1 1 1

[B] Let us now understand the subtraction of binary numbers with the help of two's complements.

Following steps are to be performed in binary subtraction using two's complements.

Example 3.

(1) Step 1. Take two binary numbers for subtraction as minuend and subtrahend.

$$\begin{array}{ccccccccc} & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 1 \longrightarrow \text{Minuend} \\ - & 1 & 0 & 0 & 1 & 0 & 1 & 1 & 0 \longrightarrow \text{Subtrahend} \end{array}$$

(2) Step 2. Reverse the subtrahend by changing zero to one and one to zero.

$$\begin{array}{ccccccccc} & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 1 \\ - & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \longrightarrow \text{Subtrahend after reversing the digits.} \end{array}$$

(3) Step 3. Add one to subtrahend to make it two's complement

$$\begin{array}{ccccccccc} & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 1 \\ - & 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \\ \hline \end{array}$$

$$\boxed{\begin{array}{cccccccc} 0 & 1 & 1 & 0 & 1 & 0 & 0 & 1 \\ & & + & & & & & 1 \\ \hline 0 & 1 & 1 & 0 & 1 & 0 & 1 & 0 \\ \multicolumn{8}{c}{\text{Two's complement of subtrahend}} \end{array}}$$

(4) Step 4. Add minuend and two's complement of subtrahend.

$$\begin{array}{ccccccccc} & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 1 \\ + & 0 & 1 & 1 & 0 & 1 & 0 & 1 & 0 \\ \hline 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \end{array}$$

(5) Step 5. Disregard the carry in the result of addition to get the correct answer.

1 0 1 0 0 0 0 1 1

↑——————— Disregard the carry. the answer will be 1 0 0 0 0 1 1.

(6) Step 6. If there is no carry in the result of addition, find out its one's complement by subtracting 1 from the number.

(7) Step 7. Now reverse the digits of one's complement to get the correct answer.

We will now solve more problems for the students.

NUMERICAL PROBLEMS

Problem 1. ***Find the binary equivalent of*** **$(39)_{10}$.**

Solution. $(39)_{10} = ?$

2	39	Remainder
2	19	1
2	9	1
2	4	1
2	2	0
2	1	0
2	0	1

(LSB)

↑ Bottom to top

(MSB)

Therefore, $(39)_{10} = (100111)_2$

Verification : $(100111)_2 = 1 \times 2^5 + 0 \times 2^4 + 0 \times 2^3 + 1 \times 2^2 + 1 \times 2 + 1 \times 2^0$

$= 32 + 0 + 0 + 4 + 2 + 1.$

$= (39)_{10}$

Problem 2. ***Convert the following decimal numbers to binary :***

(i) **$(89)_{10}$** ***(ii)*** **$(146)_{10}$**

Solution. (i) $(89)_{10} = (\ ?\ )_2$

2	89	Remainder	
2	44	1	(LSB)
2	22	0	↑
2	11	0	│
2	5	1	│
2	2	1	│
2	1	0	│
2	0	1	(MSB)

∴ $(89)_{10} = (1011001)_2$

(ii) $(146)_{10} = (\ ?\ )_2$

2	146	Remainder	
2	73	0	(LSB)
2	36	1	↑
2	18	0	│
2	9	0	│
2	4	1	│
2	2	0	│
2	1	0	│
	0	1	(MSB)

∴ $(146)_{10} = (10010010)_2$

Problem 3. ***Convert the following decimal numbers to binary :***

(i) **$(0.6875)_{10}$** *(ii)* **$(21.6)_{10}$**

		Carry	(MSB)
Solution. (i)	$0.6875 \times 2 = 1.3750$	1	│
	$0.3750 \times 2 = 0.7500$	0	│
	$0.7500 \times 2 = 1.5000$	1	↓
	$0.5000 \times 2 = 1.0000$	1	(LSB)

∴ $(0.6875)_{10} = (0.1011)_2$

Verification. $(0.1011)_2 = 1 \times 2^{-1} + 0 \times 2^{-2} + 1 \times 2^{-3} + 1 \times 2^{-4}$

$$= \frac{1}{2} + 0 + \frac{1}{8} + \frac{1}{16}$$

$$= 0.5 + 0.125 + 0.0625$$

$$= (0.6875)_{10}$$

(ii) First consider the whole number part :

2	21	Remainder	
2	10	1	(LSB)
2	5	0	↑
2	2	1	│
2	1	0	│
	0	1	(MSB)

Next consider the fractional part :

	Carry	
		(MSB)
$0.6 \times 2 = 1.2$	1	↑
$0.2 \times 2 = 0.4$	0	
$0.4 \times 2 = 0.8$	0	
$0.8 \times 2 = 1.6$	1	
$0.6 \times 2 = 1.2$	1	(LSB)

As we shall not get the fractional product equal to zero, so we terminate at the fifth bit. Therefore,

$$(21.6)_{10} = (10101.10011)_2$$

Problem 4. ***Convert : (i)* $(0.6875)_{10}$ and *(ii)* $(0.115)_{10}$ *to octal.***

Solution. (i) $(0.6875)_{10} = (\ ?\ )_8$

	Carry	
		(MSB)
$0.6875 \times 8 = 5.5000$	5	↓
$0.5000 \times 8 = 4.0000$	4	(LSB)

$\therefore \quad (0.6875)_{10} = (0.54)_8$

(ii) $(0.115)_{10} = (\ ?\ )_8$

	Carry	
		(MSB)
$0.115 \times 8 = 0.920$	0	
$0.920 \times 8 = 7.360$	7	
$0.360 \times 8 = 2.880$	2	
$0.880 \times 8 = 7.040$	7	
$0.040 \times 8 = 0.320$	0	
$0.320 \times 8 = 2.560$	2	↓
$0.560 \times 8 = 4.480$	4	(LSB)

up to 7 decimal places.

$\therefore \quad (0.115)_{10} = (0.0727024)_8$

Problem 5. ***Convert* $(564.3)_{10}$ *to octal.***

Solution. $(564.3)_{10} = (\ ?\ )_8$

8	564	Remainder	
8	70	4	(LSB)
8	8	6	↑
8	1	0	
	0	1	(MSB)

	Carry	
		(MSB)
$0.3 \times 8 = 2.4$	2	
$0.4 \times 8 = 3.2$	3	
$0.2 \times 8 = 1.6$	1	
$0.6 \times 8 = 4.8$	4	
$0.8 \times 8 = 6.4$	6	↓
$0.4 \times 8 = 3.2$	3	(LSB)

upto 6 decimal places.

$\therefore \quad (564.3)_{10} = (1064.231463)_8$

Problem 6. ***Convert* $(76.43)_8$ *to decimal.***

$$(76.43)_8 = 6 \times 8^0 + 7 \times 8^1 + 4 \times 8^{-1} + 3 \times 8^{-2}$$

$$= 6 + 56 + 4 \times 0.125 + 3 \times 0.0625$$

$$= 62 + 0.500 + 0.1875$$
$$= (62.6875)_{10}$$

Problem 7. ***Convert the following binary numbers into octal :***

(i) $\mathbf{(110101100)_2}$ ***(ii)*** $\mathbf{(1101.101)_2}$ ***(iii)*** $\mathbf{(111.1)_2}$

Solution. (i) $(110101100)_2 = (\ ?\ )_8$

$$\begin{array}{lccccc} (110101100)_2 & = & 110 & 101 & 100 \\ & & \downarrow & \downarrow & \downarrow \\ & & 6 & 5 & 4 \end{array}$$

$\therefore \quad (110101100)_2 = (654)_8$

(ii) $(1101.101)_2 = (\ ?\ )_8$

$$\begin{array}{lccccc} (1101.101)_2 & = & 001 & 101 & . & 101 \\ & & \downarrow & \downarrow & & \downarrow \\ & & 1 & 5 & . & 5 \end{array}$$

$\therefore \quad (1101.101)_2 = (15.5)_8$

(iii) $(111.1)_2 = (\ ?\ )_8$

$$\begin{array}{lcccc} (111.1)_2 & = & 111 & . & 100 \\ & & \downarrow & & \downarrow \\ & & 7 & . & 4 \end{array}$$

$\therefore \quad (111.1)_2 = (7.4)_8$

Table 6. First eight octal numbers and their binary equivalents.

Octal number	Binary
0	000
1	001
2	010
3	011
4	100
5	101
6	110
7	111

Problem 8. ***Convert the following octal numbers into binary :***

(i) $\mathbf{(537)_8}$ ***(ii)*** $\mathbf{(47.12)_8}$ ***(iii)*** $\mathbf{(160.5)_8}$

Solution. (i) $(537)_8 = (\ ?\ )_2$

$$\begin{array}{lccccc} (537)_8 & = & 5 & 3 & 7 \\ & & \downarrow & \downarrow & \downarrow \\ & & 101 & 011 & 111 \end{array}$$

$\therefore \quad (537)_8 = (101011111)_8$

(ii) $(47.12)_8 = (\ ?\ )_2$

$$\begin{array}{lcccccc} (47.12)_8 & = & 4 & 7 & . & 1 & 2 \\ & & \downarrow & \downarrow & & \downarrow & \downarrow \\ & & 100 & 111 & . & 001 & 010 \end{array}$$

$\therefore \quad (47.12)_8 = (100111.001010)_2$

(ii) $(160.5)_8 = (\ ?\ )_2$

(iii) $$(160.5)_8 = \begin{array}{ccccc} 1 & 6 & 0 & . & 5 \\ \downarrow & \downarrow & \downarrow & & \downarrow \\ 001 & 110 & 000 & . & 101 \end{array}$$

$\therefore$ $(160.5)_8 = (001110000.101)_2$

Problem 9. ***Convert the following hexadecimal numbers to decimal numbers :***

(i) $(E\,5)_{16}$ ***(ii)*** $(F\,F\,F\,F)_{16}$ ***(iii)*** $(2\,A\,.\,3\,F)_{16}$

Solution. (i) $(E\ 5)_{16} = (\ ?\ )_{10} = 5 \times 16^0 + E \times 16^1$

$$= 5 \times 1 + 14 \times 16 \quad (\because \quad E = 14)$$
$$= 5 + 224$$
$$= (229)_{10}$$

(ii) $(F\ F\ F\ F)_{16} = (\ ?\ )_{10}$

$$= F \times 16^0 + F \times 16^1 + F \times 16^2 + F \times 16^3$$
$$= 15 \times 1 + 15 \times 16 + 15 \times 256 + 15 \times 4096 \quad (\because F = 15)$$
$$= 15 + 240 + 3840 + 61440$$
$$= (65535)_{10}$$

(iii) $(2A\,.\,3F)_{16} = (\ ?\ )_{10}$

$$= A \times 16^0 + 2 \times 16^1 + 3 \times 16^{-1} + F \times 10^{-2}$$
$$= 10 \times 1 + 2 \times 16 + \frac{3}{16} + \frac{15}{256} \quad (\because \ A = 10, \ \ F = 15)$$
$$= 10 + 32 + \frac{3}{16} + \frac{15}{256}$$
$$= (42.2461)_{10}$$

Problem 10. ***Convert the following hexadecimal numbers into binary :***

(i) $(D\,4\,3\,F\,7)_{16}$ ***(ii)*** $(6\,F\,2\,E)_{16}$ ***(iii)*** $(5\,F\,4\,.\,24)_{16}$

Solution. (i) $(D\ 4\ E\ 3\ F\ 7)_{16} = (\ ?\ )_2$

$$(D\,4\,E\,3\,F\,7)_{16} = \begin{array}{cccccc} D & 4 & E & 3 & F & 7 \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 1101 & 0100 & 1110 & 0011 & 1111 & 0111 \end{array}$$

$\therefore$ $(D\,4\,E\,3\,F\,7)_{16} = (1101\ 0100\ 1110\ 0011\ 1111\ 0111)_2/$

(ii) $(6\ F\ 2\ E)_{16} = (\ ?\ )_2$

$$(6\,F\,2\,E)_{16} = \begin{array}{cccc} 6 & F & 2 & E \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 0110 & 1111 & 0010 & 1110 \end{array}$$

$\therefore$ $(6\ F\ 2\ E)_{16} = (0110\ 1111\ 0010\ 1110)_2$

(iii) $$(5\,F\,4.24)_{16} = \begin{array}{cccccc} 5 & F & 4 & . & 2 & 4 \\ \downarrow & \downarrow & \downarrow & & \downarrow & \downarrow \\ 0101 & 1111 & 0100 & . & 0010 & 0100 \end{array}$$

$\therefore$ $(5\ F\ 4.24)_{16} = (0101\ 1111\ 0100\ .\ 0010\ 0100)_2$

Problem 11. ***Convert*** $(1010\,.\,0001\ 1111\ 01011\ 000)_2$ ***into hexadecimal number.***

Solution. $(1010.0001111101011000)_2 = (\ ?\ )_6$

$$\begin{array}{ccccccc} = & 1010 & . & 0001 & 1111 & 0101 & 1000 \\ & \downarrow & & \downarrow & \downarrow & \downarrow & \downarrow \\ & A & . & 1 & F & 5 & 8 \end{array}$$

$= (A\,.\,1\,F\,58)_6$

Problem 12. ***Convert the following decimal numbers into hexadecimal numbers :***

(i) $(47)_{10}$ *(ii)* $(84.5)_{10}$ *(iii)* $(500.625)_{10}$

Solution. (i)

16	47	1	(LSB)
16	2	15 (F)	↑
	0	2	(MSB)

∴ $(47)_{10} = (2F)_{16}$ ($\because$ F = 15)

(ii) $(84.5)_{10} = (\ ?\ )_{16}$

16	84		(LSB)
16	5	4	↑
	0	5	(MSB)

$0.5 \times 16 = 8.0$ (MSB)

∴ $(84.5)_{10} = (54.8)_{16}$

(iii) $(500.625)_{10} = (\ ?\ )_{16}$

16	500		(LSB)
16	31	4	↑
16	1	15 (F)	
	0	1	(MSB)

$0.625 \times 16 = 10.00 \mid A_{(10)}$

∴ $(500.625)_{10} = (1\,F\,4.A)_{16}$

Problem 13. ***Convert the following hexadecimal numbers to their octal equivalents :***

(i) $(5F.43)_{16}$ *(ii)* $(ABAB)_6$

Solution. (i) $(5\,F.43)_{16} = (\ ?\ )_8$

$$\begin{array}{ccccc} 5 & F & . & 4 & 3 \\ \downarrow & \downarrow & & \downarrow & \downarrow \\ 0101 & 1111 & . & 0100 & 0011 \end{array}$$

$= (001\ \ 011\ \ 111\ \ .\ \ 010\ \ 000\ \ 110)_2$

$$\begin{array}{cccccccc} = & 001 & 011 & 111 & . & 010 & 000 & 110 \\ & \downarrow & \downarrow & \downarrow & . & \downarrow & \downarrow & \downarrow \\ & 1 & 3 & 7 & & 2 & 0 & 6 \end{array}$$

∴ $(5\,F.43)_{16} = (137.206)_8$

(ii) $(A\,B\,A\,B)_{16} = (\ ?\ )_8$

$$\begin{array}{cccc} A & B & A & B \\ \downarrow & \downarrow & \downarrow & \downarrow \\ 1010 & 1011 & 1010 & 1011 \end{array}$$

$= (1\ \ 010\ \ 101\ \ 110\ \ 101\ \ 011)_2$

$$\begin{array}{cccccc} = 001 & 010 & 101 & 110 & 101 & 011 \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 1 & 2 & 5 & 6 & 5 & 3 \end{array}$$

$\therefore$ $(ABAB)_{16} = (125653)_8$

Problem 14. ***Convert the following octal numbers into their hexadecimal equivalent :***

(i) $(2543)_8$ *(ii)* $(532.74)_8$

Solution. (i) $(2543)_8 = (\ ?\ )_{16}$

$$\begin{array}{llll} = (010 & 101 & 100 & 011)_2 \\ = 0101 & 0110 & 0011 & \\ \quad\downarrow & \downarrow & \downarrow & \\ \quad 5 & 6 & 3 & \end{array}$$

$\therefore$ $(2543)_8 = (563)_{16}$

(ii) $(532.74)_8 = (\ ?\ )_{16}$

$$\begin{array}{lcccccc} (532.74)_8 & = (101 & 011 & 011 & . & 111 & 100)_2 \\ & = (1 & 0101 & 1010 & . & 1111 & 00)_2 \\ & = 0001 & 0101 & 1010 & . & 1111 & 0000 \\ & \downarrow & \downarrow & \downarrow & & \downarrow & \downarrow \\ & 1 & 5 & A & . & F & 0 \end{array}$$

$\therefore$ $(532.74)_8 = (15A\,.\,F0)_{16}$

Problem 15. ***Add the following numbers :***

(i) $(101)_2$ ***and*** $(001)_2$ *(ii)* $(11)_2$ **and** $(01)_2$

Solution. (i)

$$\begin{array}{lccc} \text{Augend} & & 1 & 1 \\ \text{Addend} & & 0 & 1 \\ \hline & 1 & 0 & 0 \end{array}$$

(ii)

$$\begin{array}{lccc} \text{Augend} & 1 & 0 & 1 \\ \text{Addend} & 0 & 0 & 1 \\ \hline & 1 & 1 & 0 \end{array}$$

Problem 16. ***Add the binary numbers 1010 and 1111.***

Solution.

$$\begin{array}{lcccc} \text{Augend} & 1 & 0 & 1 & 0 \\ \text{Addend} & 1 & 1 & 1 & 1 \\ \hline \text{Carry bit} \longleftarrow 1 & 1 & 0 & 1 & 1 \end{array}$$

Problem 17. ***Subtract (i)*** $(001)_2$ ***from*** $(100)_2$ ***and (ii)*** $(011)_2$ ***from*** $(101)_2$.

Solution. (i)

$$\begin{array}{lccc} \text{Minuend} & 1 & 0 & 0 \\ \text{Subtrahend} & 0 & 0 & 1 \\ \hline & 0 & 1 & 1 \end{array}$$

(ii)

$$\begin{array}{lccc} \text{Minuend} & 1 & 0 & 1 \\ \text{Subtrahend} & 0 & 1 & 1 \\ \hline & 0 & 1 & 0 \end{array}$$

Problem 18. ***Multiply*** $(10111)_2$ ***by*** $(101)_2$.

Solution.

$$\begin{array}{lccccccc} \text{Multiplicand} & & & 1 & 0 & 1 & 1 & 1 \\ \text{Multiplier} & & \times & & & 1 & 0 & 1 \\ \hline & & & 1 & 0 & 1 & 1 & 1 \\ & & 0 & 0 & 0 & 0 & 0 & \\ & 1 & 0 & 1 & 1 & 1 & & \\ \hline \text{Product} & 1 & 1 & 1 & 0 & 0 & 1 & 1 \end{array}$$

Problem 19. ***Multiply* $(1101)_2$ *by* $(1011)_2$.**

Solution.

$$\begin{array}{lcccccccc}
\text{Multiplicand} & & & & 1 & 1 & 0 & 1 & \\
\text{Multiplier} & & & \times & 1 & 0 & 1 & 1 & \\
\hline
 & & & & 1 & 1 & 0 & 1 & \\
 & & & 1 & 1 & 0 & 1 & & \\
 & & 0 & 0 & 0 & 0 & & & \\
 & & 1 & 1 & 0 & 1 & & & \\
\hline
\text{Product} & 1 & 0 & 0 & 0 & 1 & 1 & 1 & 1
\end{array}$$

Problem 20. ***Divide* $(1111000)_2$ *by* $(100)_2$.**

Solution. The division of binary numbers is carried out in the same way as in decimal numbers. The rules for division are :

$0 \div 1 = 0 \quad ; \quad 1 \div 1 = 1$

Division by 0 is meaningless.

```
       11110
    100)1111000(
        100
        ---
        111
        100
        ---
         110
         100        [Here, divisor = 100;
         ---
          100         dividend = 1111000;
          100         quotient = 11110]
          ---
           000
           000
           ---
           000
```

$\therefore \quad (1111000)_2 \div (100)_2 = (11110)_2$

2·5. PROGRAMMING

In order to solve a problem on a computer, we have to develop an algorithm. An algorithm is a set of instructions which if strictly followed, will give a solution to the problem. In case an instruction is obeyed, we say it is executed. The following activities are involved when we solve a problem on a computer..

(a) Define the problem.

(b) Analyse the problem.

(c) Develop an algorithm or a method for solving the problem.

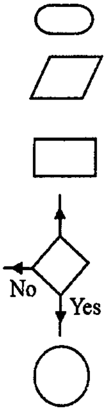
(e) Test and debug the program.

(f) Document the program.

There is normally some overlap of the above activities. For example, with a large program, a portion may be written and tested before another portion is written. For any problem, there will normally be more than one algorithm (method) to solve it. Each method will have its own advantages and disadvantages. The user will have a choice of algorithms and it will be his/her job to decide which algorithm is the best and why this is so.

[I] Flow Charts

The algorithm uses a numbered list of instructions, the instructions themselves are English-like statements of what must be done. Another method which is useful for specifying small algorithms is the ***flow chart***. A flow chart consists of ***'flow chart symbols'*** connected by arrows. Each symbol will have information about what must be done at the point and the arrows indicate the flow of execution of the algorithm, *i.e.*, they indicate the order in which the instructions must be executed. Figure (14) shows the symbols commonly used in flow charting.



Oval, indicates Start or Stop; terminator symbol)

Parallelogram, used to specify an Input or Output operation, *e.g.*, getting data or printing data; (I/O symbol)

Rectangle, used to specify an operation or process, *e.g.*, 'find average' or 'set F to 32 + C (process symbol)

Rhombus, used to specify a condition. This usually takes the form of a question with possible answers Yes or No (or True or False).
These arrows lead to the required action corresponding to the answer to the question (the decision symbol, more commonly called the decision box).

Circle, used as a connecting point for arrows coming from different directions (connector symbol).

Fig. 14. Flow chart symbols.

2·6. COMPUTER PROGRAMMING LANGUAGES

We have already discussed that computer is not merely a calculating machine but it can do something more than that. The instructions are fed into the computer in the form of a program. Program is a set of instructions. There are different programming languages used to feed the instructions into a computer. The following are the categories of programming languages.

[I] Low Level Language

Low level language is also known as machine language. Machine language is in the form of 0 and 1. When the computers were developed initially, the interpreter programs were not available to convert the program code written in plain language to 0 and 1. Computer understands the language of 0 and 1 only. The computer programs were written using the machine codes (0 and 1), that could directly be fed to computer memory for execution. We know that the characters used in computer are represented with the help of binary numbers. Each character is represented with a group of 8 bits. If the character B was to be used in computer program, the user had to type the binary code of B and not the character B. For example, if statement C = A + B was to be written as a part of a program then the user had to type the binary code of each character directly and not the characters. Low level language is computer oriented which means that program written for one machine can work only on similar type of machine.

[II] Assembly Language

Assembly language is slightly improved pattern of machine language. In this language, the instructions are written using the words of English language. These words are further decoded to 0 and 1 with the help of another program called the ***assembler***. This language is also machine dependent. This means that the program written for a particular computer cannot run on another computer.

[III] High Level Language

Understanding of assembly language is slightly difficult for every one because it requires technical knowledge of the microprocessor. To overcome these difficulties and to understand the assembly language, high level languages have been developed. In high level language, the instructions are written using English language. The examples of high level language are FORTRAN, COBOL, BASIC, PASCAL, C, C_{++} etc. These languages are procedure oriented and not the computer oriented. It means that programmer need not to worry about knowing the architecture of the microprocessor. Programs are common for each computer, which means that the program written on one computer can run on any computer. This feature of high level language has increased the portability of programs. The compiler is required to translate the language to machine code for computer. The computer will be different for different languages.

(1) FORTRAN. It means *'Formula Translation'* and is the oldest high level language. It was developed in 1956-57. It was designed to solve scientific and engineering problems and is currently the most popular language among the scientists and engineers. After 1957, it appears in different variations such as FORTRAN II, FORTRAN IV and FORTRAN 77 (a version of 1977). The updated version of FORTRAN 77 is FORTRAN 90.

(2) COBOL. It means *'Common Business Oriented Language'* and was designed to solve the data processing problems of the business community, *e.g.*, problems relating to pay roll, stock control, accounts received and paid, cheque analysis etc. The activities involve little numerical work but a large amount of data has to be processed. The processing consists in creating and updating large files of data. Unlike FORTRAN, the COBOL does not have all the commonly used mathematical functions such as square root, sine, cosine, tangent, logarithms and exponentials etc. In FORTRAN, matrices encountered in science and engineering can be manipulated easily using the FORTRAN arrays, whereas in COBOL this cannot be done.

(3) BASIC. It means *'Beginner's All-purpose Symbolic Instruction Code'* and was developed by John Kemeny and Thomas Kurtz (1963). Basic is easy to learn and use. It was mainly designed to be used as an interactive language. Almost every computer manufacturer provides BASIC on its machines. BASIC is probably the most widely used programming language in the world because of the widespread use of microcomputers.

(4) PASCAL. It was designed by Niklaus Wirth and named after the famous French mathematician, Blaise Pascal (17th century). The first Pascal compiler appeared in 1970. The language was chiefly designed as a tool for teaching structured programming concepts. Most of the colleges and universities use it to teach computer programming. Pascal has the facilities to manipulate, not only numbers, but also vectors, matrices, strings of characters, records and files etc. PASCAL is more readable and thus self documentary as compared to BASIC.

(5) C LANGUAGE. It was designed by Denis Ritchie (1972). It enables the user to perform almost everything that can be done in assembly language, but which is more readable and better structured. It is used for writing the very popular operating system UNIX.

(6) SNOBOL. It means *'String Oriented Symbolic Language'* and was designed to solve non-numeric problems.

(7) ALGOL. It means *'Algorithmic Language'*. It was the fore-runner of PASCAL language but it could not gain in popularity.

(8) ADA. It was designed particularly for complex real time problems and was named in honour of Lady Ada Augusta Lovelace who is reputed to have written the first computer program for a computer developed by Charles Babbage (1842). It was promoted by the U.S. Department of Defence for applications in the field of control of processes in military applications.

(9) PROLOG. It means *'Programming in Logic'* and was invented by Colmerauer and Roussel (1972). In this language, we specify what is to be computed and the system decides how it must be carried out. In recent years, PROLOG has been employed for teaching computer programming to children. It is sometimes known as 'language of the future.'

2·7. OPERATING SYSTEMS

Operating system is a software loaded into computer memory for ensuring the control and proper working of computer hardware. No computer can work without an operating system. The reason for it is that the system of working of each part of computer is defined in operating system program.

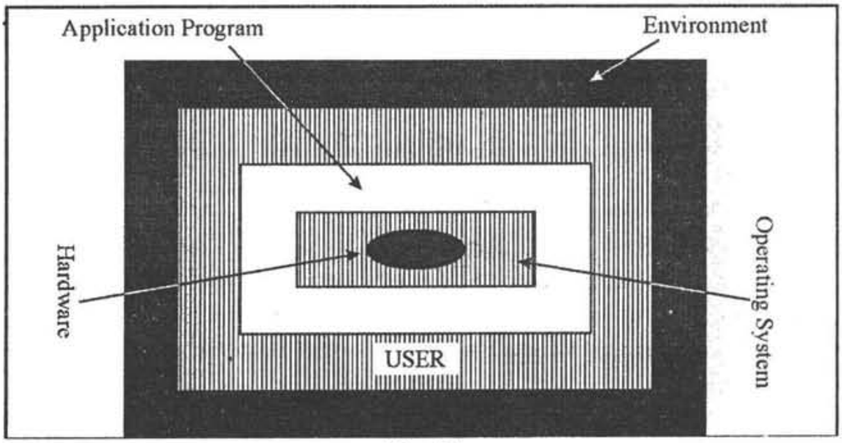
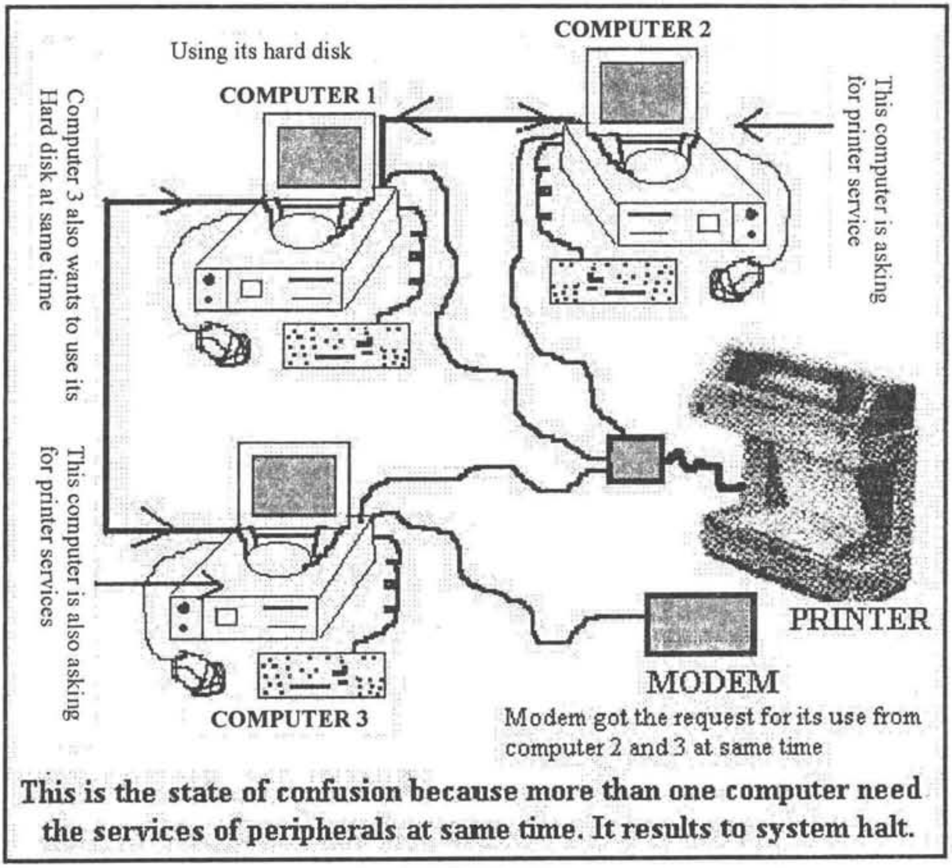


Fig. 15.

We know that many programs can be loaded in computer memory. Different parts of computer are used to operate these programs on computer. There are chances of clashing of instructions issued through different programs. It may create a halt to operation of the computer. If two different programs need the service of some part of the computer, it may create a state of confusion that whose service is to be completed first. Operating system software has been assigned this responsibility to decide the priority and conrol the entire system. Operating system is required in computer in the same way as a principal is required in a college or a vice-chancellor in a university, who takes the decision above all the teaching staff.

Operating system attends to the request of different programs running in computer memory and decides their working through the hardware. For example, suppose you want to read the data from a floppy and execute the command for this purpose. The operating system will read this command and check the availability of floppy drive before reaching the data. Similarly, if you execute the command for printing a file through printer, the operating system program will check the availability of printer. The complete control of hardware is done through operating system program. Figures (16) and (17) will make us understand the need of an operating system in any computer.



This is the state of confusion because more than one computer need the services of peripherals at same time. It results to system halt.

Fig. 16.

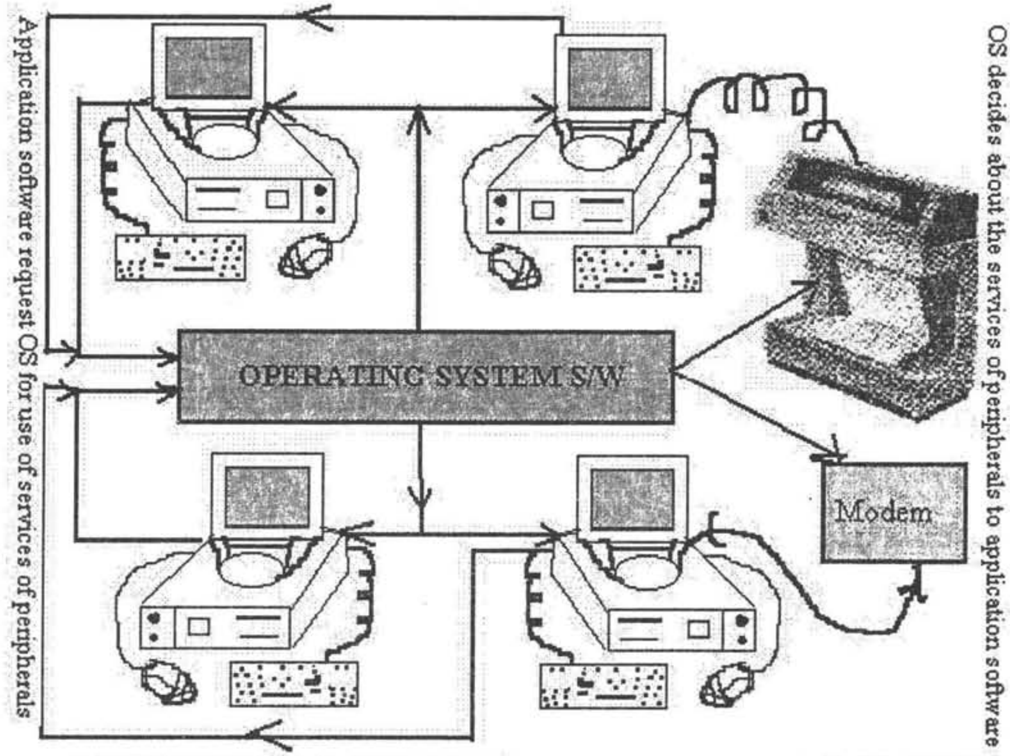


Fig. 17.

[I] Personal Computer Operating Systems

The examples of operating systems are MS-DOS, MS-WINDOWS, UNIX, ZENIX etc. The main mode of use of a personal computer (PC) is by a single user. Thus, operating systems (OS) for PCs have been constructed as a single user single task operating system, *i.e.*, it is assumed that only a single user uses the machine and runs only one program at a time. The operating system of PCs consists of two parts, *viz.*, (i) *Basic Input Output System* (BIOS) which is stored in a floppy disc or a hard disc and (ii) *Microsoft Disc Operating System* (MS DOS). This type of OS is widely used. The BIOS provides basic low level services, whereas DOS provides many user-level services. MS-DOS provides services such as editing, filing and other utility programs.

MS-Windows is an improved operating system for more powerful personal computers which have a large memory (4 to 8 MB) and disc (200 to 400 MB). This gives a very good *'Graphical User Interface'* (GUI) which simplifies the use of the computer. It also helps us to allow the multiple programs to be simultaneously stored in memory and executed.

(1) UNIX operating system. This system [figure (18)] is a very powerful operating system used in personal computers and supercomputers. UNIX is written in C, so it makes it portable. It is organised as a layered operating system. The innermost portion is known as a ***kernel.*** It provides low-level services, *e.g.*, device drivers and memory management. The next portion is known as a ***shell***. It is a command interpreter. The outermost portion is known as ***utilities portion***. It provides miscellaneous services such as text processing, text setting, games, calender, graphics, language compilers etc. The user interacts with the kernel using commands and utilities.

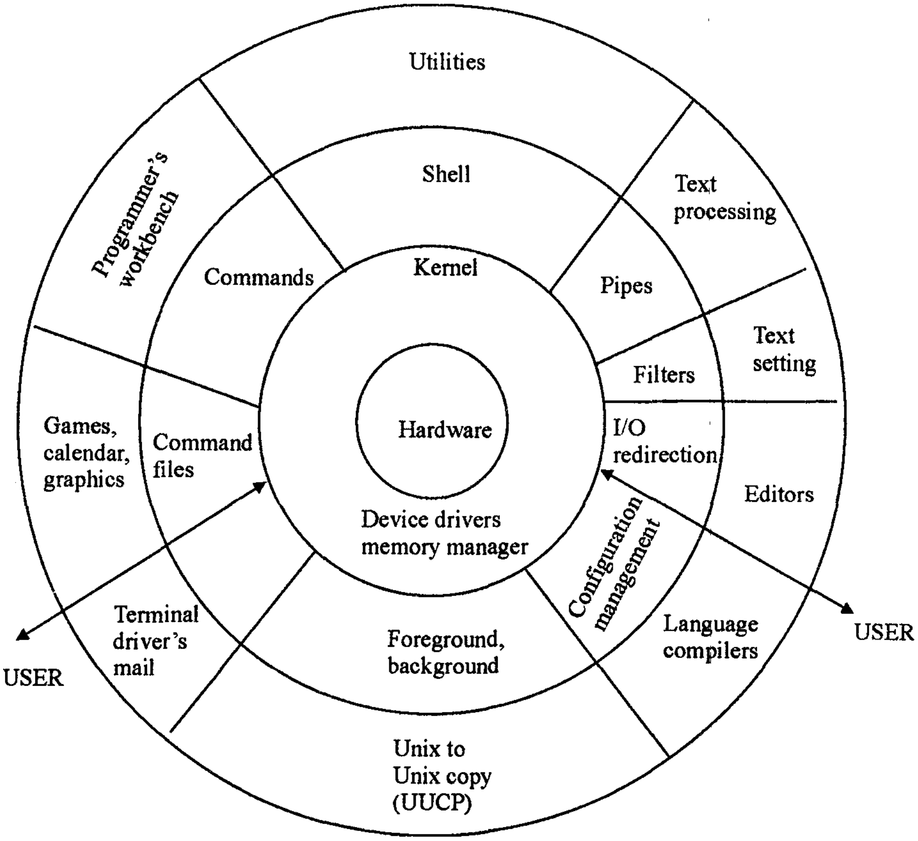


Fig. 18.

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. Explain briefly the Base 10 system of numeration.
2. Write a short note on Abacus.
3. Define the term computer. Explain briefly the working system of a computer.
4. Write a short note on personal computer.
5. Explain in brief about the main parts of a computer.
6. Write a brief note on decimal number system.
7. Describe briefly the high level languages *viz*; Fortran, Pascal, Basic, C language and Cobol.

[I] Short Answer Type Questions

8. What is the function of 'Control Unit' in a computer?
9. Explain the following terms used in computer :

(i) ALU (ii) Hard disc drive (iii) OCR

(iv) CD-ROM (v) RAM (vi) Mouse

10. How does primary memory store data? Explain.
11. Define the terms hardware and software.
12. Distinguish between first and second generation computers.

13. Explain third generation computers.

14. What do you understand by the following terms :

(i) Operating system (ii) Language processor

(iii) Utility programs (iv) Programming

15. What is a binary number system?

16. Define the terms algorithm, bit byte and word length.

17. Why should a byte be a group of 8 bits only?

18. Why do we use alphabets A to F in place of 10 to 15 in hexadecimal number system.

19. Explain the process of binary subtraction using one's complement method with example.

20. What are the functions of MS-DOS and MS-WINDOWS ?

21. Why is laser printer better than DMP ?

22. Explain the secondary storage devices.

23. What are input-output (I/O) devices?

[III] Numerical Problems

1. Convert $(11011.101)_2$ into decimal numbers.

2. Find the binary equivalent of $(99)_{10}$.

3. Convert $(11.625)_{10}$ into binary equivalent.

4. Convert $(0.6875)_{10}$ to octal equivalent.

5. Convert $(47.12)_8$ into binary equivalent.

6. Convert $(5DB9)_{16}$ into binary equivalent.

7. Convert $(B4F5)_{16}$ into decimal number.

8. Convert $(532.74)_8$ into hexadecimal equivalent.

[IV] Multiple Choice Questions

1. The Roman system uses how many symbols to represent its digits?

(a) 3 (b) 5 (c) 7 (d) 11

2. The unit used to read the exernal data and instructions in a computer is :

(a) Input unit (b) Output unit

(c) CPU (d) None of the above

3. The computer memory is measured in terms of :

(a) Units (b) Bytes (c) Binary (d) ALU

4. The hexadecimal equivalent of $(2543)_8$ is :

(a) $(253)_{16}$ (b) $(363)_{16}$ (c) $(463)_{16}$ (d) $(563)_{16}$

5. The decimal equivalent of $(100111)_2$ is :

(a) $(19)_{10}$ (b) $(29)_{10}$ (c) $(39)_{10}$ (d) $(49)_{10}$

6. The binary equivalent of octal number 6 is :

(a) 001 (b) 010 (c) 100 (d) 110

7. 1 second consists of ......microseconds?

(a) 10^3 (b) 10^6 (c) 10^9 (d) 10^{12}

8. Name the principle on which inkjet printer works :

(a) Dot (b) Spray (c) Miscible (d) None of the above

9. The following is an output device :

(a) Keyboard (b) Arithmetic logic unit

(c) Monitor (d) Scanner

10. Computers used integrated circuits as suitching devices in :
(a) First generation computers (b) Second generation computers
(d) Third generation computers (d) Fourth generation computers.

[V] Fill in the Blanks

1. A mouse is .... device generally used in graphical interface software.
2. COBOL is an example of .... level language.
3. .... beam is used for writing or reading the data on CD-ROM.
4. Printers used to print graphs and designs are called ....
5. ENAIC were the .... generation computers.
6. Large scale integration circuits were used in ....generation computers.
7. 8 bits are equal to ....byte.
8. The components which we can see and touch are known as ....
9. 15 in decimal system is equivalent to .... in hexadecimal system.
10. Octal number 1 is equivalent to .... binary equivalent.

[VI] True or False

State whether the following statements are true (T) or false (F) ?

1. In Roman system of numeration, L represents 100.
2. The speed of computer is very fast as compared to a calculator.
3. A computer consists of CPU only.
4. The computer memory is measured in terms of bytes.
5. In computer memory, 0 and 1 are called binary digits or bits.
6. Laser printers are coloured printers.
7. The computer works with 256 characters generated by the keyboard.
8. CD-ROM is a compact disc used to store data for reading purpose.
9. The octal equivalent of $(10)_{10}$ is 12.
10. The binary equivalent of $(0)_{10}$ is 1000.

ANSWERS

[III] Numerical Problems

1. $(27.101)_{10}$ **2.** $(1100011)_2$ **3.** $(1011.101)_2$ **4.** $(0.54)_8$
5. $(100111.001010)_2$ **6.** $(0101110111001)_2$ **7.** $(46325)_{10}$ **8.** $(15A.F0)_{16}$

[IV] Multiple Choice Questions

1. (c) **2.** (a) **3.** (b) **4.** (d) **5.** (c)
6. (d) **7.** (b) **8.** (b) **9.** (c) **10.** (d)

[V] Fill in the Blanks

1. input **2.** high **3.** Laser **4.** plotters **5.** first
6. fourth **7.** one **8.** hardware **9.** F **10.** 000.

[VI] True or False

1. (F) **2.** (T) **3.** (F) **4.** (T) **5.** (T)
6. (F) **7.** (T) **8.** (T) **9.** (T) **10.** (F)

❑❑❑

Chapter 3

GASEOUS STATE

In contrast with solids and liquids, gases occupy the same volume as that of the closed vessel in which they are contained. They are characterised by low density and high compressibility. When different gases in different proportions are brought in contact, they diffuse readily into each other forming a homogeneous mixture. Any gas or gaseous mixture exerts a pressure on the walls of the containing vessel, a pressure which depends on the volume and temperature of the given mass of a gas. All gases are found to expand to the same extent when heated through the same difference of temperature at constant pressure. All gases possess nearly the same coefficients of expansion.

3·1 GAS LAWS

All gases have been seen to obey some simple and common relations, which are generally called ***gas laws***. These are expressed as follows :

(a) Boyle's law : Robert Boyle (1662) measured the variation of the volume of a gas with pressure at constant temperature and the relation is known as Boyle's law. It may be stated as, ***"at constant temperature, the volume of a given mass of a gas varies inversely as its pressure."*** Mathematically,

$$V \propto 1/P, \text{ if temperature is constant}$$

or

$$PV = \text{constant}.$$

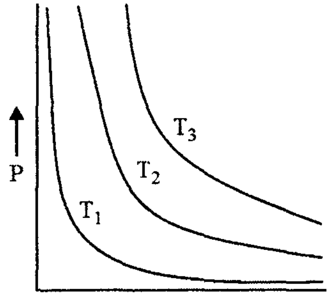


Fig. 1

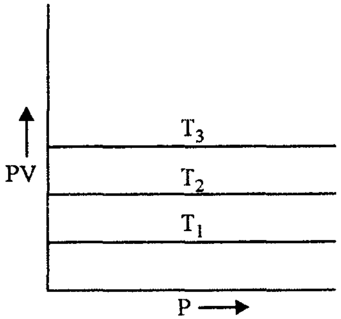


Fig. 2.

In other words, Boyle's law can be stated as, ***"at constant temperature, the product of pressure and volume of a given mass of a gas is constant"***.

If we plot the values of P as ordinate and the values of V as abscissa for a given mass of a gas at a series of constant temperatures, T_1, T_2, T_3 etc., we get rectangular hyperbolae (Fig. 1) and the curves are known as ***isotherms***. We get straight lines when values of PV are plotted against P (Fig. 2).

(b) Gay-Lussac's or Charles' law : The variation of temperature with volume of a certain mass of a gas was studied by Gay-Lussac (1782) and also by Charles (1787) independently and the relation is known as Gay-Lussac's or Charles' law, according to which, ***"at constant pressure, the volume of a given mass of a gas changes by a constant fraction of its volume at 0°C for 1°C change in temperature."***

If V_0 and V_t be the volumes at 0°C and t°C of a given mass of a gas at constant pressure, then

$$V_t = V_0 (1 + \alpha t) \qquad ...(1)$$

where, α is the *coefficient of expansion*, which is approximately the same for all gases, unlike solids or liquids. The value of α has been found to be 0.0036609 or 1/273. We can, therefore express the value of V_t as follows :

$$V_t = V_0 \left(1 + \frac{t}{273} \right) \qquad ...(2)$$

At two temperatures t_1°C and t_2°C, we can write equation (2) as :

$$V_{t_1} = V_0 \left(1 + \frac{t_1}{273} \right)$$

$$V_{t_2} = V_0 \left(1 + \frac{t_2}{273} \right)$$

or

$$\frac{V_{t_1}}{V_{t_1}} = \frac{273 + t_1}{273 + t_2} \qquad ...(3)$$

If we lower the temperature of the gas to –273°C, then according to equation (1), the volume of the gas becomes zero, *i.e.*, this temperature (–273°C) represents the limit of thermal contraction of the gas. This statement is rather hypothetical, because all gases would solidify or liquefy before attaining this limit and a temperature lower than –273°C is so far inconceivable.

A new scale of temperature with this limit as zero and having each degree equal to a centigrade degree has been proposed and is known as ***absolute scale of temperature***. Thus, we have absolute zero equal to –273°C and,

$$t\text{°C} = (273 + t)\ \text{K}$$

From equation (3), we have $\dfrac{V_{t_1}}{V_{t_2}} = \dfrac{T_1}{T_2}$ ...(4)

where, T_1 and T_2 refer to temperatures on the absolute scale.

Hence, Charles' law may be expressed as, ***"at constant pressure, the volume of a given mass of a gas varies directly with the absolute temperature."***

If we plot the values of V as ordinate and values of T as abscissa, we get straight lines passing through the origin, at constant series of pressure (Fig. 3). The curves are known as ***isobars.***

It has also been found that pressure of a given mass of a gas varies directly as the absolute temperature, if the volume is kept constant. *i.e.*, $P \propto T$, if V is constant.

If pressures be plotted against absolute temperatures at a series of constant volume, we get straight lines passing through the origin (Fig. 4). These curves are known as ***isochores.***

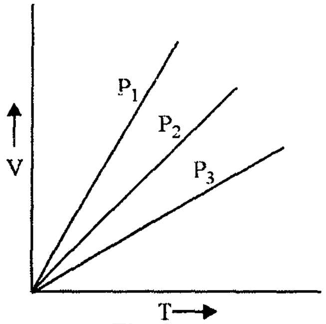


Fig. 3.

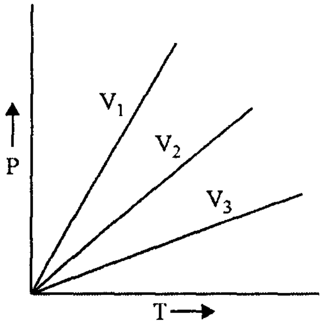


Fig. 4.

(c) Equation of state : By combining Boyle's law and Charles' law, we arrive at the following conclusions :

(i) Boyle's law : $V \propto 1/P$, if n and T are constants.

(ii) Charles' law : $V \propto T$, if n and P are constants.

If all the factors vary, then we have

$$V \propto \frac{T}{P}$$

$$V = \frac{RT}{P}, \text{ where } R \text{ is a constant.}$$

or

$$PV = RT$$

For n moles of a gas,

$$PV = nRT \qquad \ldots(5)$$

At a given temperature and pressure, the volume of one mole of a gas is the same and so 'R' is a universal constant. Equation (5) gives us a relation connecting P, V and T of a system and is known as ***'equation of state'.***

(d) Avogadro's hypothesis : Avogadro (1811) said that ***"at the same temperature and pressure, equal volumes of all gases would contain equal number of molecules."***

(e) Dalton's law of partial pressures : If a vessel contains a mixture of two or more gases, then the individual pressures of different gases will depend upon the relative amounts of the constituent gases. The individual pressures can, however, be expressed in terms of partial pressures of the constituents. The partial pressure of a gas is defined as, ***"the pressure it would exert if it alone occupied the whole volume of the vessel at the same temperature."***

Dalton on studying the relation between individual partial pressures of the constituents and the total pressure of the system enunciated his law of partial pressures, according to which, ***"the total pressure of a mixture of gases is equal to the sum of the partial pressures of the sum of the constituent gases, at the same temperature."***

If a mixture of gases contain $n_1, n_2, n_3, \ldots$ moles of different gases at temperature T, whose partial pressures are represented by $p_1, p_2, p_3, \ldots$

respectively, then according to Dalton's law of partial pressures, the total pressure (P) of the system will be given by,

$$P = p_1 + p_2 + p_3, \ldots \qquad \ldots(6)$$

According to the equation of state, we have

$$P = \frac{n}{V} . RT$$

where, V is the total volume of the system, and n is the total number of moles of gases, *i.e.*,

$$n = n_1 + n_2 + n_3 + \ldots$$

Therefore, individual partial pressures are given by,

$$p_1 = \frac{n_1}{V} . RT; p_2 = \frac{n_2}{V} . RT; p_3 = \frac{n_3}{V} RT. \qquad \ldots(7)$$

$$\therefore \quad p_1 + p_2 + p_3 + \ldots = \left(n_1 + n_2 + n_3 + \ldots\right) \frac{RT}{V} . = \frac{n}{V} RT. \qquad \ldots(8)$$

$$\therefore \quad P = p_1 + p_2 + p_3, \ldots$$

From equations (7) and (8), we have

$$p_1 = \frac{n_1}{n} . P ; \quad p_2 = \frac{n_2}{n} . P ; \quad p_3 = \frac{n_3}{n} . P$$

Problem 1. ***200 g of hydrogen mixed with 700 g of nitrogen are kept at a pressure of 100 atmospheres. Calculate the partial pressures of hydrogen and nitrogen.***

Solution. $n_{H_2} = \frac{200}{2} = 100; \quad n_{N_2} = \frac{700}{28} = 25.$

$\therefore$ Total number of moles = 100 + 25 = 125.

Now, $p_{H_2} = \frac{100}{125} \times 100 = 160$ atmospheres

$p_{N_2} = \frac{25}{125} \times 100 = 20$ atmospheres

(f) Amagat's law of partial volumes : This law is quite analogous to the preceding law. According to this law, ***"the total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases."***

In other words, if $v_1, v_2, v_3, \ldots$ be the partial volumes of the constituent gases and V be the total volume, then we have

$$V = v_1 + v_2 + v_3 + \ldots$$

The partial volume of a constituent is defined as the ***volume which the particular constituent would occupy at the total pressure of the mixture, at the same temperature.***

From equation of state, we have $V = \frac{n}{P} . RT$

The partial volumes will then be given by,

$$v_1 = \frac{n_1}{P} . RT; v_2 = \frac{n_2}{P} . RT; v_3 = \frac{n_3}{P} . RT.$$

$$v_1 + v_2 + v_3 + \ldots = \left(n_1 + n_2 + n_3 + \ldots\right)\frac{RT}{P} = \frac{n}{P} \cdot RT.$$

$$\therefore \qquad V = v_1 + v_2 + v_3 + \ldots$$

Similarly, we can also write, $v_1 = \frac{n_1}{n} \cdot V$; $v_2 = \frac{n_2}{n} \cdot V$; $v_3 = \frac{n_3}{n} \cdot V$.

(g) Graham's law of effusion : Effusion is a process in which a gas passes through a fine orifice made in the wall of the containing vessel. The rate of effusion, however, depends upon the density, pressure and temperature of the gas. Graham (1827) found a mathematical relation connecting all the above factors and gave it in the form of law known as Graham's law of effusion. According to it, ***"at constant temperature and pressure, the rate of effusion of a gas is inversely proportional to the square root of its density."***

Diffusion, on the other hand, is a process in which a gas passes through a porous wall (unglazed earthern ware or compressed graphite). The law of effusion also applies to diffusion.

If r_1 and r_2 be the rates of diffusion (or effusion) of two gases of densities d_1 and d_2 at constant temperature and pressure, then

$$r_1 \propto \frac{1}{\sqrt{(d_1)}} \quad \text{and} \quad r_2 \, \alpha \, \frac{1}{\sqrt{(d_2)}}$$

$$\frac{r_1}{r_2} = \sqrt{\left(\frac{d_2}{d_1}\right)}$$

or $$r\sqrt{d} = \text{constant.}$$

If t_1 and t_2 be the times required for the passage of the volume (V) of two gases through the same orifice, then

$$r_1 = \frac{V}{t_1} \text{ and } r_2 = \frac{V}{t_2}$$

$$\therefore \qquad \frac{r_1}{r_2} = \frac{V/t_1}{V/t_2} = \frac{t_2}{t_1} = \sqrt{\left(\frac{d_2}{d_1}\right)}$$

Since, $$\text{Vapour density} = \frac{\text{Molecular weight}}{2}$$

$$\therefore \qquad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\left(\frac{M_2/2}{M_1/2}\right)} = \sqrt{\left(\frac{M_2}{M_1}\right)} \qquad \ldots(9)$$

where, M_1 and M_2 are the respective molecular weights.

Equation (9) enables us to calculate the molecular weight of a gas provided the ratio of rates of effusion with a known gas is known. This is done with the help of an ***effusiometer.***

Graham's law helps us to separate the gas components in a given mixture partially. If a mixture of gases is passed through a tube made of porous walls, then in a given time, lighter constituent will diffuse out more than the heavier one. By repeating this process, we can considerably increase the concentration of one component. This process known as ***atmolysis*** has been used to concentrate argon in nitrogen. A number of isotopes of gases have been separated by this process.

Nature and Numerical Values of R

The value of gas constant, R is given by,

$$R = \frac{PV}{T} \quad \text{(For 1 mole of a gas)}$$

$$R = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}} = \frac{\frac{\text{Force}}{\text{Area}} \times \text{Volume}}{\text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work}}{\text{Temperature}}$$

So, the units of R will be unit of work divided by that of temperature. Hence, in C.G.S. system, the unit of R will be erg per degree per mole, in S.I. system it will be joule per kelvin per mole and in F.P.S. system, it will be foot poundal per degree per mole.

We know that one mole of any gas at N.T.P. occupies a volume of 22.4 litres. From this statement, we can calculate the values of R in different units as follows :

(i) In litre-atmosphere per degree per mole.

$$P = 1 \text{ atmosphere}, V = 22.4 \text{ litres}, T = 273 \text{ K}$$

$$\therefore \quad R = \frac{1 \times 22.4}{273} = 0.0821 \text{ lit. atm. deg}^{-1} \text{ mole}^{-1}$$

(ii) In erg per degree per mole.

$$P = 1 \times 76 \times 13.6 \times 981 \text{ dyne/sq cm},$$

$$V = 22{,}400 \text{ c.c.}, T = 273 \text{ K}$$

$$\therefore \quad R = \frac{1 \times 76 \times 13.6 \times 981 \times 22400}{273}$$

$$= 8.31 \times 10^7 \text{ erg deg}^{-1} \text{ mole}^{-1}$$

(iii) In calorie per degree per mole.

As 4.18×10^7 ergs = 1 calorie,

$$\text{so} \quad R = \frac{8.31 \times 10^7}{4.18 \times 10^7} = 1.99 = 2 \text{ cal lit deg}^{-1} \text{ mole}^{-1}.$$

3.2 KINETIC THEORY OF GASES

It was observed that the gas laws mentioned earlier were based on experimental observations. The theoretical foundation or mathematical representation was missing. However, several workers studied the properties of gases and found that the gases are essentially composed of freely moving molecules. The basic ideas of the workers were mentioned to explain the behaviour of gases called the ***kinetic theory of gases***. This theory succeeded to attain a rigid mathematical form due to the efforts of Joule, Krönig, Clausius, Maxwell, Boltzmann etc. The main postulates of the kinetic theory of gases may be given as follows :

(i) Every gas consists of a large number of tiny discrete particles called ***molecules.*** For the same gas, all molecules are of same the size and mass.

(ii) The molecules are always in a state of constant rapid zig-zag motion in all directions. These molecules collide with each other and with the walls of the containing vessel. A molecule moves in a straight line with uniform velocity between two collisions.

(iii) The pressure of a gas is due to the unequal bombardment of the molecules on the walls of the vessel. The average force per unit area which the molecules exert in their impacts with the walls per unit time is the pressure. Greater the number of collisions, greater will be the pressure.

(iv) The molecules are supposed to be perfectly elastic as a result of which no energy is lost in their collisions with one another or with the walls of the containing vessel.

(v) The molecules are negligibly small in comparison to the volume of the vessel. At relatively low pressures, the forces of attraction between the molecules are also negligible because of the comparatively large distances between them.

(vi) The temperature of a gas is a measure of the average kinetic energy of the gas molecules.

If temperature is raised, the molecules will move more vigorously thus making more impacts on the walls of the containing vessel at a constant volume. Therefore, we observe an increase of pressure with rise in temperature at constant volume.

[I] Derivation of Kinetic Equation of Gases

On the basis of the above postulates of the kinetic theory, we can calculate the pressure of a gas in terms of molecular quantities. The kinetic equation is the same whether the vessel is spherical or cubical in nature, but for the sake of clarity, we will deduce kinetic equation by taking both the cases separately.

(i) For Cubical Vessel : Suppose a volume of gas is enclosed in a cubical vessel (Fig. 5) of side 1 cm. Suppose the number of molecules present in it be n and the mass of each molecule be m.

The molecules move with different velocities in different directions colliding with each other and with the walls of the containing vessel. Suppose u is the velocity of a molecule at any instant. This velocity may be resolved in three rectangular components u_x, u_y and u_z along the three axes X, Y and Z of the cube. Then, we have

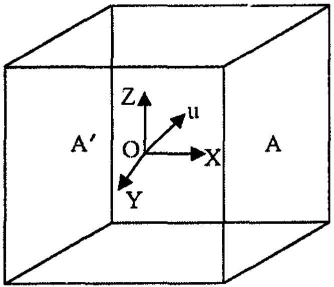


Fig. 5.

$$u^2 = u_x^2 + u_y^2 + u_z^2 \qquad ...(1)$$

Now consider the molecule moving with a velocity u_x along X axis striking the walls A and A′. Since the collisions are perfectly elastic, the molecule after colliding with the wall A would rebound with exactly the same velocity but in opposite direction.

The momentum of the molecule before it strikes A $= mu_x$

The momentum of the molecule after impact $= m(-u_x) = -mu_x$

$\therefore$ Change of momentum due to one impact $= mu_x - (-mu_x) = 2\,mu_x$.

After colliding with the wall A, it will travel a distance l cm to strike the face A′ (*i.e.*, opposite to A) and then return to face A again. Hence, after traversing a distance of l every time, it will make one impact on the wall. The total number of impacts the molecule makes on the two walls A and A′ per unit time would thus be u_x/l.

∴ Total change of momentum per molecule along X-axis per second

$$= 2mu_x \times \frac{u_x}{l} = \frac{2mu_x^2}{l}.$$

Similarly, the total change of momentum per molecule along Y-axis and Z-axis per second would be $\frac{2mu_y^2}{l}$ and $\frac{2mu_z^2}{l}$, respectively.

Therefore, the total change of momentum along all the three axes per second per molecule

$$= \frac{2mu_x^2}{l} + \frac{2mu_y^2}{l} + \frac{2mu_z^2}{l} = \frac{2m}{l}\left(u_x + u_y^2 + u_z^2\right) = \frac{2mu^2}{l} \quad \text{(vide eqn. 1)}$$

Now we consider all the molecules having different velocities $u_1, u_2, u_3, \ldots$ etc. The change of momentum per second of all the molecules on all the walls of the cube

$$= \frac{2mnu_1^2}{l} + \frac{2mnu_2^2}{l} + \frac{2mnu_3^2}{l} + \ldots + \frac{2mnu_n^2}{l} = \frac{2m}{l}\left(u_1^2 + u_2^2 + u_3^2 + \ldots + u_n^2\right) = \frac{2mnu^2}{l}$$

where, u is the root mean square velocity*

According to Newton's second law of motion, the change of momentum per unit time is the force (F) exerted by the molecules on the walls of the cube.

$$\therefore \qquad F = \frac{2mnu^2}{l}$$

Since, pressure is the force per unit area (A), we have

$$P = \frac{F}{A} = \frac{2mnu^2}{l.A} = \frac{2mnu^2}{l.\,6l^2} \qquad \text{(As } A = \text{area of cube} = 6l^2\text{)}$$

$$P = \frac{1}{3}\frac{mnu^2}{V} \qquad \text{(As } l^3 = \text{volume of cube} = V\text{)}$$

or

$$PV = \frac{1}{3}\,mnu^2. \qquad \ldots(2)$$

---

*On the basis of kinetic theory of gases, we have three types of velocities, *viz*, average velocity, root mean square velocity and most probable velocity. Suppose in a gas, there are $n_1, n_2, n_3, \ldots$molecules possessing velocities $u_1, u_2, u_3, \ldots$, respectively. The average velocity (v) is then given by,

$$v = \frac{n_1u_1 + n_2u_2 + n_3u_3 + \ldots}{n_1 + n_2 + n_3 + \ldots}.$$

The root mean square velocity (u) is defined as the square root of the mean of squares of all the velocities and is given by

$$u = \sqrt{\left(\frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \ldots}{n_1 + n_2 + n_3 + \ldots}\right)}$$

Most probable velocity ($\bar{u}$) is defined as the velocity possessed by the maximum number of molecules of the gas. We have

$$v = 0.9213 \times u \quad \text{and} \quad \bar{u} = \sqrt{\left(\frac{2u}{3}\right)}.$$

If d the density of the gas, then from equation (2), we have

$$P = \frac{1}{2}\frac{mN}{V} \cdot u^2 = \frac{1}{3} du^2 \qquad \ldots(3)$$

For 1 mole of a gas, n can be replaced by N (Avogadro number). Expressions (2) and (3) are different forms of kinetic equation of gases.

Derivation of Kinetic Equation

For Spherical Vessel

Figure (6) is a planar section through the centre of a spherical vessel of radius r. A particle that collides elastically with the wall of this vessel rebounds from the vessel at an angle θ equal to its angle of approach. Moreover, since the sphere is symmetrical, one particle in such a vessel will remain in the same plane and this plane will pass through the centre of the sphere. The distance between collisions is $2r \cos \theta$. If u be the velocity of the particle, the time Δt between collisions is $2r \cos \theta/u$. So, the number of collisions of a particle with the vessel per unit time is given by

$$\frac{1}{\Delta t} = \frac{u}{2r \cos \theta} \qquad \ldots(\text{i})$$

The component of velocity along the perpendicular to the spherical surface is $u \cos \theta$. Since this component of momentum of a particle of mass m before collision $= mu \cos \theta$, and afterward $= - mu \cos \theta$, because the component of velocity is in the opposite direction, the change in momentum, Δp per collision is

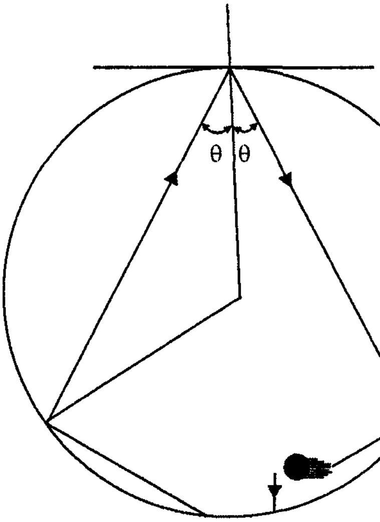


Fig. 6.

$$\Delta p = mu \cos \theta - (- mu \cos \theta) = 2mu \cos \theta \qquad \ldots(\text{ii})$$

The total outward force exerted equally on an average in all directions by the collisions of n molecules is n times as great as due to one average molecule. If collisions between or among molecules should prevent any one particular molecule from traversing a simple path along a chord, its momentum is in any event conserved and it ultimately reaches the wall and is reflected. Hence, for n molecules, the total outward force is the time rate of change of momentum, which by equations (i) and (ii) is

$$n \cdot \frac{\Delta p}{\Delta t} = n \cdot \frac{mu^2}{r}$$

Since this force is exerted on an area $4\pi r^2$ of the sphere, the force per unit area or pressure, P is given by

$$P = \frac{nmu^2/r}{4\pi r^2} = \frac{nmu^2}{4\pi r^3}$$

Since the volume V of the sphere is $\frac{4}{3}\pi r^3$, therefore,

$$PV = \frac{1}{3} mnu^2 \qquad \ldots(\text{iii})$$

[II] Derivation of Gas Laws From Kinetic Equation

(1) **Boyle's law :** We know that,

$$PV = \frac{1}{3} mNu^2 = \frac{2}{3} N \times \frac{1}{2} mu^2 \qquad \text{...(4)}$$

In a given mass of a gas, the number of molecules N remains constant. Similarly, at constant temperature, mean kinetic energy of a molecule, *i.e.*, $\frac{1}{2} mu^2$ also remains constant, therefore, from equation (4) it follows that,

PV = constant, which is Boyle's law.

(2) **Charles' law :** From equation (4), we have

$$V = \frac{2}{3} \cdot \frac{N}{P} \cdot \frac{mu^2}{2} = \frac{2}{3} \cdot \frac{N}{P} \cdot kT$$

(As mean kinetic energy $\frac{1}{2} mu^2$ is proportional to absolute temperature T, *i.e.*, $\frac{1}{2} mu^2 = kT$, where k is a constant).

So, $V = \text{Constant} \times kT = \text{Constant} \times T$

or $V \propto T$

This is Charles' law.

(3) **Avogadro's hypothesis :** If two gases are represented by subscripts 1 and 2, then we have for both the gases the following two kinetic equations :

$$P_1 V_1 = \frac{1}{3} m_1 n_1 u_1^2$$

$$P_2 V_2 = \frac{1}{3} m_2 n_2 u_2^2$$

At the same pressure and same volume, $P_1 = P_2$ and $V_1 = V_2$, so

$$\frac{1}{3} m_1 n_1 u_1^2 = \frac{1}{3} m_2 n_2 u_2^2 \qquad \text{...(5)}$$

If the temperatures of the gases are the same, then their mean kinetic energies will also be the same, *i.e.*,

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2 \qquad \text{...(6)}$$

Dividing equation (5) by (6), we get $n_1 = n_2$. This is Avogadro's law.

(4) **Ideal gas equation :** Combining Boyle's law, Charles' law, Avogadro's law, we find that the volume of a gas depends on the pressure, temperature and number of moles, as follows :

$V \propto \frac{1}{P}$ (at constant T and n) [Boyle's law]

$V \propto T$ (at constant P and n) [Charle's law]

$V \propto n$ (at constant P and T) [Avogadro's law]

So, V should be proportional to the product of the above three terms, *i.e.*,

$$V \propto \frac{nT}{P} = R\left(\frac{nT}{P}\right)$$

or

$$PV = nRT \qquad \text{...(7)}$$

where R, the proportionality constant, is known as **gas constant**. Equation (7) is known as **ideal gas equation**.

(5) Graham's law of diffusion : We have from kinetic equation,

$$P = \frac{1}{3}\frac{mNu^2}{V}$$

or $$P = \frac{1}{3}du^2 \qquad \left(\text{where, } \frac{mN}{V} = d, \text{ the density of the gas}\right)$$

or $$u = \sqrt{\left(\frac{3P}{d}\right)}$$

At constant pressure, $u = \text{constant} \times \frac{1}{\sqrt{d}}$ or $u \propto \frac{1}{\sqrt{d}}$

The velocity of a molecule u, is directly proportional to its rate of diffusion, r, *i.e.*, $u \propto r$. Therefore,

$$r \propto \frac{1}{\sqrt{d}}$$

This is Graham's law.

(6) Dalton's law of partial pressures : Consider a vessel containing a mixture of gases of densities $d_1, d_2, d_3 \ldots$ having root mean square velocities $u_1, u_2, u_3 \ldots$ The molecules of all gases will make collisions with the walls. The total pressure P exerted would then be given by

$$P = \frac{1}{3}d_1 u_1^2 + \frac{1}{3}d_2 u_2^2 + \frac{1}{3}d_3 u_3^2 + \ldots \qquad \text{(cf. eqn. 2)}$$

The individual pressures of the constituent gases would, therefore, be given by

$$P = \frac{1}{3}d_1 u_1^2; \quad P_2 = \frac{1}{3}d_2 u_2^2; \quad P_3 = \frac{1}{3}d_3 u_3^2$$

Therefore, $$P = p_1 + p_2 + p_3 + \ldots$$

This is Dalton's law of partial pressures.

3·3 KINETIC ENERGY AND TEMPERATURE OF A GAS

As mentioned in the postulates of the kinetic theory, the temperature, T, of a gas is a measure of the average kinetic energy, E, of the molecules, *i.e.*, if two gases are at the same temperature, then their average kinetic energies would be the same. Now we have

$$PV = \frac{1}{3}mnu^2$$

or $$PV = \frac{2}{3}n \cdot \frac{1}{2}mu^2 = \frac{2}{3}n.E' \qquad \ldots(1)$$

where E' = translational kinetic energy of the gas molecules.

For one mole of a gas, the number of molecules would be replaced by Avogadro's number (N). Therefore,

$$PV = \frac{2}{3}N \,.\, E = RT \qquad \text{(From gas laws)}$$

where E = translational kinetic energy of one mole of the gas.

$$\therefore \qquad E = \frac{3}{2}RT = \frac{3}{2}PV \qquad \ldots(2)$$

Equation (2) gives us a quantitative relation between absolute temperature and kinetic energy of gas molecules. Thus, the *translational kinetic energy of an ideal (or perfect) gas is directly proportional to the absolute temperature.* If we divide gas constant, R by Avogadro's number N, we get another constant, k, where $k = R/N$. The constant k is a universal constant and is called *Boltzmann's constant.* Its value is 1.38×10^{-16} erg degree^{-1}.

Problem 1. Calculate the kinetic energy of one gram of oxygen at 47°C.

Solution. 1 g oxygen = 1/32 mole.

Kinetic energy of one mole, $E = \frac{3}{2} RT$

$\therefore$ Kinetic energy of 1 g $O_2 = \frac{E}{32} = \frac{3}{64} RT = \frac{3}{64} \times 8.314\ JK^{-1} \times 320\ K = \mathbf{124.7\ J}$.

3·4 MAXWELL'S LAW OF DISTRIBUTION OF MOLECULAR VELOCITIES

If in a pure gas, all the molecules have velocities exactly equal in magnitude, but differ in direction, the gas as a whole would not behave non-isotropically and then this extraodinary state would soon be modified by collisions. In a head-on collision, in which the motion of two spheres is along the line between their centres at impact, there is an interchange of velocities if the collision is elastic and the masses of the two bodies are equal. For example, if a moving sphere collides head-on and elastically with another sphere at rest, then the moving sphere comes to rest and the one struck moves off with the velocity of the first. As viewed from a system of coordinates moving with half the velocity of the moving sphere, this process would be a head-on collision of two identical spheres each moving at half speed towards each other. After the collision, they will separate at the same rate but in directions from which they first approached the collision.

When trajectories are in the same plane, similar facts apply to components of velocity. If two identical spheres with the same kinetic energy collide, then one retires from the collision with all their kinetic energy to leave the other at rest. Suppose a sphere collides elastically with another that is proceeding in the same plane at right angles to its path. If their trajectories are in the same plane and the collision occurs at the very instant and that the centre of the second sphere lies along the projected trajectory of the first identical sphere, the first sphere will stop and the second will not only have all its own original velocity but will have gained all the velocity of the first sphere. These two equal perpendicular velocity components would add as vectors and the second sphere would proceed at an angle of 45°, with a velocity of magnitude $\sqrt{2}$ times that of either sphere before collision. In this collision, linear momentum and kinetic energy are conserved and the first sphere is stopped, while the kinetic energy of the other is doubled. Other types of collisions would be expected to effect a lesser transfer of energy. Thus, a system of particles with uniform velocities would rapidly achieve a range of velocities from zero to large values.

Therefore, as a result of random collisions of gaseous molecules, the molecular speeds (or velocities) keep on changing. Consider a gas molecule of mass m with a velocity component u. The kinetic energy (E) associated with this velocity component is $\frac{1}{2} mu^2$. The probability that this molecule has its velocity component between u and $u + du$ is given by $p(u)\,du$. Boltzmann in the 19th century showed that the probability that a molecule with energy E occupied a given energy level was proportional to $e^{-E/kT}$. It is apparent that we can equate this probability with $p(u)\,du$. Therefore,

$$p\,(u)\,du \propto e^{-E/kT} \propto e^{-mu^2/2kT} \qquad \left(\therefore\ E = \frac{1}{2}mu^2\right)$$

$$= A\,e^{-mu^2/2kT}\,du \qquad \text{...(1)}$$

where, A is a constant of proportionality. The value of A can be evaluated by requiring that the total probability must be unity. Thus,

$$\int_{-\infty}^{\infty} p(u)\,du = A\int_{-\infty}^{\infty} e^{-mu^2/2kT}\,du = 1 \qquad \text{...(2)}$$

The range of integration of velocity component u is $-\infty$ to $+\infty$, since velocity has both magnitude and direction. Putting $m/2kT = a$, it is found from calculus that,

$$\int_{-\infty}^{\infty} e^{-au^2}\,du = \left(\frac{\pi}{a}\right)^{3/2} = \left(\frac{\pi\,.\,2kT}{m}\right)^{3/2} \qquad \text{...(3)}$$

From equations (2) and (3), $A = (2\pi kT/m)^{3/2} = 1$, so that

$$A = (m/2\pi kT)^{1/2} \qquad \text{...(4)}$$

Substituting the value of A in equation (1), we have

$$p(u)\,du = \left(\frac{m}{2\pi\,kT}\right)^{3/2} e^{-mu^2/2kT}\,du \qquad \text{...(5)}$$

Equation (5) is known as ***Maxwell's distribution of velocities*** in one dimension. We can derive Maxwell's distribution of velocities in three dimensions by multiplying the three one-dimension distributions. So,

$$p\,(u, v, w) = p\,(u)\,p\,(v)\,p\,(w) \qquad \text{...(6)}$$

where, $p\,(v)$ and $p\,(w)$ are the velocity components in the other two dimensions.

$$p\,(u, v, w)\,du\,dv\,dw = p\,(u)\,du \times p\,(v)\,dv \times\ p\,(w)\,dw$$

$$= \left(\frac{m}{2\pi\,kT}\right)^{3/2} \exp\left[\frac{-m\,(u^2 + v^2 + w^2)}{2kT}\right] du\,dv\,dw \qquad \text{...(7)}$$

An expression can be found which gives the fraction of molecules with a speed between c and $c + dc$ $(c^2 = u^2 + v^2 + w^2)$ regardless of the direction. These are molecules whose velocity points lie within a spherical shell of thickness dc from the origin. This shell has a volume of $4\pi c^2\,dc$, which is the integral of $du\,dv\,dw$ in equation (7) over the spherical shell. So,

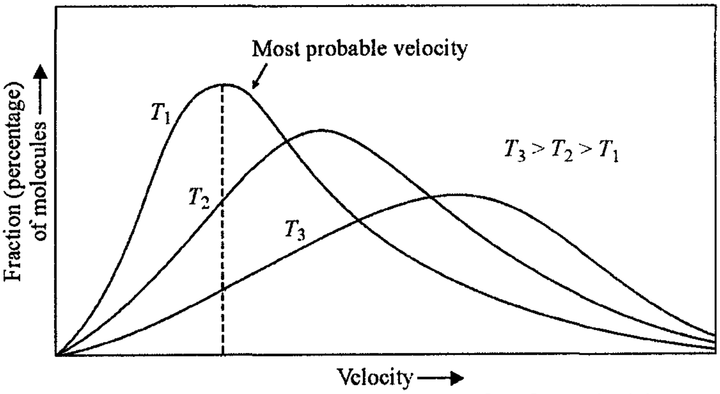


Fig. 7. The Maxwell's distribution of molecular velocities.

$$p(c)\,dc = 4\pi\left(\frac{m}{2\pi kT}\right)^{32} c^2 \exp\left(-\frac{mc^2}{2kT}\right)dc \qquad \ldots(8)$$

The equation (8) is known as ***Maxwell's distribution of molecular speeds***. It is customary to write $p(c)\,dc$ as $\frac{dN_c}{N_c}$, where N_c is the total number of gas molecules. The quantity $\frac{dN_c}{N_c}$, gives the fraction of molecules with speeds between c and $c + dc$. The mass $m = M/N$, where M is molar mass and N is Avogadro's number. So, equation (8) can be written as,

$$\frac{dN_c}{N_c} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \exp\left(-\frac{Mc^2}{2RT}\right)dc \qquad \ldots(9)$$

The Maxwell's distribution of molecular speeds is plotted in figure (7).

We see that the fraction of molecules having velocities greater than zero increases with an increase in velocity, reaches a maximum and then falls off to zero again at higher velocities. The salient features of the curves are as follows :

(a) The fraction of molecules with too low or too high velocities is very small.

(b) There is a certain velocity for which the fraction of molecules is maximum. This is called the ***most probable velocity***. This corresponds to the peak of the curve. Its value at a given temperature, depends upon the volume of the gas.

[I] Effect of Temperature on Distribution of Molecular Velocities

As shown in figure (7), the most probable velocity increases with rise in temperature. The entire distribution curve shifts to the right with rise in temperature, as shown. The rise in temperature, increases the fraction of the molecules having high velocities considerably. This can be understood from the presence of the factor, $\exp(-mc^2/2kT)$ in equation (8). The component has a negative sign and a temperature T is in the denominator. The factor, thus, increases appreciably with rise in temperature. This factor is known as ***Boltzmann factor.***

Knowing that $1/2mc^2$ is the kinetic energy of one molecule of gas with velocity c, the factor

$$\exp(-mc^2/2kT) = \exp(-E/kT)$$

where, $E\ (= \frac{1}{2}mc^2)$ is the kinetic energy per molecule of the gas. Therefore, greater the temperature, the greater is the value of E. So, Boltzmann's factor increases rapidly with increase in temperature.

[II] Validity of Maxwell's Distribution Law

The validity of Maxwell's distribution law can be checked by an apparatus shown in figure (8). A beam of metal atom is created by heating a metal like silver or bismuth in an oven. The two discs are mounted on a rotating axis. The slit in one disc comes in the path of vapour molecules coming out of slit in second disc after an interval of time determined by the rate of rotation of the axis. Particles

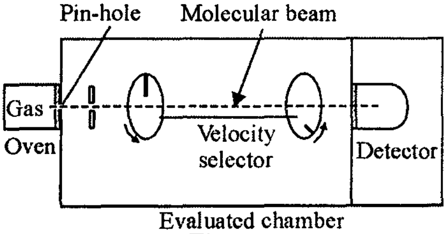


Fig. 8.

moving with different velocities can be collected in the detector by adjusting the rotation rate of the discs. On plotting a function of number of particles collected in the detector and the velocities of the particles as given by rotation rate of discs, we obtain curves as shown in figure (9).

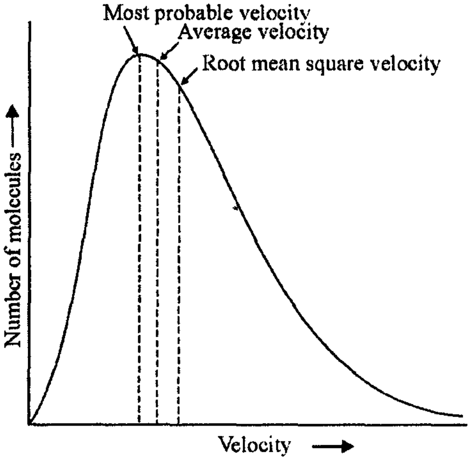


Fig. 9.

[III] Types of Molecular Velocities

We come across with three types of molecular velocities in the study of gases. These are : (i) *average velocity* (ii) *root mean square velocity* (iii) *most probable velocity.*

(1) Average velocity : The average velocity is defined as the *arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.* If $u_1, u_2, u_3, \ldots, u_n$ are the individual velocities of the gas molecules and n is their total number, then average velocity is given by

$$v = \frac{u_1 + u_2 + u_3 + \ldots + u_n}{n}$$

If, however, $u_1, u_2, u_3 \ldots$ are the velocities possessed by groups of $n_1, n_2, n_3, \ldots$ molecules of the gas, respectively, then average velocity is given by,

$$v = \frac{n_1u_1 + n_2u_2 + n_3u_3 + \ldots}{n_1 + n_2 + n_3 + \ldots}$$

(2) Root mean square velocity : The root mean square velocity is defined as the *square root of the mean of the squares of different velocities possessed by molecules of a gas at a given temperature.* It is given by

$$u = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + \ldots + u_n^2}{n}}$$

where $u_1, u_2, u_3, \ldots, u_n$ are the individual velocities of n molecules of the gas.

Alternatively,

$$u = \sqrt{\frac{n_1u_1^2 + n_2u_2^2 + n_3u_3^2 + \ldots}{n_1 + n_2 + n_3 + \ldots}}$$

where $u_1, u_2, u_3, \ldots$ are the velocities possessed by groups of $n_1, n_2, n_3 \ldots$ molecules, respectively.

(3) Most probable velocity : It is defined as the *velocity possessed by the maximum number of molecules of a gas at a given temperature.*

With the help of Maxwell equation (8), we can derive mathematical expressions for the above three types of velocities *viz.*, average velocity (v), root mean square velocity (u) and most probable velocity ($\overline{u}$). These relations are as follows :

$$v = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$u = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$\overline{u} = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

It is found that,

$$u : v : \overline{u} = 1.00 : 0.92 : 0.82$$

[IV] Derivation of Expressions for Various Types of Molecular Velocities

(1) ***Expression for average velocity*** : The average velocity will be given by the expression

$$v = \int_0^\infty c\,p(c)\,dc \qquad \ldots(10)$$

Substituting the value of $p(c)\,dc$ from equation (8), we have

$$v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty c^3 \exp\left(-\frac{mc^2}{2kT}\right)dc \qquad \ldots(11)$$

Let $$\frac{mc^2}{2kT} = x^2 \quad \text{or} \quad c^2 = \frac{2kTx^2}{m} \qquad \ldots(12)$$

Differentiating both sides, we have $dc = \dfrac{2kTx\,dx}{mc}$ ...(13)

From equation (12), $$c = \left(\frac{2kTx^2}{m}\right)^{1/2} = \left(\frac{2kT}{m}\right)^{1/2} x \qquad \ldots(14)$$

Substituting the value of c in equation (13), we get

$$dc = \frac{2kT\,x\,dx}{m\,(2kT/m)^{1/2}x} = \left(\frac{2kT}{m}\right)^{1/2} dx$$

From equation (14), $$c^3 = \left(\frac{2kT}{m}\right)^{3/2} x^3$$

$$\therefore \quad \int_0^\infty c^3 \exp\left(-\frac{mc^2}{2kT}\right)dc = \int_0^\infty \left(\frac{2kT}{m}\right)^{3/2} x^3 e^{-x^2}\left(\frac{2kT}{m}\right)^{1/2} dx$$

$$= \left(\frac{2kT}{m}\right)^2 \int_0^\infty x^3 e^{-x^2}\,dx = \left(\frac{2kT}{m}\right)^2\left(\frac{1}{2}\right) \qquad \ldots(15)$$

$$\left[\because \int_0^\infty x^3 e^{-x^2}\,dx = \frac{1}{2}\right]$$

From equations (11) and (15),

$$v = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{2kT}{m}\right)^2\left(\frac{1}{2}\right) = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

or $$v = \left(\frac{8RT}{\pi m}\right)^{1/2} \qquad \ldots(16)$$

(2) ***Expression for root mean square velocity*** : The root mean square velocity would be defined as,

$$u^2 = \int_0^\infty c^2\, p(c)\, dc$$

From equation (8),

$$\int_0^\infty c^2\, p(c)\, dc = 4\pi\left(\frac{m}{2\pi\, kT}\right)^{3/2} \int_0^\infty c^4 \exp\left(\frac{-mc^2}{2kT}\right) dc \qquad ...(17)$$

Let

$$\frac{mc^2}{2kT} = x^2 \qquad ...(18)$$

$$\therefore \qquad c^4 = \left(\frac{2kT}{m}\right)^2 x^4 \qquad ...(19)$$

From equation (14),

$$\therefore \qquad c = \left(\frac{2kT}{m}\right)^{1/2} x \qquad ...(20)$$

$$dc = \left(\frac{2kT}{m}\right)^{1/2} dx$$

From equations (17), (19) and (20), we have

$$\int_0^\infty c^2\, p(c)\, dc = 4\pi\left(\frac{m}{2\pi\, kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^2 \left(\frac{2kT}{m}\right)^{1/2} \int_0^\infty x^4 e^{-x^2} dx \qquad ...(21)$$

From the table of definite integrals, we know that,

$$\int_0^\infty x^4 e^{-x^2} dx = \frac{3}{8}\pi^{1/2}$$

So, combining this equation with equation (21), we get

$$\int_0^\infty c^2\, p(c)\, dc = u^2 = \left(\frac{3kT}{m}\right)$$

or

$$u = \left(\frac{3RT}{M}\right)^{1/2} \qquad ...(22)$$

(3) ***Expression for most probable velocity*** **:** Differentiating equation (9), with respect to c and setting the result to zero, as required for a maximum, we get

$$\frac{d}{dc}\left(\frac{dN_c}{N_c}\right) = \left(\frac{m}{2\pi\, kT}\right)^{3/2} \left(e^{-mc^2/2kT}\right)\left[8\pi c + 4\pi c^2\left(-\frac{mc}{kT}\right)\right] = 0$$

The factor $\left(\frac{m}{2\pi\, kT}\right)^{3/2}$ is constant which is different from zero. The factor $\exp\left(-\frac{mc^2}{2kT}\right)$ is also not equal to zero. So, the third factor, $8\pi c + 4\pi c^2\left(-\frac{mc}{kT}\right) = 0$

$$\therefore \qquad c = \overline{u} = \left(\frac{2kT}{m}\right)^{1/2}$$

or

$$\overline{u} = \left(\frac{2RT}{M}\right)^{1/2} \qquad \left(\because\ k = \frac{R}{N} \text{ and } M = N.m\right) \qquad ... (23)$$

The molecular distribution of the three types of velocities is shown in figure (9).

[V] Maxwell's Distribution of Molecular Energies

From equation (8), it is possible to know how the kinetic energies of translation of molecules are distributed amongst the various molecules. The fraction of molecules having kinetic energies in the range of E and $E + dE$, *viz.*, $\frac{dN_{c(E)}}{IN_c}$ can be determined as follows :

$$\therefore \qquad E = \frac{1}{2}mc^2 \qquad \therefore \quad c = \left(\frac{2E}{m}\right)^{1/2}$$

$$\therefore \qquad 2c\,dc = \left(\frac{2}{m}\right)dE \text{ or } cdc = \frac{dE}{m}$$

$$\text{So,} \qquad c^2\,dc = c\,\frac{dE}{m} = \left(\frac{2E}{m}\right)^{1/2}\left(\frac{dE}{m}\right) = \frac{(2E)^{1/2}}{m^{3/2}}\,dE$$

Substituting the value of $c^2\,dc$ in equation (9), we get

$$\frac{dN_{c\,(E)}}{N_c} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{(2E)^{1/2}}{m^{3/2}}\right)dE\,\exp\left(-\frac{E}{kT}\right)$$

$$= \frac{2(E)^{1/2}}{(\pi)^{1/2}\,(kT)^{3/2}}\exp\left(-\frac{E}{kT}\right)dE \qquad \ldots (24)$$

The above equation is known as ***Maxwell's equation for distribution of kinetic energies of molecules.***

Maxwell's distribution of kinetic energies at two different temperatures is shown in figure (10) in which the factor $\frac{1}{N_c}\left[\frac{dN_{c\,(E)}}{dE}\right]$ is plotted against E.

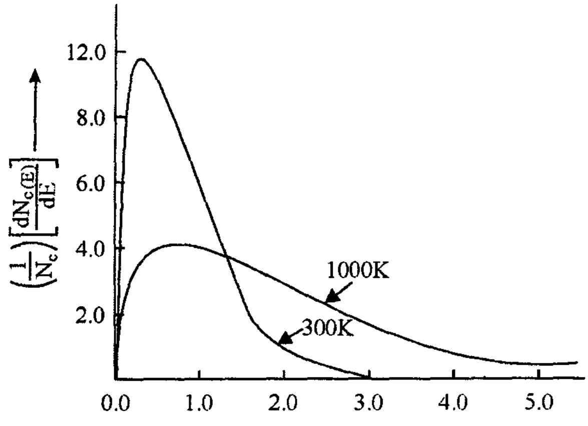


Fig. 10.

As seen, the distribution of kinetic energies depends on the temperature and is independent of the mass of the gas. The maximum in the probability function corresponds to the ***most probable kinetic energy***.

From equation (23), it is clear that,

(i) the most probable kinetic energy is given by $kT/2$ per molecule or $RT/2$ per mole of the gas.

(ii) the average kinetic enrgy per molecule is given by

$$\frac{3}{2}NkT = \frac{3}{2}kT$$

The above results are in perfect agreement with the obtained from kinetic theory.

Problem 1. ***Derive an expression for the root mean square velocity u of an ideal gas in terms of pressure and density of the gas.***

Solution. We know that, $u = \left(\frac{3RT}{M}\right)^{1/2}$ ...(i)

For an ideal gas, $PV = nRT = \frac{wRT}{M}$ (where w is the mass of the gas)

$\therefore \quad P = \frac{wRT}{VM} = \frac{PRT}{M}$ (where $\rho = w/V$ = density of the gas)

$\therefore \quad \frac{RT}{M} = \frac{P}{\rho}$

Substituting the value of RT/M in equation (i), we get

$$u = \left(\frac{3P}{\rho}\right)^{1/2}$$

Problem 2. ***Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 20K.***

Solution. Average velocity, $v = \left(\frac{3RT}{M}\right)^{1/2}$, *i.e.*, $v \propto \left(\frac{T}{M}\right)^{1/2}$

Suppose v_1 and v_2 are the average velocities of O_2 and H_2, respectively.

$$\therefore \quad \frac{v_1}{v_2} = \left(\frac{T_1/M_1}{T_2/M_2}\right)^{1/2} = 1 \text{so that } T_1/M_1 = T_2/M_2$$

or

$$\frac{T_1}{32 \text{ g mol}^{-1}} = \frac{T_2}{2\text{g mol}^{-1}}$$

$$\therefore \quad T_1 = (32/2)\, T_2 = 16 \times T_2 = 16 \times 20 \text{ K} = \mathbf{320\ K}$$

Problem 3. ***Calculate the temperatures at which the average velocity, root mean square velocity and most probable velocity of oxygen gas are all equal to 1500 ms***$^{-1}$.

Solution. (i) Let the respective temperatures be T_1, T_2 and T_3.

Average velocity, $v = \left(\frac{8RT_1}{\pi M}\right)^{1/2} = 1.5 \times 10^3 \text{ ms}^{-1}$

$$\therefore \quad T_1 = \frac{(1.5 \times 10^{-3} \text{ ms}^{-1})^2 (32 \times 10^{-3} \text{ kg mol}^{-1})(3.1416)}{(8)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})} \quad (\because M = 32 \text{ g mol}^{-1})$$

$$= \mathbf{3399\ K}$$

(ii) Root mean square velocity, $u = \left(\frac{3RT_2}{M}\right)^{1/2} = 1.5 \times 10^3 \text{ ms}^{-1}$

$$\therefore \quad T_2 = \frac{(1.5 \times 10^3 \text{ ms}^{-1})^2 (32 \times 10^{-3} \text{ kg mol}^{-1})}{(3)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})} = \mathbf{2886\ K}$$

(iii) Most probable velocity, $\bar{u} = \left(\frac{2RT_3}{M}\right)^{1/2} = 1.5 \times 10^3 \text{ ms}^{-1}$

$$\therefore \quad T_3 = \frac{(1.5 \times 10^3 \text{ ms}^{-1})^2 (32 \times 10^{-3} \text{ kg mol}^{-1})}{(2)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})} = \mathbf{4330\ K}$$

3·5 MOLECULAR VELOCITY

The molecules of different gases move with different velocities and the values are as high as the speed of a bullet. The numerical values of molecular velocity can be calculated in a number of cases as follows :

(i) When only temperature is given.

We have, $PV = \frac{1}{3} mNu^2 = RT$ or $u^2 = \frac{3RT}{mN}$

For 1 mole of a gas, mN = total mass of the gas = molecular weight M.

$$u = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.31 \times 10^7 \times T}{M}\right)}$$

$$= 1.58 \times 10^4 \times \sqrt{\left(\frac{T}{M}\right)} \qquad \ldots (1)$$

Hence the value of u can be calculated at any temperature, provided the value of M is known.

Problem 1. ***At what temperature will the R.M.S. velocity of hydrogen be one and half time of its value at N.T.P. ?***

Solution : We have $\frac{1}{2} . \mu^2 = \frac{3}{2} . kT$ or $u \propto \sqrt{T}$

If the required temperature is T_1 when its velocity is (3/2). u, then

$$\frac{u_1}{u} = \sqrt{\left(\frac{T_1}{T}\right)}$$

$$\frac{(3/2)\, u}{u} = \sqrt{\left(\frac{T_1}{273}\right)}$$

$$T_1 = \frac{9}{4} \times 273 = \mathbf{614.25\ K}$$

Problem 2. ***Calculate the root mean square velocity of hydrogen molecules at 100°C.***

Solution. The molecular weight M of hydrogen is 2.016, therefore, according to equation (1), we get

$$u = 1.58 \times 10^4 \times \sqrt{\left(\frac{273}{2.016}\right)} = \mathbf{21.49 \times 10^4\ cm.\ sec^{-1}}.$$

(ii) When both pressure and density are given.

We have from kinetic equation, $P = \frac{1}{3} du^2$ or $u = \sqrt{\left(\frac{3P}{d}\right)}$ ... (2)

This is the required relation.

Problem 1. ***What is the R.M.S. velocity of air at N.T.P., if its density is 0.00129 g cc⁻¹ ?***

Solution. We have, $u = \sqrt{\left(\frac{3P}{d}\right)} = \sqrt{\left(\frac{3 \times 76 \times 13.6 \times 981}{0.00129}\right)} = \mathbf{4.86 \times 10^4\ cm\ sec^{-1}}$.

(iii) When both pressure and temperature are given.

We have from kinetic equation, $PV = \frac{1}{3} mNu^2$

or $u = \sqrt{\left(\frac{3PV}{M}\right)}$ (where mN = mol. wt. = M) ... (3)

The value of V can be calculated by means of the expression

$$\frac{P_0V_0}{T}=\frac{PV}{T}$$

and the fact that at N.T.P. 1 mole of a gas occupies a volume of 22400 c.c., where P_0, V_0 and T_0 represent the respective values at N.T.P. Therefore,

$$\frac{76\times 13.6\times 981\times 22400}{273}=\frac{PV}{T}$$

Since the values of P and T are known, we can calculate V. Hence, from equation (3) we can calculate the value of R.M.S. velocity, u,

---

Problem 1. ***Calculate the root mean square velocity of nitrogen at 27°C and 70 cm. pressure. Density of Hg = 13.6 g cm^{-3}.***

Solution. We have, $$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$$

or $$\frac{76\times 22400}{273}=\frac{70\times V_2}{300}$$

$$V=26{,}730 \text{ ml.}$$

From equation (1), we have $$u=\sqrt{\left(\frac{3\times 70\times 13.6\times 981\times 26730}{28}\right)}$$

$$=\mathbf{5.17\times 10^4 \ cm\ sec^{-1}}.$$

3·6 EXPANSIVITY AD COMPRESSIBILITY

Fluids, *i.e.*, gases and liquids expand on heating, though the expansion of gases is much more than that of liquids. Similarly, they can be compressed. The variation of volume (V) with temperature (T), at constant pressure (P) is known as ***coefficient of thermal expansion***, ***coefficient of isobaric expansion*** or ***expansivity*** (α) of the fluid. Therefore,

$$\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Similarly, the variation of V with P, at constant temperature, is known as ***coefficient of isothermal compressibility*** or simply ***compressibility*** (β) of the fluid. Therefore,

$$\beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Generally, the volume of a gas decreases with an increase of pressure, so the quantity $\left(\frac{\partial V}{\partial P}\right)_T$ is negative. So, a minus sign is included in the definition of β so as to make β positive. The dimensions of α and β are T^{-1} and P^{-1}, respectively.

Problem 1. ***Show that for an ideal gas, $\alpha=\frac{1}{T}$ and $\beta=\frac{1}{P}$***

Solution. For n mole of an ideal gas, $PV=nRT$ or $V=\frac{nRT}{P}$ ...(i)

Differentiating equation (i) with respect to T at constant P, we get

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{nR}{P}=\frac{PV}{PT}=\frac{V}{T}$$

$$\therefore \qquad \alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P=\left(\frac{1}{V}\right)\left(\frac{V}{T}\right)=\frac{1}{T}$$

Differentiating equation (i) with respect to P at constant T, we get

$$\left(\frac{\partial V}{\partial P}\right)_T=-\frac{nRT}{P^2}=\left(\frac{nRT}{P}\right)\left(-\frac{1}{P}\right)=\left(-\frac{V}{P}\right)$$

$$\therefore \qquad \beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T=\left(-\frac{1}{V}\right)\left(-\frac{V}{P}\right)=\frac{1}{P}$$

Problem 2. ***For a fluid show that,*** $\left(\frac{\partial P}{\partial T}\right)_V=\frac{\alpha}{\beta}$

where α ***and*** β ***are expansivity and compressibility of the gas. Show also that for an ideal gas,***

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{R}{V}$$

Solution. A gas can be defined by any two of the parameters P, V and T. So we can write

$$V=f(T,P)$$

V is a state function, so its total differential can be written as

$$dV=\left(\frac{\partial V}{\partial T}\right)_P dT+\left(\frac{\partial V}{\partial P}\right)_T dP \qquad \text{... (i)}$$

By definiton, $\alpha=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, so that $\left(\frac{\partial V}{\partial T}\right)_P=\alpha V$

and $\quad \beta=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, so that $\left(\frac{\partial V}{\partial P}\right)_T=-\beta V$

Substituting for α and β in equation (i), are get

$$dV=\alpha V\,dT-\beta V\,dP$$

When V is constant, $dV=0$, so

$$\alpha V\,dT-\beta V\,dP=0$$

or $\quad V(\alpha\,dT-\beta\,dP)=0$

But $V\neq 0$, so $\quad \alpha\,dT-\beta\,dP=0$

or $\quad \alpha\,dT=\beta\,dP$

or $\quad \left(\frac{\partial P}{\partial T}\right)_V=\frac{\alpha}{\beta}$

We can show that for an ideal gas (see preceding problem)

$$\alpha=\frac{1}{T}\text{ and }\beta=\frac{1}{P}$$

$$\therefore \qquad \left(\frac{\partial P}{\partial T}\right)_V=\frac{\alpha}{\beta}=\frac{1/T}{1/P}=\frac{P}{T}=\frac{R}{V}$$

3·7 MEAN FREE PATH

The average distance traversed by a molecule between two successive collisions is known as its *mean free path*. The calculation of mean free path for rigid spheres is straight forward but tedious. The following approximate derivation gives us a method of measurement and it yields correct order of magnitude and correct functional form.

Suppose that molecules of type 1 have a radius r_1 and that molecules of type 2 have a radius r_2. If the molecules are rigid, the distance between the centres at impact is $r_1 + r_2$. Whenever their centres approach the distance $r_1 + r_2$, a collision occurs. It is convenient, therefore, to picture the collision as occurring when a point molecule comes within a distance of $r_1 + r_2$ of another molecule and is assigned an effective radius of $r_1 + r_2$.

Suppose that the point molecules are projectiles fixed into gas molecules with radii $r_1 + r_2$. The number of point molecules dN lost by collision on penetrating a distance dx into the target gas is proportional to dx and to the number of point molecules N that are fired at the target, *i.e.*,

$$dN = -kN\,dx \qquad ...(1)$$

The negative sign implies that N decreases as x, the depth of penetration, increases. The value of proportionality constant k is positive and is a function of the target. The equation (1) is then integrated, *i.e.*,

$$\int \frac{dN}{N} = -k \int dx$$

or
$$\log N = -kx + C \qquad ...(2)$$

where, C is the integration constant, whose value can be evaluated by assuming that N_0 is the number of point molecules that enter the target gas at $x = 0$. On substituting these values in equation (2), we get

$$\log N_0 = -k \times 0 + C$$

$$C = \log N_0$$

Therefore, equation (2) becomes, $\log N = -kx + \log N_0$

or
$$N = N_0\, e^{-kx}.$$

The same result might be obtained by definite integration of equation (1), *i.e.*,

$$\int_{N_0}^{N} \frac{dN}{N} = -k \int_0^x dx$$

or
$$\log\left(\frac{N}{N_0}\right) = -kx$$

or
$$N = N_0\, e^{-kx} \qquad ...(3)$$

The average distance (λ) traversed by a point molecule is the sum of the expected values of x, *i.e.*, it is the sum of the distances x times the fraction of molecules dN/N_0 that penetrate to a depth x. Therefore, upon summation over all molecules N_0, we get

$$\lambda = \int_0^{N_0} x \cdot \frac{dN}{N_0} \qquad ...(4)$$

Equation (3) yields, $dN = -k\, N_0\, e^{-kx} \cdot dx.$ ...(5)

Since all molecules are absorbed after passing through a target of infinite thickness, $N = 0$, when $x = \infty$, but since $N = N_0$ at $x = 0$, it follows from equations (4) and (5) that,

$$\lambda = \int_0^{\infty} -kx \,.\, e^{-kx} \,.\, dx \qquad ...(6)$$

Interchanging the limits of the definite integral is equivalent to reversing the sign of the summation, and this involves a negative sign. So,

$$\lambda = \int_{\infty}^{0} kx \,.\, e^{-kx} \,.\, dx.$$

Put $y = kx$, then $dy = k\, dx$. So

$$\lambda = \frac{1}{k} \int_{\infty}^{0} y\, e^{-y}\, dy = \frac{1}{k} \Gamma\,(2) = \frac{1}{k} \qquad ...(7)$$

The proportionality constant k is characteristic of the target gases. According to equation (1), it is the fraction of molecules dN/N that collides in the distance dx. As such, it is the ratio of the total area of N_2 target molecules, each of area $\pi\,(r_1 + r_2)^2$, to the cross-sectional area in which they are seen by the approaching point molecules. If this cross-sectional area be unit area, and N_2 molecules exist in volume V, and if possible overlaps are ignored, then

$$k = \pi\,(r_1 + r_2)^2 \,.\, \frac{N_2}{V} \qquad ...(8)$$

From equations (7) and (8), it follows that $\lambda = \dfrac{V}{\pi\, \sigma^2 N}$ ...(9)

where a distance, σ, characteristic of the molecules is substituted for $(r_1 + r_2)$, and where the subscript of N is ignored. When an appropriate average over all angles is calculated and when account is taken of the Maxwell-Boltzmann distribution in velocities, the correct formula for mean free path is given by,

$$\lambda = \frac{V}{\sqrt{2}\pi\, \sigma^2 N} \qquad ...(10)$$

In view of real indefiniteness of σ, the mean effective collision distance, this factor of $\sqrt{2}$ is almost negligible. Since $PV = NkT$, equation (10) becomes

$$\lambda = \frac{kT}{\sqrt{2}\pi\, \sigma^2 P} \qquad ...(11)$$

The value of λ at 300 K at several pressures have been seen to be $\sqrt{10} \times 10^{-8}$ cm.

3·8 COLLISION DIAMETER

When two molecules of a gas approach each other, they continue moving each other till a point is reached when the mutual repulsion between the molecules (resulting from electronic and nuclear repulsions) is so great that they have to retrace their path. *The distance between the centres of such molecules at the point of closest approach, i.e., when they are about to retrace their path, is known as*

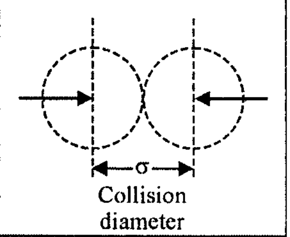


Fig. 11.

collision diameter. It is represented by the Greek symbol, sigma (σ). Evidently, a gaseous molecule can be regarded as a rigid or hard sphere of radius σ. The volume $\frac{4}{3}\pi\sigma^3$ is known as the effective volume of the molecule. Molecules though infinitesimally small have an effective collision diameter. It can be easily seen that if the distance between the centres of two molecules is less than σ, there would be a collision between them. So, collision is an event in which the centres of two identical molecules come within a distance σ from each other. The collision diameters of H_2, He, N_2, O_2 are 0.274 nm, 0.318 nm, 0.375 nm and 0.361 nm, respectively.

3·9 COLLISION NUMBER

It can be shown by kinetic considerations that the number of molecules with which a single molecule will collide per unit time is given by $\sqrt{2\pi}\ \sigma^2 v\rho$, where v is the average velocity of the molecules and ρ is the number density, *i.e.*, the number of molecules per unit volume of the gas. This value thus gives the *number of collisions suffered by a single molecule per unit time per unit volume of the gas*. This is known as ***collision number*** (Z_1). So,

$$Z_1 = \sqrt{2}\ \pi\sigma^2 v\rho \qquad ...(12)$$

The total number of molecules colliding per unit time per unit volume of the gas is given by $\sqrt{2}\pi\sigma^2 v\rho^2$. Since each collision involves two molecules, the number of collisions of like molecules occurring per unit time per unit volume of the gas is given by,

$$Z_{1,1} = \frac{1}{2}\left(\sqrt{2}\ \pi\sigma^2 v\rho^2\right) = \frac{1}{\sqrt{2}}\left(\pi\sigma^2 v\rho^2\right) \qquad ...(13)$$

3·11 COLLISION FREQUENCY

The number Z_1 as given by equation (12) gives the collision frequency of the gas. So, ***collision frequency***, is defined as the *number of molecular collisions occurring per unit time per unit volume of the gas*.

The number of collision of molecules of type 1 with those of type 2, would be given by,

$$Z_{1,2} = \frac{1}{\sqrt{2}}\left(\pi\ \sigma^2\ v\ \rho_1\ \rho_2\right) \qquad ...(14)$$

where ρ_1 and ρ_2 are the number densities of the molecules of type 1 and 2, respectively. The number density (ρ) is equal to P/kT, as shown below.

For an ideal gas, $PV = nRT = nNkT$

or $$P = \frac{nNkT}{V} = \frac{N'kT}{V} \qquad ...(15)$$

where N' (= nN) is the total number of molecules in n moles of the gas. As ρ is the number of molecules per unit volume, so $\rho = N'/V$, therefore,

$$P = \rho kT \text{ or } \rho = \frac{P}{kT}$$

Equations (12) and (13) may be written as

$$Z_1 = \frac{\sqrt{2}\pi\sigma^2 vP}{kT} \qquad ...(16)$$

$$Z_{1,2} = \frac{\pi \sigma^2 vP}{\sqrt{2} \cdot (kT)^2} \qquad ...(17)$$

It may be noted that units of Z_1 and $Z_{1,2}$ are s^{-1} and $s^{-1}\ m^{-3}$ respectively.

Problem 1. ***For oxygen gas at 25°C, calculate (a) mean free path at 1 atm pressure (b) mean free path at 10^{-3} mm Hg pressure (c) number of collisions per second per molecule (d) number of collisions per cubic metre per second (e) number of molecular collisions per dm^3 per second. Collision diameter of O_2 is 361 pm.***

Solution. **(a)** 1 atm = 1.01325×10^5 Nm^{-2}, T = 298K, σ = 361 pm = 361×10^{-12} m = 3.61×10^{-10} m

From equation (11),

$$\lambda = \frac{kT}{\sqrt{2}\pi \sigma^2 P} = \frac{(1.38 \times 10^{-23}\ \text{JK}^{-1})\ (298\text{K})}{(1.4142)\ (3.1416)\left(3.61 \times 10^{-10}\ \text{m}\right)^2 \left(1.01325 \times 10^5\ \text{Nm}^{-2}\right)}$$

$= 7.02 \times 10^{-8}$ m = **70.2 nm** (J = kg m^2 s^{-2} = 1 Nm)

(b) $$P = 10^{-3}\ \text{mm Hg} = \frac{(10^{-3}\ \text{mm Hg})\ (1.01325 \times 10^5\ \text{Nm}^{-2}\ \text{atm}^{-1})\ (298\text{K})}{760\ \text{mm Hg atm}^{-1}}$$

$= 0.1333$ Nm^{-2} $\qquad$ ($\because$ 1 mm Hg = 133.322 Nm^{-2})

$$\lambda = \frac{(1.38 \times 10^{-23}\ \text{JK}^{-1})\ (298\text{K})}{(1.4142)\ (3.1416)\left(3.61 \times 10^{-10}\ \text{m}\right)^2 \left(0.1333\ \text{Nm}^{-2}\right)} = \mathbf{5.3 \times 10^{-2}\ m}$$

(c) From equation (12), $Z_1 = \sqrt{2}\pi\sigma^2 v\rho = \dfrac{\sqrt{2}\pi \sigma^2 vP}{kT}$ $\qquad \left(\because \rho = \dfrac{P}{kT}\right)$

We know that average velocity,

$$v = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{(8)\ (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\ (298\ \text{K})}{(3.1416)\ (32 \times 10^{-3}\ \text{kg mol}^{-1})}\right]^{1/2} = 444.0\ \text{ms}^{-1}$$

P = 1 atm = 1.01325×10^5 Nm^{-2}

$$\therefore \quad Z_1 = \frac{(1.4142)\ (3.1416)\ (3.61 \times 10^{-10}\ \text{m})^2\ (444\ \text{ms}^{-1})\ (1.01325 \times 10^5\ \text{Nm}^{-2})}{(1.38 \times 10^{-23}\ \text{JK}^{-1})\ (298\text{K})} = \mathbf{6.32 \times 10^9\ s^{-1}}$$

(d) From equation (13), $Z_{1,1} = \dfrac{1}{\sqrt{2}} \pi \sigma^2 v\rho^2 = \dfrac{\pi\sigma^2 vP^2}{\sqrt{2}\ (kT)^2}$ $\qquad \left(\because \rho = \dfrac{P}{kT}\right)$

$$\therefore \quad Z_{1,1} = \frac{(3.1416)\ (3.61 \times 10^{-10}\ \text{m})^2\ (444\ \text{ms}^{-1})\ (1.01325 \times 10^5\ \text{Nm}^{-2})}{(1.4142)\ (1.38 \times 10^{-23}\ \text{JK}^{-1})^2\ (298\text{K})^2} = \mathbf{7.77 \times 10^{34}\ m^{-3}\ s^{-1}}$$

(e) 1 litre = 1 dm^3 = 10^3 m^{-3}, $n = 6.023 \times 10^{23}$ mol^{-1}

$$\therefore \quad Z_{1,1} = \frac{(7.77 \times 10^{34}\ \text{m}^{-3}\ \text{s}^{-1})\ (10^{-3}\ \text{m}^3\ \text{dm}^{-3})}{6.023 \times 10^{23}\ \text{mol}^{-1}}$$

$$= \mathbf{1.29 \times 10^8\ mol\ dm^{-3}\ s^{-1}}.$$

3·11 VISCOSITY OF GASES

Viscosity is a measure of a fluid's resistance to flow quite apart from its inertia. Viscosity measures the steady-state transfer of momentum due to a difference in velocities within the fluid. If the flow pattern involves parallel layers flowing past each other at differing velocities, the flow is called *laminar.* The phenomenon of viscosity is shown by liquids as well as gases. *The resistance which is met by one portion of a liquid in flowing over another portion is known as* ***viscosity*** *of the liquid.* It has been proved experimentally that the tangential force F, which is necessary to maintain a constant difference in the velocities of two adjacent parallel layers of a liquid, flowing in the same direction is proportional to the difference in the velocities v and area A, of the surface of contact of the two layers and inversely proportional to the distance r between the two layers. Hence,

$$F = \eta \,.\, \frac{Av}{r},$$

where η is a constant and is known as *coefficient of viscosity* of the liquid.

If $A = 1$, $v = 1$ and $r = 1$, then $\eta = F$.

Therefore, ***coefficient of viscosity*** is defined *as the tangential force necessary to maintain a difference in velocity of unity between two parallel layers one cm apart, having a surface of contact of unity between them.* Its unit is *poise*, which in CGS system is dyne per cm^2.

The coefficient of viscosity is measured by means of *Poiseuille's equation* by noting the time of flow of a definite volume of the liquid through a capillary tube under a definite difference of pressure. The Poiseuille's equation is represented as

$$\eta = \frac{\pi P r^4 t}{8 V l}, \qquad \ldots(18)$$

where V is the volume of the liquid flowing through a capillary tube of radius r and length l under a pressure P in time t.

When a spherical body of radius r and density s falls under gravity through a fluid of density d, it is acted on in the downward direction by force F' which is given by

$$F' = \frac{4}{3} \pi r^3 (s - d) g \qquad \ldots(19)$$

Because of the viscosity of the fluid, this force is opposed by a frictional force which increases in magnitude with the increase in the velocity of the falling body until the body acquires a constant velocity v, known as ***terminal velocity.*** The force F'' acting on the body is given by Stokes law as,

$$F'' = 6\pi r \eta v. \qquad \ldots(20)$$

We have $F' = F''$.

$$\therefore \quad 6\pi r \eta v = \frac{4}{3} \pi r^3 (s - d) g$$

or

$$v = \frac{2}{9} g r^2 \left(\frac{s - d}{\eta}\right) \qquad \ldots(21)$$

Equation (21) holds good when the sphere is falling through an appreciable volume of a liquid. In case a small sphere falls coaxially through a too viscous liquid in a cylindrical tube of radius r_1, the height of the liquid being h, two corrections, *viz., wall effect* and *end effect* have to be incorporated. By making these two corrections, equation (21) becomes,

$$v = \frac{2}{9} gr^2 \frac{(s-d)}{\eta\,(1 + 2.4\, r/r_1)\,(1 + 3.3\, r/h)} \qquad \ldots(22)$$

By measuring the time of fall t, through a distance l, we can write equation (22) as :

$$\eta = \frac{2}{9} gr^2 \frac{(s-d)\,t}{l\,(1 + 2.4\, r/r_1)\,(1 + 3.3\, r/h)}$$

If a layer of gas is caused to stream over another in a given layer, then as a result of the continual interchange of molecules between streaming layer and its adjacent one on account of their continued movement, some of the momentum of the streaming layer is transferred to the layer next to it and this transfer will continue from layer to layer. Hence, the whole bulk of the gas would begin to stream except the layer closest to the walls of the container. But different layers will have different velocities, the velocity decreasing with the increase in the distance from the streaming layer. This will cause a velocity gradient (dv/dr), where dv is the change of velocity at a distance dr.

In the case of thin layer of a gas, we see that its adjacent layer, nearer to the original streaming layer than it, will exert a force which will tend to increase its velocity in the same direction, but the other continuous layers move apart from the streaming layer than it, will exert a force on it in the opposite direction. These forces are known as *forces of viscosity* or *internal friction* and the retarding influence of a slower moving layer of a gas over a faster moving layer is called the *viscosity of the gas*. If F is the retarding force which the slower moving layer exerts over A cm^2 of the adjacent faster moving one and if dv/dr is the velocity gradient, then we have

$$F = -\eta A \cdot \frac{dv}{dr} \qquad \ldots(23)$$

Thus, the coefficient of viscosity, η, of the gas is defined as the *force in dynes per cm^2 exerted between two parallel layers at a unit distance apart for a unit velocity gradient.*

The value of η of gas can be determined by measuring :

(a) the flow of a gas through a capilliary tube,

(b) the damping of the oscillations of a pendulum.

(c) the retarding effect of a gas on a rotating cylinder.

For an accurate determination, Rankine's method is more commonly used.

Rankine's Method : The rate of flow of the gas under study through a cylindrical capillary tube of known radius is measured by employing the following modified form of Poiseuille's expression,

$$\eta = \frac{\pi\,(P_1 - P_2)\, r^4\, t}{8l\, V} \qquad \ldots(24)$$

where t is the time of flow of volume V of a gas to pass through a capillary tube of length l and radius r and under a pressure difference $(P_1 - P_2)$. The value of v is taken under the mean value of two pressures P_1 and P_2, *i.e.*, under $\frac{P_1 + P_2}{2}$.

By using a standard apparatus under a constant difference of pressure, η will according to equation (24) be directly proportional to the time of flow t, as all other terms therein will be constant. So, for two gases say 1 and 2, we have

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \qquad \ldots(25)$$

If the value of η of a standard gas, say dry air is known, the value of η of the unknown gas can be calculated.

The Rankine's apparatus (Fig. 12) consists of a closed rectangular glass tube ABCD provided with two stop cocks at the two ends. One arm AB of the glass is a capillary of 0.02 cm diameter, while the other arm CD is a narrow tube of 0.3 cm bore. In the wider tube a small pellell of mercury about 4 cm in length is placed which may move between A and B when desired forcing the gas to pass through the capillary arm. The apparatus is thoroughly cleaned and dried and filled with gas under 1 atm. It is then inverted to bring the lower end of the mercury pellet at mark A. It is then brought to its normal position and thermostated. The time taken by the pellet to bring its lower end to mark B is noted. The experiment is repeated three or four times and the average time is observed. The value gives the time of flow of the gas through the capillary tube under a pressure gradient, determinend by the weight of the pellet and the length of the tube. Similarly, experiments are performed with dry air and the average time of fall of the pellet is determined as before. Thus, we can calculate the coefficient of viscosity of the gas vide equation (25).

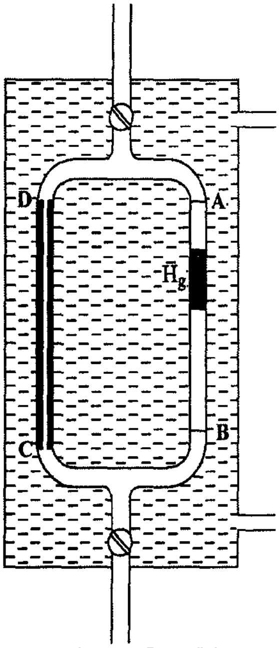


Fig. 12. Ramkine's apparatus

[I] Viscosity of Gases and Mean Free Path

Suppose a gas flows over a horizontal surface OX (Fig. 13) with a velocity as small as compared to the thermal velocity of the molecules in the direction OX. The velocity of the layer in contact with the surface is zero and it increases as we travel along OY in a direction perpendicular to OX at a uniform rate *dv/dy*.

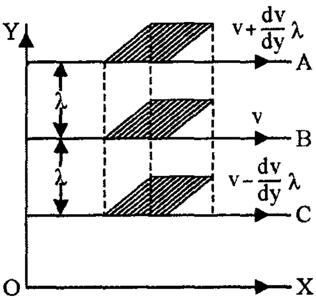


Fig. 13.

Consider a layer B at a certain distance from the fixed surface OX. The velocity with which the gas flows in this layer is v. Consider two layers A and C above and below B, respectively at a distance λ equal to the mean free path of the molecules, so that the molecules moving vertically up or down do not have any collisions while moving between the two layers.

The velocity of gas in the layer $A = v + \frac{dv}{dy} . \lambda$

The velocity of gas in the layer C $= v - \frac{dv}{dy} . \lambda$

Now due to thermal velocities, the molecules are moving in all directions, we can imagine them to be divided into three parts moving in either direction parallel to X, Y and Z axes, respectively, so that on an average one sixth of the molecules move parallel to any one axis in one particular direction. There is thus a continuous interchange of molecules between the layers A and C. If n is the number of molecules per ml, m is the mass of each and v the average velocity, then the number of molecules passing downwards from A to C per unit area of the layer B in one second $= nv/6$.

Hence, forward momentum lost per unit area per second by the layer A

$$= m . \frac{nv}{6}\left(v + \frac{dv}{dy} . \lambda\right)$$

Similarly, the number of molecules passing upwards per unit area of the layer B in one second $= nv/6$.

Therefore, forward momentum gained per unit area per second by the layer A.

$$= m . \frac{nv}{6}\left(v - \frac{dv}{dy} . \lambda\right)$$

∴ Net momentum lost by the layer A per unit area per second

$$= \frac{mnv}{6}\left[\left(v + \frac{dv}{dy} . \lambda\right) - \left(v - \frac{dv}{dy} . \lambda\right)\right] = \frac{1}{3} mnv \, \lambda . \frac{dv}{dy}$$

The layer C below B gains the same amount of momentum.

Hence, the layer A above B tends to accelerate its motion and the layer C below B tends to retard its motion.

The backward dragging force per unit area

= Gain or loss of momentum per unit area per second

$$= \frac{1}{3} mnv \, \lambda . \frac{dv}{dy}$$

This force must be equal to the tangential force $\eta . dv/dy$ acting per unit area of the layer B due to viscosity, η, being the coefficient of viscosity of the gas.

$$\eta . \frac{dv}{dy} = \frac{1}{3} mvv \, \lambda \frac{dv}{dy}$$

or

$$\eta = \frac{1}{3} mnv \, \lambda = \frac{1}{3} \rho \, v \, \lambda \qquad (\because \rho = mn) \qquad \ldots(26)$$

The density of a gas increases with pressure, but λ decreases in the same ratio, so that $m\lambda$ remains constant. Hence, η is independent of pressure.

The density of gas decreases with temperature, whereas λ increases in the same ratio. But the molecular velocity v, is proportional to $\sqrt{T}$ where T is the absolute temeprature, so that

$$\eta \propto \sqrt{T}.$$

Thus, viscosity of a gas increases with an increases of temperature.

A more vigorous treatment given by Chapman, shows that the numerical coefficient in equation (26) is 1/2 rather than 1/3, so that

$$\eta = \frac{1}{2} \rho V \lambda \qquad \ldots(27)$$

This equation is known as ***Chapman's equation.***

(1) Calculation of mean free path : The Chapman equation permits calculation of mean free path from viscosity measurements. According to this equation,

$$\lambda = \frac{2\eta}{\rho v} \qquad \ldots(28)$$

where ρ is the density of the gas.

Since $V = \frac{RT}{P}$, hence $\rho = M/V = PM/RT$. We also know that,

$$V = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Substituting the values of v and ρ in equation (28), we get

$$\lambda = \frac{1}{\sqrt{2}.P} \left(\frac{\pi RT}{M}\right)^{1/2} \eta \qquad \ldots(29)$$

Thus, knowing the value of η, the mean free path can be calculated at a given temperature and pressure from equation (29).

(2) Calculation of collision diameter : As already described, the mean free path is given by the equation,

$$\lambda = \frac{kT}{\sqrt{.2}\, P\pi\, \sigma^2} \qquad \text{[cf. equation (11)]} \qquad \ldots(30)$$

From equations (29) and (30)

$$\frac{1}{\sqrt{2}.P}\left(\frac{\pi\, RT}{M}\right)^{1/2} \eta = \frac{kT}{\sqrt{2}.\, P\pi\, \sigma^2}$$

Since Boltzmann constant, $k = R/N$, so

$$\sigma^2 = \frac{(MRT)^{1/2}}{\pi^{3/2} N . \eta} \qquad \ldots(31)$$

Thus, knowing the viscosity of a gas, the collision diameter can be easily calculated from equation (31).

Problem 1. ***At N.T.P. the viscosity of hydrogen is* 8.4×10^{-5} *poise and the average velocity of the molecules is* 1.7×10^{5} *cm/sec. Calculate the mean free path and the molecular diameter. Density of hydrogen* = $0.00009\ g\ cm^{-3}$.**

Solution. From equation (26), we have $\lambda = \frac{3\eta}{\rho v} = \frac{3 \times 8.4 \times 10^{-5}}{9 \times 10^{-5} \times 1.7 \times 10^{5}} = \mathbf{1.6 \times 10^{-5}}$ **cm.**

As, molecular diameter (σ) is given by, $\sigma = \left(\frac{V}{\sqrt{2}\pi\, lN}\right)^{1/2}$ (vide equation 10)

$$= \left(\frac{22400}{\sqrt{2} \times 3.14 \times 1.6 \times 10^{-5} \times 6.023 \times 10^{23}}\right)^{1/2} = \mathbf{2.24 \times 10^{-8}\ cm.}$$

Problem 2. ***The coefficient of viscosity has the units of kg*** $m^{-1}\ s^{-1}$ ***in the SI system. Show that it can be written as Pa s (i.e., Pascal second).***

Solution. Pa s = Pressure × time = (Nm^{-2}) (s) = $(kg\ ms^{-2}\ m^{-2})$ (s) = $kg\ m^{-1}\ s^{-1}$.

Problem 3. ***At 27°C and 1 atm pressure, the coefficient of viscosity of nitrogen gas is 178 μP (i.e., micropoise). Calculate (a) the mean free path (λ) and (b) the collision diameter (σ) of nitrogen molecule using the Chapman equation.***

Solution. **(a)** According to equation (29),

$$\lambda = \frac{1}{\sqrt{2}P}\left(\frac{\pi RT}{M}\right)^{1/2} \eta$$

$$P = 1\text{ atm} = 1.01325 \times 10^5\ \text{Nm}^{-2},\quad \eta = 178\ \mu\text{K} = 1.78 \times 10^{-5}\ \text{kg m}^{-1}\ \text{s}^{-1}$$

$$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1},\ T = 300\text{K},\ M = 28\ \text{g mol}^{-1} = 28 \times 10^{-3}\ \text{kg mol}^{-1}$$

$$\therefore\quad \lambda = \frac{1}{(\sqrt{2})\,(1.01325 \times 10^5\ \text{Nm}^{-2})}\left[\frac{(3.14)\,(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\,(300\text{K})}{(28 \times 10^{-3}\ \text{kg mol}^{-1})}\right]^{1/2}$$

$$= 6.602 \times 10^{-8}\ \text{m} = \mathbf{66.02\ nm}$$

(b) From equation (31),

$$\sigma^2 = \left[\frac{(MRT)^{1/2}}{\pi^{3/2}\,N.\eta}\right]$$

$$= \left\{\frac{[(28 \times 10^{-3}\ \text{kg mol}^{-1})\,(8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\,(300\ \text{K})]^{1/2}}{(3.14)^{3/2}\,(6.023 \times 10^{23}\ \text{mol}^{-1})\,(1.78 \times 10^{-5}\ \text{kg m}^{-1}\ \text{s}^{-1})}\right\}$$

$$= 13.9129 \times 10^{-20}\ \text{m}$$

$$\therefore\quad \sigma = 3.73 \times 10^{-10}\ \text{m} = \mathbf{373\ pm}$$

3.12 HEAT CAPACITY OF GASES

The quantity of heat required to raise the temperature of the body by one degree is known as its ***heat capacity***. Heat capacity depends upon the amount of the material in the system. If the amount of the substance is one gram, the heat capacity is the same as the specific heat. If 1 g mole of a gas is taken, the heat capacity is called the ***molar heat capacity***. When a gas is heated, ordinarily there is an increase in volume as well as pressure in addition to the rise of temperature. For the sake of simplicity, either the volume or the pressure may be kept constant, therefore, a gas has two heat capacities, *i.e.*,

(a) Heat capacity at constant volume (C_v),

(b) Heat capacity at constant pressure (C_p).

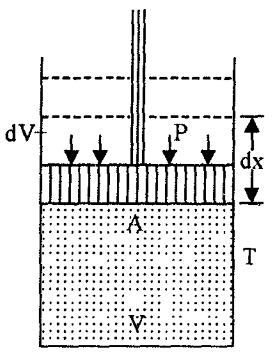


Fig. 14.

[I] Difference Between the Two Heat Capacities

Consider 1 g mole of a gas having a volume *V* ml at a pressure *P* dyne per sq cm and temperature *T* K, contained in a cylinder enclosed by a piston, as shown in figure (14). Because the heat supplied is used to increase the speed and kinetic energy of the molecules, and the molecules are monoatomic, there cannot be any absorption in vibrational or rotational energy and further, no energy can be utilised to do any mechanical work, as the volume remains constant. From kinetic equation, we have deduced that the kinetic energy (*E*) of one g mole of a gas at temperature *T*, is

$$E = \frac{3}{2}RT$$

At temperature $(T + 1)^\circ$, the kinetic energy (E) is given by

$$E_1 = \frac{3}{2} R\,(T + 1).$$

The increase in kinetic energy for 1° rise in temperature, *i.e.*,

$$E_1 - E = \Delta E = \frac{3}{2}\,[R\,(T + 1) - T] = \frac{3}{2} R \approx 3 \text{ calories}$$

The heat supplied at constant volume is equal to increase in kinetic energy, so that $C_v = \Delta E = 3$ calories, for a monoatomic gas.

If instead of volume, the pressure is kept constant and the volume is allowed to increase, the heat supplied now does two things :

(a) It raises the temperature of the gas.

(b) It does work in expanding the gas against the external pressure.

The amount of heat required to raise the temperature of the gas in this case is the same as in the first case, (when the volume is kept constant), but in addition more heat energy has to be supplied to do external work. Hence, heat capacity at constant pressure is greater than the heat capacity at constant volume by an amount which is thermal equivalent of the work done in expanding the gas against thermal work.

$$\therefore \qquad C_p = C_v + \text{Work done.}$$

Let A be the area of the piston which moves outwards due to the expansion of the gas. The force on piston $= P \times A$.

If it moves outwards by a distance dx, then

Work done $= P.\,A\,dx = P.\,dV$, where dV is the increase in volume.

If V_1 and V_2 be the initial and final volumes of the gas at constant pressure P, the work done W is given by

$$W = P \times \text{change in volume} = P\,(V_2 - V_1) = R\,(T_2 - T_1).$$

For 1° rise in temperature, $W = R \approx 2$ calories

$$\therefore \qquad C_P = C_V + R = \frac{3}{2} R + R = \frac{5}{2} R.$$

For 1 g mole of a monatomic gas, the difference of heat capacities at constant pressure and volume, is given by

$$C_p - C_v = R = 2 \text{ calories.}$$

The ratio of the heat capacities is generally expressed by the symbol γ.

$$\therefore \qquad \gamma = \frac{C_P}{C_V} = \frac{5/2R}{3/2R} = \frac{5}{3} = 1.66 \quad \text{(For monatomic gas)}$$

For a polyatomic gas, the heat supplied is utilised in not only increasing the translational kinetic energy, but also in increasing the vibrational and rotational energies of the molecules. If x calories be used for increasing the latter energies, then

$$C_v = \frac{3}{2} R + x = 3 + x$$

$$C_p = \frac{5}{2} R + x = 5 + x$$

In general, $\frac{C_p}{C_v} = \gamma = \frac{5+x}{3+x}$

For a monotomic gas, $x = 0$.

$$\therefore \quad \gamma = \frac{5}{3} = 1.66$$

For a diatomic gas, $x = R = 2$ calories.

$$\therefore \quad \gamma = \frac{5+2}{3+3} = \frac{7}{5} = 1.40.$$

For a triatomic gas, $x = 3/2\ R = 3$ calories.

$$\therefore \quad \gamma = \frac{5+3}{3+3} = \frac{8}{6} = 1.33.$$

[II] Variation of Heat Capacity with Temperature

For monotomic gases, like inert gases, the heat capacity at constant volume C_v is constant at all temperatures. For some other gases, the values of C_v are found to be constant in the ordinary range of temperatures.

The heat capacity of all gases, including monoatomic, increases with temperature at high temperatures and decreases at low temperatures, and finally approaches the limiting value of 3.0 cals. This leads us to conclude that at sufficiently low temperatures all gases have the same value of C_v which is equal to that for monoatomic gases. This fact coupled with the increase in heat capacity with the rise in temperature has been explained by Einstein on the basis of quantum theory.

The molecules of the gases are sufficiently far apart so that these motions of translation, rotation and vibration are independent of each other. The total energy for one gram mole of a gas is, therefore, the sum of three kinds of energies of individual molecules. If we denote contributions of translational, rotational and vibrational energies by C_t, C_r and C_b, respectively, then

$$C_v = C_t + C_r + C_b$$

The quantum laws are applicable only to the energies of rotation and vibration as these are not periodic and not to translational energy which is periodic. At low temperatures, the total energy of the molecules is very small and is less than the minimum energy required for rotation and vibration. Hence, only motion of translation is possible due to which the value of $C_v = C_t \approx 3$ calories.

At slightly higher temperature, rotation develops progressively and one molecule after the other begins to rotate. As the energy required for rotation has to be supplied now, the heat capacity increases gradually to the value of $C_t + C_r$. At still higher temperatures, atomic vibrations within the molecules are set up and as energy has to be supplied for the purpose, the heat capacity now increases rapidly and finally approaches the constant value which is given by,

$$C_v = C_t + C_r + C_b.$$

[III] Determination of Heat Capacity at Constant Volume

The heat capacity of a gas at constant volume can be accurately determined by means of Joly's differential steam calorimeter.

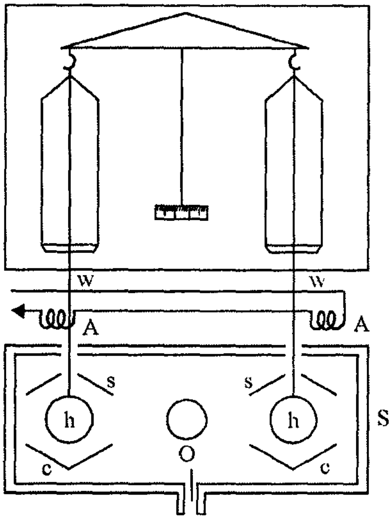


Fig. 15. Joly's calorimeter.

The apparatus (Fig. 15) consists of a double walled metal enclosure S known as steam chamber. It is placed below a sensitive balance. From either arm of the balance are freely suspended, by thin platinum wires *ww*, two equal hollow spheres *hh* of copper. In Joly's actual experiment each sphere was 6.7 cm in diameter and weighed 92.2 g. Each sphere is provided with a small tray *c* at the bottom known as *catch-water* to hold the condensed steam and is provided with a *shelter s* above it so that the steam condensed on the ceiling of the chamber may not fall on the sphere or catch-water.

The holes through which the suspension wires enter the chamber are made narrow so that any steam escaping through them may not disturb the weighing, and are lined with *plaster of paris* to absorb any condensed steam. Some steam also condenses on the suspending wires *ww* and the surface tension of the water renders weighing difficult and inaccurate. To remove this difficulty, thin platinum spirals AA surround the wires and are heated by an electric current, thus preventing condensation of steam.

To test that the two spheres have the same thermal capacity, both are exhausted and counter-poised. Dry steam is then made to enter the chamber through an opening O at the back and leaves at the bottom. Steam condenses on both the spheres and if the balance remains undisturbed, when the steady state has reached, the two spheres have equal thermal capacities. The chamber and the spheres are dried. One of the spheres is filled with gas at the desired pressure. The two are counter-poised by adding weights, say m on the empty sphere side. Thus, m gives the mass of the gas. The temperature of the enclosure, t_1, is carefully noted. Dry steam is again admitted into the chamber and it condenses on the two spheres. More condensation takes place on the sphere containing the gas. Additional weights are placed in the other and the excess of steam condensed m_1, due to the gas is noted. The temperature of steam, t_2, is also noted.

If C_v be the heat capacity of the gas at constant volume and L the latent heat of steam, then

$$\text{Heat gained by the gas} = mC_v(t_2 - t_1) \text{ cals.}$$

$$\text{Heat lost by steam} = m_1L \text{ cals.}$$

But, $$\text{Heat gained} = \text{Heat lost}$$

$$\therefore \quad mC_v(t_2 - t_1) = m_1L$$

Corrections : (i) The first weighing is made at atmospheric pressure at t_1°C, whereas the second weighing is made in steam at t_2°C. Hence, it is necessary to reduce both the weighings to vacuum to avoid error due to *buoyancy*.

(ii) The spheres are not exactly equal. The experiment is repeated by filling the evacuated sphere with the gas and exhausting the other. The mean of the two observations gives the corrected value.

(iii) Corrections are also necessary for (a) the expansion of the sphere with increased temperature and consequent work done by the gas, (b) the expansion of the sphere to the increased pressure of the gas and consequent thermal effects, and (c) increased buoyancy of the sphere due to its increased volume at higher temperature.

[IV] Determination of Heat Capacity at Constant Pressure

An accurate method for measuring the heat capacity of a gas at constant pressure has been designed by Scheel and Heuse. The apparatus (Fig. 16) consists of a glass calorimeter C of special shape as shown in the figure. In the innermost part of the calorimeter there is a coil of platinum wire H which is sealed into the glass and is heated by connecting the leads L_1 and L_2 to a battery through a rheostat, key and an ammeter. A voltmeter is connected across the leads to measure the potential difference. The calorimeter is sealed into an outer vacuum jacket to reduce the loss of heat due to radiation. The gas enters the calorimeter through a long metal tube M in which is sealed a platinum resistance thermometer P_1 which measures its initial temperature. A similar platinum resistance thermometer P_2 is provided on the other side to measure the temperature of the out-going gas.

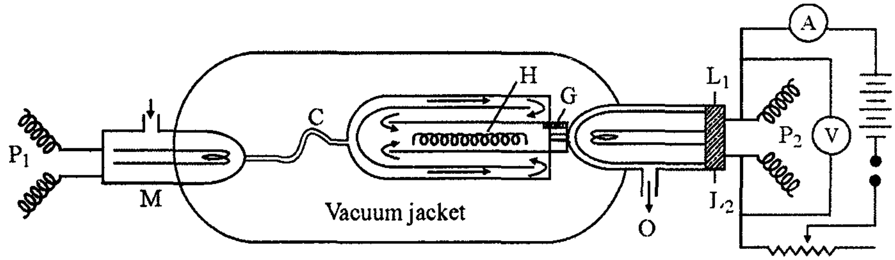


Fig. 16.

To perform the experiment the apparatus is placed in a constant temperature bath. The gas is passed slowly at constant pressure through a long metal tube which is also placed in the same bath into the calorimeter. The gas travels in the direction of the arrows through a zig-zag path and finally comes in contact wtih the heating element. The advantage of the zig-zag path is that any heat lost by the heated gas is brought back into it by the incoming steam of the gas and there is no wastage. The gas then passes through the copper gauge packing G where it is thoroughly mixed so as to attain a uniform temperature throughout. It finally flows past the platinum resistance thermometer P_2.

When the steady state has reached the initial and the final temperatures of the gas, *i.e.*, t_1° and t_2° are measured. The mass of the gas, m flowing through the calorimeter per second is measured by noting the initial and final pressures of the gas in the reservoir. If E is the reading of the voltmeter and I that of the ammeter (A), then

$$\frac{EI}{4.18} = m\, C_p\, (t_2 - t_1) + L \qquad \text{...(1)}$$

where, C_p is the heat capacity of the gas at constant pressure and L the loss of heat per second (in calories) due to radiation. Usually the value of L is negligible. In such a case,

$$C_p = \frac{EI}{4.18 \times m\, (t_2 - t_1)} \qquad \text{...(2)}$$

If L is not negligible it can be eliminated by taking another observation. The rate of flow and the current through the coil are so adjusted that the same difference of temperature, is obtained. If E and I are the values of the potential difference and the current and m' is the mass of the gas flowing per second. then

$$\frac{EI}{4.18} = m'\,C_p\,(t_2 - t_1) + L \qquad ...(3)$$

Subtracting equation (3) from (2), we get

$$\frac{EI - EI'}{4.18} = (m - m')\,C_p\,(t_2 - t_1)$$

or
$$C_p = \frac{EI - EI'}{4.18 \times (m - m')\,(t_2 - t_1)}$$

The advantages of measuring C_p by this method are as follows :

(a) The loss of heat due to radiation is negligible and can also be eliminated for accurate work.

(b) The amount of heat generated can be measured accurately as it is produced accurately.

(c) The thermal capacity of calorimeter is automatically eliminated as the temperatures are noted when they are steady. Moreover, steady temperatures can be read with greater accuracy than the varying temperatures.

(d) The method can be used to study the variation of C_p with temperature. To find the heat capacity at very low temperatures, the gas is passed through a low temperature bath in which the calorimeter is also immersed.

[V] Determination of Heat Capacity Ratio

The determination of γ, the ratio of heat capacities is based on a method known as Clement and Disorme's method. The apparatus (Fig. 17) consists of a bit, thick walled glass flask placed in a wooden box packed with saw dust, cotton wool or some other non-conducting material to avoid loss of heat. It is provided with a wide-bore stop cock S, a side tube having a gas tight tap T and a manometer M, as shown in figure (17). The manometer contains either sulphuric acid or some oil of low density and negligible vapour pressure at the room temperature. In order to completely dry the gas inside the flask some sulphuric acid is kept in the vessel.

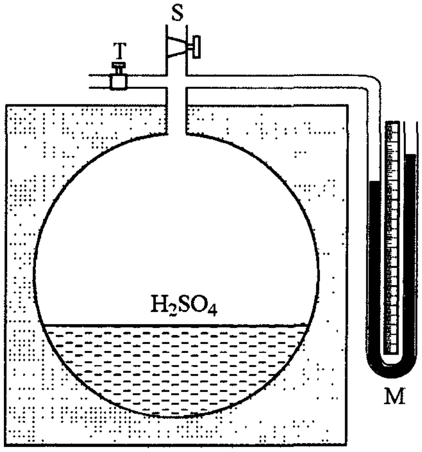


Fig. 17. Determination of γ.

Working : The stop cock S is closed and the tap T is opened and dry air is compressed into the vessel. The tap T is then closed and the gas itself is allowed to acquire the temperature of the surroundings. When a steady state has been reached, the difference h_1 in the level of the liquid in the two limbs of the manometer is noted. If P is the atmospheric pressure, the pressure P_1 of the enclosed gas is given by,

$$P_1 = P + \frac{h_1\,\rho}{D}$$

where ρ is the density of the oil and D the density of mercury.

The stop cock S is opened and closed suddenly by giving a half-turn. During the time the stop cock S remains open, the gas in the flask rushes out to equalise the pressure and just when the stop cock is closed the gas inside it is at the atmospheric pressure. Because the flask is completely insulated, no heat is either gained or lost and the process is adiabatic.

Due to the expansion of the gas under the adiabatic conditions the temperature falls. The apparatus is then left in this condition for sometime. The enclosed air slowly gains heat from the surroundings and the pressure increases. It is supposed that volume remains constant. A very small change in volume does take place due to the change in the level of the liquid column in the manometer, but it is negligible.

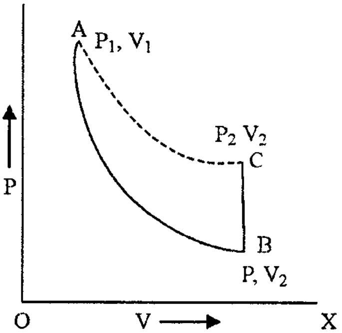


Fig. 18.

When the gas acquires the temperature of the surroundings and a steady state has been reached, the difference h_2 in the level of the liquid in the two limbs is again noted. The pressure P_2 of the enclosed gas is then given by

$$P_2 = P + \frac{h_2 \rho}{D}$$

Let P_1 and V_1 be the initial pressure and volume of the enclosed gas as shown at A in figure (18). If P is the atmospheric pressure which is the pressure of the gas after adiabatic expansion and V_2 the corresponding volume which the gas should possess, as shown at B, then the points A and B lie on the same adiabatic AB. It will be seen in thermodynamics that

$$PV_1^\gamma = PV_2^\gamma$$

or
$$\left(\frac{V_2}{V_1}\right)^\gamma = \frac{P_1}{P} \qquad \ldots(4)$$

If P_2 is the pressure and V_2 the corresponding volume which the gas should possess after the room temperature has been attained as shown at C, then the points A and C will lie on the same isothermal as there is no change in temperature from A to C.

$$\therefore \quad P_1V_1 = P_2V_2$$

or
$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \ldots(5)$$

From equations (4) and (5), we get

$$\left(\frac{P_1}{P_2}\right)^\gamma = \frac{P_1}{P}$$

or
$$\gamma (\log P_1 - \log P_2) = \log P_1 - \log P$$

or
$$\gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}$$

If the changes in pressures are small, then

$$\gamma = \frac{P_1 - P}{P_1 - P_2} = \frac{\left(P + \frac{h_1 \rho}{D}\right) - P}{\left(P + \frac{h_1 \rho}{D}\right) - \left(P + \frac{h_2 \rho}{D}\right)} = \frac{h_1}{h_1 - h_2} \qquad \ldots(6)$$

This relation is fairly accurate and convenient to calculate the value of γ in the laboratories.

3·13 REAL GASES AND IDEAL GASES

[I] Ideal or Pefect Gas

A gas which strictly obeys Boyle's and Charles' laws at all temperatures and pressures is known as an *ideal* or *perfect gas*. The characteristics of an ideal gas are as follows :

(i) The compressibility (Z) of an ideal gas is unity, *i.e.*,

$$Z = \frac{PV}{nRT} = 1$$

(ii) The product of pressure and volume of an ideal gas at constant temperature is constant.

(iii) If an ideal gas is cooled at constant pressure, the volume decreases continuously, till at –273°C, its volume becomes zero.

(iv) If it is allowed to expand without doing any external work, it shows no thermal effect.

(v) There is no force of attraction between molecules of an ideal gas.

[II] Differences Between an Ideal and Real Gas

(i) A real gas does not obey various gas laws particularly at low temperatures and high pressures. Only at high temperatures and low pressures, real gas tends towards ideal behaviour.

(ii) The volume of a real gas does not become zero at –273°C. In fact, when cooled sufficiently, a real gas is suddenly converted into liquid state.

3·14 DEVIATIONS OF REAL GASES FROM THE IDEAL GAS LAWS

It has been experimentally observed that the ideal gas laws are inadequate for representing the behaviour of the real gases. Some of the results are discussed below:

(i) According to Boyle's law $P \propto 1/V$, at constant temperature. When pressure of a gas is plotted against its volume we should get a rectangular hyperbola. At very high temperatures, the $P - V$ curves are found to be hyperbolic, but do not coincide with the theoretical rectangular hyperbola.

(ii) At constant pressure, the volume of a gas increases with increase of temperature. The change in volume per c.c. per unit rise in temperature, known as ***coefficient of isobaric expansion*** (α), is given by,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Since $PV = nRT$, therefore, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$

$$\therefore \qquad \alpha = \frac{1}{V} \cdot \frac{nR}{P} = \frac{nR}{nRT} = \frac{1}{T}$$

In other words, α will be independent of the nature of the gas and will be a function of temperature. At normal pressures, α for different gases would be different and will also depend upon the pressure. This is, however, contrary to gas laws. Thus, at ordinary temperatures and 500 atmospheric pressures, the values of α for H_2, N_2 and CO_2 are 278×10^{-5}, 315×10^{-5} and 349×10^{-5}, respectively.

(iii) At constant temperature, there is a decrease in the volume of the gas with increase of pressure. The coefficient of isothermal compressibility (β) is given as the change in volume per c.c. per unit rise in pressure. Thus

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

The negative sign implies the decrease in volume.

As $$PV = nRT, \text{ so } \left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

$$\therefore \quad \beta = -\frac{1}{V}\left(\frac{-nRT}{P^2}\right) = \frac{nRT}{nRT.P} = \frac{1}{P}$$

In other words, β should be independent of the nature of the gas and should be a function of pressure only. However, experiments have shown β to be an individualistic property.

Regnault and Amagat made experimental observations and plotted the values of *PV* against *P* for a number of gases. The curve of an ideal gas should be a straight line parallel to the *P*-axis. But it can be seen (Fig. 19) that none of the curves are linear or parallel to the *P*-axis. In the case of nitrogen, ethylene and carbon dioxide, the *PV*-value first decreases, reaches a minimum and then increases, forming a cup, with increase in pressure. But in the case of hydrogen and helium, the *PV*-values begin to increase right from the very beginning, *i.e.*, from zero pressure. If temperature is sufficiently lowered, hydrogen and helium would also exhibit the same curves as for nitrogen etc.

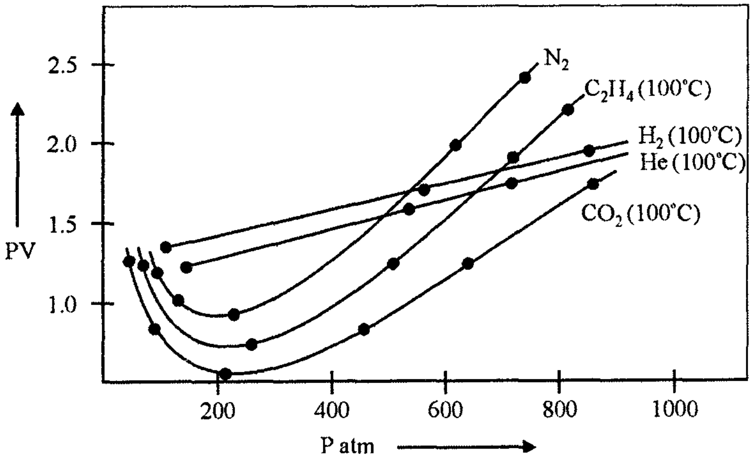


Fig. 19.

(iv) The volume of one gram mole of a gas at constant pressure and temperature should be the same, according to Avogadro's hypothesis. The molecular volumes of a number of gases at N.T.P. have been experimentally seen to vary. Thus, the Avogadro's hypothesis is only an approximate one for real gases.

From the above observations, we can safely show that the kinetic theory does not correctly represent the behaviour of real gases. Several attempts have been made to modify the equation of state ($PV = nRT$) for ideal gases and transform it into a form which would represent the P—V—T relations of real gases.

3·15 VANDER WAALS EQUATION OF STATE

[I] Derivation of Vander Waals Equation

In the derivation of perfect gas laws on the basis of the kinetic theory of gases, some assumptions were made which do not hold true for real gases. These are :

(i) The volume occupied by the molecules is regarded to be negligible as compared to the total volume of the gas, i.e., the molecules are regarded as mere mass points having no volume. At very low pressures, when the volume of the gas is quite appreciable the small volume of the molecules can be neglected in comparison to the large volume of the gas. But at high pressures, the volume of the gas is small and now the small volume of the molecules cannot be neglected in comparsion to the total volume of the gas.

(ii) The collisions between the molecules are perfectly elastic and there is no intermolecular forces of attraction between the molecules. Again when the pressure of the gas is very low, its volume is very large. The molecules remain farther apart and do not exert appreciable mutual attraction. But at high pressure, the volume of the gas is small and the molecules come closer together to exert mutual attraction.

(a) Volume Correction. Let n moles of a gas is filled in a container of volume V. If the volume of gas molecules is negligible, then the total volume V is available for movements of each molecule. As molecules have finite size, the space in which they are free to move is less than the total volume of the gas. If the actual volume of n molecules is subtracted from the gas volume V, we obtain the correct volume. If b is the volume of 1 mole of gas, the corrected volume is $(V-nb)$, where b is known as ***co-volume, effective volume*** or ***excluded volume.*** The factor b is nearly four times the actual volume of the molecules.

The fact that the co-volume is nearly four times the actual volume of the molecules is shown as below :

Consider two gas molecules unpenetrable and incompressible spheres. Let d be the diameter of the molecule. It is clear that the centres of the two spheres cannot approach each other more closely than the distance d. For this pair of molecules, a sphere of radius d and so of volume $\frac{4}{3}\pi d^3$ constitutes what is known as ***excluded volume***. The excluded volume per molecule is thus half the above volume, *i.e.*, $\frac{2}{3}\pi d^3$. The actual volume of one gas molecule of radius r is given by,

$$\frac{4}{3}\pi r^3.$$

or $$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{1}{6}\pi d^3$$

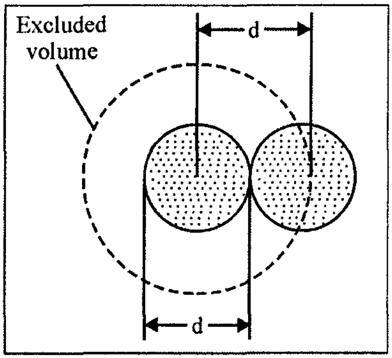


Fig. 20.

∴ Excluded volume per molecule

$$= \frac{2}{3}\pi d^3 = 4\left(\frac{1}{6}\pi d^3\right)$$

$$= 4 \times \text{Actual volume of the gas molecule.}$$

Thus, the excluded volume is 4 times the actual volume of the molecule. As b is the excluded volume per mole, we have,

$$b = 4N\left(\frac{4}{3}\pi r^3\right)$$

where N = Avogadro's number.

(b) Pressure Correction. If we again consider the molecule A well inside the vessel, it is attracted by other molecules in all directions with the same force and the net force on it is zero. But when it strikes the wall ED of the vessel it is pulled back by other molecules (Fig. 21). Its velocity and hence the momentum with which it strikes the wall would be less than the momentum with which it will strike in the absence of the forces of attraction. Naturally, when the momentum becomes less the pressure decreases.

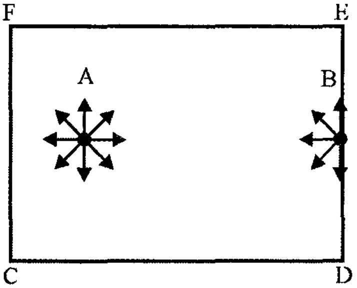


Fig. 21.

It is evident that if we double the number of molecules per c.c. of the gas, the decrease in pressure will be four times as great. It is due to the fact that the decrease in pressure is proportional to :

(i) the number of attracting molecules per unit volume.

(ii) the number of attracted molecules striking a unit area of the walls of the containing vessel per unit time.

Both the above factors are proportional to the number of molecules per c.c. or density of the gas.

∴ Force of attraction, $p \propto (\text{Density of the gas})^2$

$$\propto \left(\frac{n}{V}\right)^2 = \frac{n^2a}{V^2}$$

where a is the proportionality constant known as ***coefficient of attraction***. The factor, a/V^2 is known as ***cohesive pressure***.

Hence, Ideal pressure = Observed pressure + Force of attraction

$$= P + \frac{n^2a}{V^2}$$

This value of real pressure should be substituted in the perfect gas equation. Now substituting $(V - nb)$ for V and $\left(P + \frac{n^2a}{V^2}\right)$ for P in gas equation $PV = nRT$, we get,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \qquad \text{... (1)}$$

Equation (1) is known as *vander Waals equation of state.* For 1 mole of a gas, vander Waals equation can be written as,

$$(P + \frac{a}{V^2})\ (V - b) = RT \qquad \ldots (2)$$

[II] Units of Vander Waals Constants

The values of a and b depend on the units used for expressing pressure and volume. If the pressure is expressed in atmospheres and volume in litres, then

$$a = \frac{PV^2}{n^2} = \frac{\text{Pressure} \times (\text{Volume})^2}{(\text{Mol})^2}$$

$$= \frac{(\text{atm})\ (\text{litre})^2}{(\text{mol})^2} = \text{atm litre}^2\ \text{mol}^{-2}$$

Similarly, $$b = \frac{\text{Volume}}{\text{mol}} = \frac{\text{litre}}{\text{mol}} = \text{litre mol}^{-1}$$

In S.I. units, $$a = \frac{(\text{Pressure} \times \text{Volume})^2}{(\text{mol})^2} = \frac{(\text{Nm}^{-2})\ (\text{m}^3)^2}{(\text{mol})^2}$$

$$= \text{Nm}^4\ \text{mol}^{-2}$$

$$b = \text{Volume mol}^{-1}$$

$$= \text{m}^3\ \text{mol}^{-1}$$

[III] Applications of Vander Waals Equation to Real Gases

Equation (2) can explain the behaviour of real gases as follows :

(a) When the pressure is not too high. If the pressure is not very high, the value of V should be large and b may be neglected in comparison to V, hence equation (2) for 1 mole becomes,

$$\left(P + \frac{a}{V^2}\right) . V = RT$$

or $$PV + \frac{a}{V} = RT$$

or $$PV = RT - \frac{a}{V}$$

$$= P_i V_i - \frac{a}{V}$$

In other words, the value of PV is less than RT (or ideal product of PV) by an amount equal to (a/V) and this explains the dip in the curves of CO_2, O_2, C_2H_4 (c.f. fig. 16) at not too high pressures.

(b) When the pressure is too high. If the pressure is considerably high, the value of V will be very small and now we cannot neglect b. But since P is very large, the quantity (a/V^2) becomes small and can be neglected in comparison to high value of P. Thus equation (2) for 1 mole becomes,

$$P\ (V - b) = RT$$

or $$PV - P.b = RT$$

or $$PV = RT + P.b = P_i V_i + P.b$$

In other words, the product PV becomes greater than RT (or ideal product of PV) by an amount equal to $P.b$. This explains why the curves start rising at high pressures. (cf. fig. 19).

(c) When the temperature is high. When at a given pressure, the temperature is very high, the volume becomes sufficiently large to make the value of (a/V^2) negligibly small. At this stage, the value of b also becomes negligible in comparsion to V. Under these conditions, equation (2) for 1 mole becomes $PV = RT$, *i.e.*, approaches the ideal gas equation. This explains why the deviations become less at high temperatures.

(d) Exceptional behaviour of hydrogen and helium. We see from figure (19), that the curves for H_2 and He do not show a dip even when the pressure is moderate and the curves start rising right from the very beginning. This fact can be explained as both hydrogen and helium have comparatively small masses and so the attractive forces between the molecules become too small even at low pressures. In simpler words, the pressure correction term (a/V^2), due to the attractive forces between the molecules is always negligible. Hence, equation (2) for 1 mole becomes,

$$PV = RT + P.b$$
$$= P_iV_i + P.b$$

Therefore, there is a continuous rise in the values of PV with increase of pressure in the case of hydrogen and helium.

[IV] Modified Form of Vander Waals Equation

vander Waals equation may be written as

$$P\left(1+\frac{a}{PV^2}\right)V\left(1-\frac{b}{V}\right)=RT$$

or

$$PV\left(1+\frac{a}{PV^2}\right)\left(1-\frac{b}{V}\right)=RT$$

or

$$PV=RT\left(1+\frac{a}{PV^2}\right)^{-1}\left(1-\frac{b}{V}\right)^{-1}=RT\left(1-\frac{a}{PV^2}\right)\left(1+\frac{b}{V}\right)$$

[Neglecting higher powers]

$$=RT\left(1-\frac{b}{V}-\frac{a}{PV^2}\right)\quad\left[\text{Neglecting}\,\frac{ab}{PV^3}\right]\qquad\ldots(3)$$

We can write equation (3) on a first approximation as

$$PV=RT\left(1+\frac{Pb}{RT}-\frac{aP}{R^2T^2}\right)=RT\left[1+P\left(\frac{b}{RT}-\frac{a}{R^2T^2}\right)\right]$$

or

$$PV = RT\,(1 + X\,.\,P)$$

where

$$X=\frac{b}{RT}-\frac{a}{R^2\,T^2}=\frac{b}{RT}\cdot\left(1-\frac{a}{bRT}\right).$$

On substituting the values of a and b in terms of critical constants, *i.e.*, $a = 3P_cV_c^2$ and $b = \frac{V_c}{3}$, we get

$$X=\frac{1}{8}\cdot\frac{RT_c}{P_c}\cdot\frac{1}{RT}\cdot\left[1-\frac{27}{64}\cdot\frac{R^2\,T_c^2}{P_c}\cdot\frac{8P_c}{RT_c}\cdot\frac{1}{RT}\right]$$

$$=\frac{T_c}{8P_cT}\left[1-\frac{27}{8}\cdot\frac{T_c}{T}\right]\qquad\ldots(4)$$

[V] Methods for Calculating the Values of Vander Waals Constants

A number of methods have been given to calculate the values of vander Waals constants a and b, the principles of some of which are discussed below :

(a) From compressibility coefficient (β) : We know that

$$\beta = -\frac{1}{V}\left(\frac{\partial P}{\partial V}\right)_T$$

or
$$\left(\frac{\partial P}{\partial V}\right)_T = -\beta V$$

From vander Waals equation, we have

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

or
$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = -\beta V \qquad ...(5)$$

i.e,
$$\beta V = \frac{RT}{(V-b)^2} - \frac{2a}{V^3} \qquad ...(6)$$

Knowing the value of β, we can calculate the values of a and b by solving equations (5) and (6).

(b) From pressure coefficient (α') : We know that,

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2}$$

or
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{V-b} = \frac{1}{T}\left(P + \frac{a}{V^2}\right)$$

or
$$\frac{a}{V^2} = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Since
$$\alpha' = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad \left[\text{where } \alpha' = \frac{a}{V^2}\right]$$

$\therefore$
$$\frac{a}{V^2} = TP\left(\alpha' - \frac{1}{T}\right) \qquad ...(7)$$

From an experimental determination of α' and parameter of the system, we can calculate the value of a from equation (7).

$\because$
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

$\therefore$
$$b = V - \left\{R\Big/\left(\frac{\partial P}{\partial T}\right)_V\right\}$$

$$= V - \frac{R}{\alpha' P} \qquad ...(8)$$

From equation (8), we can easily calculate the value of b.

Problem 1. ***Show that for a vander Waals gas, the Boyle's temperature, $T_B = a/Rb$.***

Solution : Boyle's temperature is a temperature at which a gas obeys Boyle's law, *i.e.*, PV remains constant for an appreciable range of pressure from zero pressure. Mathematically, Boyle's temperature is the temperature at which,

$$\lim_{P \to 0} \left[\frac{\partial (PV)}{\partial P}\right]_T = 0$$

For n moles of a gas, vander Waals equation is

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} \text{ or } PV = \frac{nRTV}{V - nb} - \frac{n^2 a}{V}$$

$$\therefore \quad \left[\frac{\partial (PV)}{\partial P}\right]_T = \left[\frac{nRT}{V - nb} - \frac{nRTV}{(V - nb)^2} + \frac{n^2 a}{V^2}\right]\left[\frac{\partial V}{\partial P}\right]_T = 0, \text{ at Boyle's temperature.}$$

Since $\left(\frac{\partial V}{\partial P}\right)_T$ is always negative and is not equal to zero, so the expression in square bracket on the right hand side is equal to zero. Therefore,

$$\frac{nRT}{V - nb} - \frac{nRTV}{(V - nb)^2} + \frac{n^2 a}{V^2} = 0$$

or $$nRTV^2 (V - nb) - nRTV^3 + n^2 a (V - nb)^2 = 0$$

or $$n^2 a (V - nb)^2 = - nRT [V^2 (V - nb) - V^3]$$

or $$na (V - nb)^3 = - RT (V^3 - nbV^2 - V^3) = nbRTV^2$$

$$\therefore \quad RT = \frac{a}{b}\left(\frac{V - nb}{V}\right)^2 = \frac{a}{b}\left(1 - \frac{nb}{V}\right)^2$$

At Boyle's temperature, $T = T_B$

$$\therefore \quad T_B = \frac{a}{Rb}\left[1 - \frac{nb}{V}\right]^2$$

When $P \to 0$, the volume will be infinitely large, so that $\frac{nb}{V} \to 0$.

$$\therefore \quad T_B = \frac{a}{Rb}.$$

3·17 CRITICAL PHENOMENON

The deviations of various gases from the gas laws are intimately connected with the process of liquefaction of gases, as the deviations are more marked when a gas is nearing liquefaction. To determine the exact conditions required to liquefy a gas, Andrews undertook a detailed study of the effect of pressure and temperature on the volume of carbon dioxide.

Andrew's Experiment : The apparatus (Fig. 22) consists of a thick walled glass tube A ending in a capillary C at its upper end. It is filled with pure dry carbon dioxide and sealed at both the ends. The wider end is then opened under mercury so that some of it rises in the tube and encloses a column of carbon dioxide as shown at m. The tube A is enclosed in a strong metallic tube B filled with water and having a steel screw plunger S at the bottom. By screwing in the plunger, the water is compressed and the pressure is communicated to the gas. Pressures of the order of 400 atmospheres can be produced.

To find the value of the pressure, a similar tube A′ containing air above the mercury thread m is kept in a metal tube B′ having a steel screw plunger S′ at the bottom. The two metal tubes B and B′ are connected by a side tube T. By screwing in either S or S′, the pressure is communicated to both the sides. The pressure is

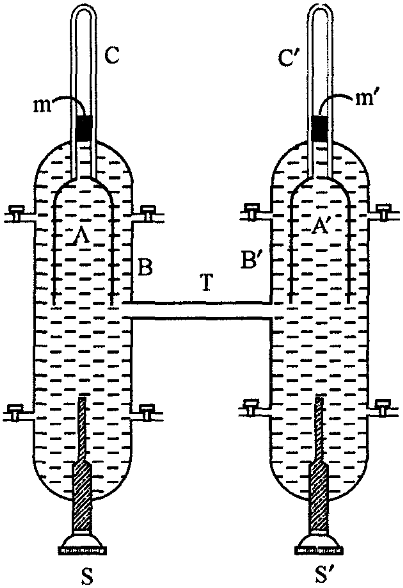


Fig. 22. Andrews apparatus

determined from the volume occupied by air for which the relation between pressure, volume and temperature is accurately known.

The capillary C containing carbon dioxide is surrounded by a bath which can be maintained at any suitable temperature. A number of observations between pressure and volume at various temperatures are taken and a number of isothermals are drawn. ***An isothermal is a curve which shows the relation between pressure and volume at constant temperature.***

In Andrew's actual experiment, isothermals were draw at temperatures 13.1°, 21.1°, 31.1° and 51.1°C, respectively as shown in figure (23). The amount of departure of any gas from being perfect can be determined by Andrew's experiment. The gas under test is put in place of carbon dioxide.

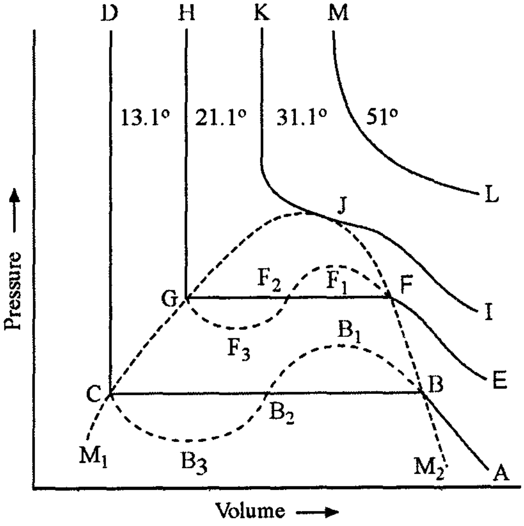


Fig. 23. Different isotherms of CO₂.

Consider the isothermal corresponding to the temperature 13.1°C. To start with, let the gas has a volume and pressure corresponding to the point A. As the pressure is increased, the volume decreases roughly according to Boyle's law upto the point B, where the gas behaves as a saturated vapour. If the pressure is increased further, the gas begins to liquefy, even if the pressure remains constant. But the volume decreases upto the point C when the whole of the gas is liquefied. Any further increase of pressure brings about a negligibly small decrease in volume as the liquids are almost incompressible. This is shown by the part CD which is straight line almost parallel to Y-axis.

The general shape of isothermal for temperatrue 21.1°C is again the same. The gas obeys Boyle's law in the portion EF which is greater than AB. From F to G, the gas behaves as saturated vapour in contact with its own liquid, the volume decreases and the pressure remains constant. From G to H it is in the liquid state and increase of pressure produces no decrease in volume. The second isothermal differs from the first in the following respects :

(i) The volume occupied by a given mass of the saturated vapour when condensation starts is smaller; (ii) The volume of the liquid when condensation is complete is larger than that in the first case and (iii) The horizontal part FG is smaller than the part BC. This shows that with rise of temperature, the density of saturated vapour increases and that of the liquid decreases.

For the isothermal at 31.1°C, the horizontal portion of the curve almost disappears. The curve shows that from I to J to L, Boyle's law is obeyed. In fact, the highest temperature at which the liquefaction occurs and isotherm shows a horizontal portion is 31.1°C. This temperature is known as ***critical temperature*** and the isothermal corresponding to it is known as ***critical isothermal***. So, 31.3°C is the critical temperature of CO_2 and IJK is the critical isothermal.

The isothermals for temperatures 51°C, much above the critical temperature do not show any horizontal portion and obey Boyle's law from one end to the other. The isothermal for 51°C is similar to the isothermal for air.

The dotted curve joining the extremities of the horizontal part of these isothermals is called the ***border curve***. Its apex J is called the ***critical point*** and it lies on the critical isothermal. The border curve M_1 J M_2 clearly indicates the different states of a substance. To the right of the border curve the substance is unsaturated vapour, within it, it is a mixture of saturated vapour and liquid and to its left it is entirely in the liquid state.

For every gas there is a critical temperature below which a gas must be cooled in order to liquefy it by means of pressure alone. At this critical temperature, the volume and density of the saturated vapour become equal to the volume and density of the liquid. It is not possible to distinguish the vapour (or gas) from the liquid.

The gas behaves almost a perfect gas above the critical temperature but shows large deviations from Boyle's law at temperatures below the critical value. The pressure necessary to liquefy a gas at the critical temperature is called the ***critical pressure*** and the volume occupied by a unit mass of a gas at critical temperature is called the ***critical volume***.

[I] Continuity of State

There exists a continuity of state between the liquid and the gaseous phases. Let us start with a given mass of the substance in the state represented by the point M_2, heat it at constant volume till the point F is reached and then cool it at constant pressure, till the point G is reached. The substance then changes from the gaseous to liquid form without the occurrence of any discontinuity.

Hence, the gaseous the liquid state may be regarded as distinct stages of a series of continuous physical changes. In other words, a gas and liquid are widely separated forms of the same condition of matter, which can be made to pass from one to the other by a series of changes so graded that no breach of continuity occurs. Thus, at high temperatures and low pressures, the substance approximates to the condition of an ideal gas obeying Boyle's law. As the temperature is lowered and the pressure increased, deviation from Boyle's law takes place. The substance slowly acquires the property of a liquid and gradually loses the properties of the gas. At sufficiently low temperature and high pressure, the substance entirely becomes a liquid.

[II] Application of Vander Waals Equation to Critical Phenomenon

For one mole of a gas, vander Waals' equation,

$$\left(P+\frac{a}{V^2}\right)V(V-b)=RT$$

may be simplified as $PV-Pb+\frac{a}{V}-\frac{ab}{V^2}-RT=0$

Multiplying throughout by V^2 and dividing by P, we get

$$V^3-bV^2+\frac{aV}{P}-\frac{ab}{P}-\frac{RTV^2}{P}=0$$

Arranging in descending powers of V, we get

$$V^3-\left(b+\frac{RT}{P}\right)V^2+\frac{aV}{P}-\frac{ab}{P}=0 \qquad \ldots (1)$$

This equation is cubic in V and as such there may be three real roots or one real and two imaginary roots of V for each value of P and T. In other words, for given values of P and T, there will be either three real values or one real and two imaginary values of V. This behaviour is not shown by isotherms of CO_2 in figure (7).

At 51^o and 31.1^o, there is only one volume for each pressure. At 12.1^o, there are two different values of V corresponding to points B and C for the same pressure. However, the third volume predicted by equation (1) is missing.

By substituting the experimental values of a and b in equation (1), Thomson (1871) calculated the values of V for different values of P and T. He plotted these calculated values of V against P and the isotherms obtained by him are shown by dotted curves in figure (23). The isotherms for temperature 31.1^o and above are exactly of the same form as obtained by Andrews. However, the theoretical isotherms below the critical temperature differ from experimental isotherms (of Andrews). They have no sharp breaks and the horizontal portions of the curves are replaced by wave like portions. For example, the experimental isotherms ABCD and EFGH are replaced by theoretical isotherms $ABB_1B_2B_3CD$ and $EFF_1F_2F_3GH$, respectively. In these, there are obviously three volumes represented by B, B_2 and C (and F, F_2 and G), corresponding to one pressure as predicted by equation (1). As the temperature rises, the wave portion of the curve becomes smaller and smaller and the three values of volume get closer and closer until they merge into one point J at 31.1° (critical temperature). At J, the three roots of V (say x, y and z) of equation (1) are identical. Since the temperature is critical, the value of V represents the critical volume of the gas, *i.e.*, $V = V_c$. The three values of V can be represented as,

$$(V-x)(V-y)(V-z)=0,$$

At critical point, $x = y = z = V_c$

$$\therefore \qquad (V-V_c)^3 = 0$$

Expanding and writing in decreasing powers of V, we get

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad \text{...(2)}$$

This equation must be identical with vander Waals' equation (1) at critical temperature and pressure, which may be written as

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \qquad \text{...(3)}$$

Since equations (2) and (3) are identical, the coefficients of equal powers of V in the two equations must be equal to one another. Therefore,

$$3V_c = b + \frac{RT_c}{P_c} \qquad \text{...(4)}$$

$$3V_c^2 = \frac{a}{P_c} \qquad \text{...(5)}$$

$$V_c^3 = \frac{ab}{P_c} \qquad \text{...(6)}$$

Dividing equation (6) by (5), we get

$$V_c = 3b \qquad \text{...(7)}$$

Substituting the values of V_C in equation (5), we get

$$P_c = \frac{a}{3V_c^2} = \frac{a}{3 \times (3b)^2} = \frac{a}{27b^2} \qquad \text{...(8)}$$

Substituting the values of P_c and V_c in equation (4), we get

$$T_c = \frac{8}{3} \cdot \frac{P_cV_c}{R} = \frac{8}{3} \cdot \frac{(a/27b^2) \times 3b}{R}$$

or

$$T_c = \frac{8a}{27bR} \qquad \text{...(9)}$$

From equations (7), (8) and (9), we can calculate the values of a, b and R in terms of critical constants. We thus have

$$b = \frac{V_c}{3} \qquad \text{...(10)}$$

$$a = 3P_c V_c^2 \qquad \text{...(11)}$$

$$R = \frac{8}{3} \cdot \frac{P_c V_c}{T_c} \qquad \text{...(12)}$$

From equation (12), we have

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.66$$

The ratio $\frac{RT_c}{P_c V_c}$ often called the critical coefficient is constant.

Problem 1. ***If vander Waals equation of a gas is given by***

$$\left(P + \frac{0.00786}{V^2}\right)(V - 0.00224) = 0.0041\ (273.16 + t),$$

calculate the values of T_c and P_c of the gas.

Solution. From the given question, we can compute that : $a = 0.00786$, $b = 0.00224$, $R = 0.0041$, $T = (273.16 + t)$.

Now $$P_c = \frac{a}{27b^2} = \frac{0.00786}{27 \times (0.00224)^2} = \mathbf{0.7382\ atm}$$

$$T_C = \frac{8a}{27R\,b} = \frac{8 \times 0.00786}{27 \times 0.0041 \times 0.00224}$$

or $$T_C = \mathbf{25.36\ K}$$

Problem 2. ***Two moles of CO_2 at 27°C is filled in a five litre flask. Calculate its pressure using the following : (1) Ideal gas equation (ii) vander Waals equation***

For CO_2 : $a = 3.6$ atm lit^2 mole^{-2}, $b = 4.28 \times 10^{-2}$ lit mole^{-1}, $R = 0.082$ lit atm deg^{-1} mole^{-1}.

Solution. (i) *Pressure from ideal gas equation*

$$PV = nRT \text{ or } P = \frac{nRT}{V}$$

$$\therefore \qquad P = \frac{2 \times 0.082 \times 300}{5} = \mathbf{9.84\ atm.}$$

(ii) *Pressure from vander Waals equation*

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

or $$\left(P + \frac{4 \times 3.6}{25}\right)(5 - 0.0428 \times 2) = 2 \times 0.082 \times 300$$

On solving, $P = \mathbf{9.43\ atm.}$

[IV] Experimental Determination of Critical Constants

(i) *Critical temperature and pressure* : These values can be determined by a simple method which is based on the principle that at the critical temperature, the surface of separation, *i.e.*, meniscus between the liquid and the vapour phase disappears. It is generally used when the substance is in liquid state at ordinary temperatures.

The experimental liquid is taken in a vessel V enclosed in a glass jacket J [Fig. (24)]. The temperature of J can be varied gradually by circulating a suitable liquid from a thermostat. The vessel V is connected to a mercury manometer M containing air. The temperature is first lowered so that the vessel is cooled and the surface of separation between the liquid and its vapour becomes sharp. The temperature of the jacket is raised slowly. This rise is continued till the meniscus between the liquid and its vapour just disappears. This temperature say t_1° is noted. The jacket is then cooled slowly till cloudiness due to the condensation of vapours appears again. This temperature t_2° is again noted. The ***critical temperature*** will thus be $\left(\frac{t_1+t_2}{2}\right)$.

The mean of the pressures read from the manometer M, corresponding to temperatures t_1° and t_2° ; gives the value of ***critical pressure.***

(ii) Critical volume : The determination of V_c takes the advantage of the observations made by Calliatet and Mathias that when mean values of the densities of liquid and saturated vapour of a substance are plotted against the corresponding temperatures, a straight line is obtained.

In figure (25), the curves VC and LC show the plots of the densities of saturated vapours and those of liquid against the corresponding temperatures. The point C, where the two curves meet gives the *critical temperature.* This point is not sharp as the curve in this range is rather flat. Therefore, the mean densities are then plotted against different temperatures when a straight line MC is obtained. The point C where this line cuts the curve VCL, gives the critical temperature as the density of the liquid now becomes identical with that of vapour. The point C gives the critical density of the substance. The ***critical volume*** is obtained by dividing the molecular weight of the substance by the critical density.

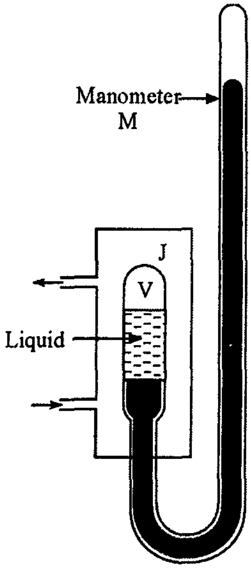


Fig. 24

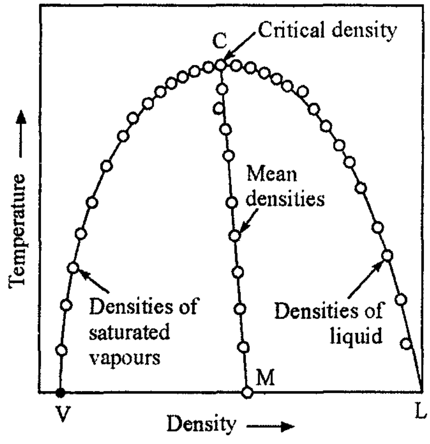


Fig. 25

3·17 LAW OF CORRESPONDING STATES

An equation which expresses the relation between pressure, volume and temperature of a gas is called *the equation of state* or *the characteristic equation*. If we express the actual pressure, volume and temperature as fractions of the critical pressure, volume and temperature, respectively, we get the reduced equation of state.

To get the reduced equation of state from vander Waals equation, assume that

$$\pi = \frac{P}{P_c};\ \phi = \frac{V}{V_c};\ \theta = \frac{T}{T_c}$$

where π, ϕ and θ are known as ***reduced pressure, reduced volume*** and ***reduced temperature,*** respectively.

Substituting the values of P, V and T in vander Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT,$$

we get

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi\, V_c - b) = R\theta T_c$$

Substituting the values of critical constant P_c, V_c and T_c (derived earlier), we get

$$\left\{\pi \,.\, \frac{a}{27b^2} + \frac{a}{\phi^2 (3b)^2}\right\}(\phi \,.\, 3b - b) = R\theta \,.\, \frac{8a}{27b.R}$$

or

$$\left(\pi + \frac{3}{\phi^2}\right) = (3\phi - 1) = 8\theta \qquad ...(1)$$

Equation (1) in terms of the reduced parameter of the system is called the *vander Waals reduced equation of state.* It is applicable to all gases and is independent of the constants a, b and R.

According to equation (1), *if two gases have the same reduced pressure and are also at the same reduced temperature, then their reduced volumes should be the same.* Gases or substances under such conditions are said to be in ***corresponding states*** and the principle is called the ***law of corresponding states.***

[I] Tests of Law of Corresponding States

Equation (1) can be written as

$$\pi = \frac{8\theta}{3\phi - 1} - \frac{3}{\phi^2}$$

At constant reduced volume, *i.e.,* ϕ = constant, there is a linear relationship between π and θ, as clear from the above relation. This shows that π, ϕ and θ are related in the same way for all gases in corresponding states as P, V and T in case of ideal gases.

When compressibility $\beta = PV/RT$ is plotted against reduced pressure, π for different gases studied at the same reduced temperature, the values for different gases lie more or less on the same curve. This shows that all gases, in corresponding states deviate almost equally from ideal behaviour.

The reduced equation of state helps us to test the validity of vander Waals equation, by maintaining a number of gases at the same π and θ and then finding whether ϕ is also the same. It has been, however, observed that the law of corresponding states is approximately obeyed. In other words, vander Waals equation is not quantitatively valid and it is only an aproximate equation.

3·18 OTHER EQUATIONS OF STATE

[I] The Dieterici Equation

Dieterici proposed the following equation of state :

$$P = \frac{RT}{V-b} \cdot e^{-a/RTV}$$

The volume correction introduced by Dieterici (1897) was the same as introduced by vander Waals. The pressure correction was introduced by Jeans who stated that a molecule coming to the wall of the vessel from its interior overcomes a certain force of attraction and so attains a potential energy higher than that occupied by a molecule in the bulk. Thus, the density of molecules near the walls will be less than that in the interior. Let n and n_0 represent the number of molecules per c.c. at the walls and in the interior, then according to Maxwell's distribution law, we have,

$$\frac{n}{n_0} = e^{-A/RT}$$

where A represents the excess energy per g mole at the walls.

If d and d_0 and P and P_0 be the densities and pressures of the gas at the walls and in the interior, respectively then

$$\frac{n}{n_0} = \frac{d}{d_0} = \frac{P}{P_0}$$

$$\therefore \qquad \frac{P}{P_0} = e^{-A/RT}$$

or

$$P_0 = P \cdot e^{A/RT}$$

The pressure P_0 in the interior is the ideal pressure, as all the attractive forces cancel each other. So, introducing the pressure correction in $PV = RT$, we get

$$P \cdot e^{A/RT}(V-b) = RT$$

$$P = \frac{RT}{V-b} \cdot e^{-A/RT}$$

Jeans found that A depends upon volume as observed, so we can write Dieterici's equation of state as

$$P \cdot e^{a/RTV}(V-b) = RT \quad (\because A = a/V)$$

or

$$P = \frac{RT}{V-b} \cdot e^{-a/RTV} \qquad \ldots(1)$$

Equation (1) is known as ***Dieterici's equation.***

On expansion of equation (1), we get $P = \frac{RT}{V-b}\left[1 - \frac{a}{RTV} + \frac{1}{2}\left(\frac{a}{RTV}\right)^2 + \ldots\right]$

Neglecting higher powers, we get $P = \frac{RT}{V-b} - \frac{a}{V(V-b)}$

At low pressures, the value of V is very large and $(V-b)$ is approximately equal to V, so

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \text{ or } \left(P + \frac{a}{V^2}\right)(V-b) = RT$$

This is vander Walls equation. Thus, at low pressures, the two equations would respond to the same extent.

Dieterici's Reduced Equation of State : By introducing the concept of reduced pressure, volume and temperature in Dieterici's equation (1), we get

$$\pi P_c = \frac{R\theta\, T_c}{\phi\, V_c - b} .6e^{-a/R\theta T_c \,.\, \phi\, V_c}$$

Substituting the values of critical constants, *i.e.*,

$$V_c = 2b; P_c = \frac{a}{4b^2} \,.\, e^{-2}; T_c = \frac{a}{4bR},$$

In the above equation, we get $\pi e^{-2} = \frac{\theta}{2\phi - 1} \,.\, e^{-2/(\theta\phi)}$

or $$\pi\,(2\phi - 1) = \theta \,.\, e^{2 - [2/(\theta\phi)]} \qquad \text{...(2)}$$

Equation (2) is required Dieterici's reduced equation of state.

(II) The Berthelot Equation

Berthelot (1898) introduced the same volume correction as in vander Waals equation, but the pressure correction was different. He introduced the correction as a/TV^2 in place of a/V^2. So, the required equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or $$PV = RT + Pb - \frac{a}{TV} + \frac{ab}{TV^2} \approx RT + Pb - \frac{aP}{RT^2}$$

$$\left(\text{Neglecting } \frac{ab}{TV^2} \text{ and assuming } V = \frac{RT}{P}\right)$$

$$\therefore \qquad PV = RT\left[1 + \frac{Pb}{RT} - \frac{aP}{R^2T^3}\right] = RT\left[1 + \frac{P}{T}\left(\frac{b}{R} - \frac{a}{R^2T^2}\right)\right] \qquad \text{...(3)}$$

Berthelot accepted the experimental values for a, b and R as follows :

$$b = \frac{V_c}{4}\,;\; a = \frac{16}{3} P_c V_c^2 T_c\,; \quad \text{and } R = \frac{32}{9}\frac{P_c V_c}{T_c}$$

Substituting the values of a, b and R in equation (3), we get

$$PV = RT\left[1 + \frac{P}{T}\left(\frac{V_c}{4} \cdot \frac{9T_c}{32P_c V_c} - \frac{16}{3} P_c T_c V_c^2 \frac{81T_c^2}{(32P_c V_c)^2} \cdot \frac{1}{T^2}\right)\right]$$

or $$PV = RT\left[1 + \frac{9}{128} \cdot \frac{PT_c}{TP_c}\left(1 - \frac{6T_c^2}{T^2}\right)\right] \qquad \text{... (4)}$$

Equation (4) has been found to be useful in the calculation of densities, heat capacities and free energy changes etc.

On differentiating equation (4) with respect to P, we get

$$\frac{d\,(PV)}{dP} = RT \,.\, \frac{9}{128} \cdot \frac{T_c}{TP_c}\left(1 - \frac{6T_c^2}{T^2}\right) \qquad \text{... (5)}$$

At Boyle's point, *i.e.*, T_B, $\frac{d\,(PV)}{dT} = 0$. So, equation (5) becomes

$$\frac{T_c^2}{T_B^2} = \frac{1}{6} \quad \text{or} \quad \frac{T_B}{T_C} = \sqrt{6} = 2.45$$

The value of 2.45 is less than the experimental results.

Reduced Berthelot equation. From equation (4),

$$PV = RT\left[1 + \frac{9}{128} \cdot \frac{PT_c}{TP_c}\left(1 - \frac{6T_c^2}{T^2}\right)\right]$$

or
$$\pi\,\phi \,.\, P_c\,V_c = R\theta T_c\left[1 + \frac{9}{128} \cdot \frac{\pi}{\theta}\left(1 - \frac{6}{\theta^2}\right)\right]$$

or
$$\pi\,\phi = \theta \,.\, \frac{RT_c}{P_cV_c}\left[1 + \frac{9}{128} \cdot \frac{\pi}{\theta}\left(1 - \frac{6}{\theta^2}\right)\right]$$

or
$$\pi\,\phi = \left[\frac{32\theta}{9} + \frac{\pi}{4}\left(1 - \frac{6}{\theta^2}\right)\right] \qquad \dots (6)$$

Equation (6) is known as reduced form of Berthelot's equation.

(III) The Kammerling Onnes Equation

Onnes gave a general and more satisfactory equation of state. He expressed the product PV as a power series in $1/V$ as shown below :

$$PV = RT\left[1 + \frac{B_2(T)}{V} + \frac{B_3(T)}{V^4} + \frac{B_4(T)}{V^3} + \dots\right]$$

where $B_2(T), B_3(T), B_4(T)$ ... are called the first, second, third, fourth, etc. virial coefficients, respectively. These coefficients are constant at constant temperature. The virial equation can also be expressed as a power series in pressure, as shown below :

$$PV = RT\;[1 + A_2(T)\,P + A_3(T)\,P^2 + A_4(T)\,P^3 + \dots]$$

where $A_2(T), A_3(T), A_4(T)$, etc. are new temperature dependent virial coefficients. At low pressures, only the first virial coefficient ($= RT$) is important. It is always positive. It increases with rise in temperature. The second virial coefficient is negative at low temperatures, becomes zero at a particular temperature and then becomes increasingly positive as temperature is continuously increased.

The temperature at which second virial coefficient disappears is known as ***Boyle's temperature*** (T_B). At this temperature while second virial coefficient disappears, the third, fourth and higher virial coefficients become insignificant. At this temperature, PV becomes almost equal to RT. So, at ***Boyle's temperature, the gas behaves ideally over an appreciable range of pressure***.

Holborn used a virial equation in which the value of PV is expressed in terms of power series of pressure, *i.e.*,

$$PV = A_1 + B_1P + C_1P^2 + D_1P^3 + E_1P^4 + \dots$$

We thus have, $A = A_1 = RT$. In these equations, the second virial coefficient is of great importance, whereas the higher virial coefficient become significant only at high pressures.

3·19 LIQUEFACTION OF GASES

It was observed that substances which were gaseous at ordinary temperatures could be converted into liquid state if sufficiently cooled and simulatenously subjected to a high pressure. Faraday (1825) attempted to liquefy certain gases and was successful in his attempt in liquefying ammonia, chlorine, carbon dioxide and sulphur dioxide. But attempts to liquefy, nitrogen and hydrogen failed and thus these gases were termed a ***permanent gases***.

[I] Liquefaction of Chlorine

The apparatus employed is shown in figure (26). It consists of a strong V-shaped glass tube closed at both the ends. One end of the bent glass tube contains crystals of chlorine hydrate, while the other end is immersed in a freezing mixture. On heating the end containing chlorine hydrate, chlorine is evolved in large quantities and a high pressure is developed. When cooling is caused by the freezing mixture, it is liquefied into an oily liquid under its own pressure.

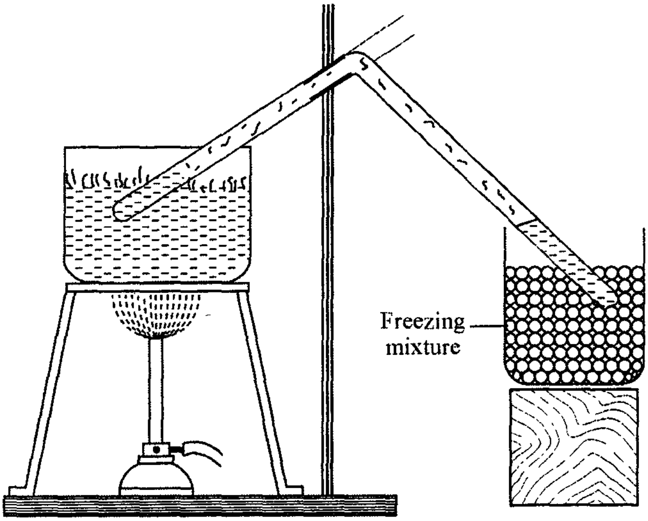


Fig. 26.

[II] Liquefaction of Carbon Dioxide

The above method is used for the liquefaction of carbon dioxide also. A strong cylinder is filled one-third with sodium bicarbonate. An open copper tube containing sulphuric acid is introduced and the apparatus is fitted as shown above. When the cylinder is inverted, the acid reacts with sodium bicarbonate and carbon dioxide under pressure. The pressure produced in this way is of the order of 50–80 atmospheres and hence the gas is liquefied and distils over the other end. If liquid carbon dioxide is allowed to escape through a jet, solid carbon dioxide is produced.

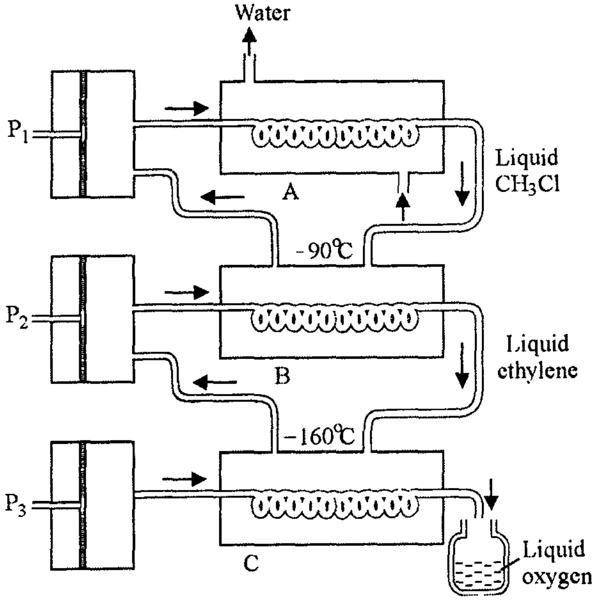


Fig. 27.

[III] Liquefaction of Oxygen

It was found that even gases like oxygen, nitrogen, hydrogen, carbon monoxide, etc., when subjected to a pressure of 3000 atmospheres, could not be liquefied. The cause of these failures was explained by Andrew's discovery of critical temperature for various gases. It was shown that every gas when it is above a certain temperature (*called critical temperature*) cannnot be liquefied, however, high pressure it may be subjected to. It was found that the critical temperature of oxygen is –148°C. Oxygen, therefore, must be cooled to a temperature below this particular temperature if it were to be liquefied. The apparatus used by Kammerlingh-Onnes is shown in figure (27).

It consists of three compressor machines A, B and C worked by three pumps P_1, P_2 and P_3, respectively. Machine A is used to liquefy methyl chloride (CH_3Cl) whose critical temperature is 143°C. Hence, it can be liquefied by a pressure of a few atmospheres at the room temperature by making it to flow through a spiral surrounded by water jacket. Liquid methyl chloride is made to flow round a spiral in B which is connected to the suction side of the compressor P_1. Liquid methyl chloride evaporates in B under reduced pressure and thus results in a fall of temperature to about –90°C in this chamber.

Inside the jacket B is placed a condenser coil through which ethylene passes from the compressor P_2 and is cooled to –90°C. It is liquefied as its critical temperature is 9.5°C. Liquid ethylene is then made to flow round the spiral in C and is allowed to evaporate under reduced pressure by connecting it to the suction side of the compressor P_2. The temperature falls to about –160°C which is well below the critical temperature of oxygen.

Through the spiral in C, oxygen passes under pressure, which gets liquefied and is collected in the vacuum flask. The lowest temperature attained by boiling liquid oxygen under reduced pressure is –218°C.

[IV] Liquefaction of Air (Linde's Method)

Linde and Hampson (1895) used Joule-Thomson effect and the principle of regenerative cooling in the liquefaction of air. This principle consists in cooling the incoming gas by the gas which has already undergone cooling due to Joule-Thomson effect. By maintaining a continuous cycle of operation, the initial temperature can be progressively lowered whereby the cooling effect is enormously enhanced.

The apparatus employed by Linde for liquefaction of air is shown in Fig. (28). It consists of two stage compressors P_1 and P_2. The compressor P_1 compresses the incoming air to a pressure of 20 atmospheres. The compressed air is then cooled by passing it through the water bath. It is then led through a caustic soda bath to free it from carbon dioxide. It this is not done, carbon dioxide solidifies and chokes the valves.

The gas then enters the compressor P_2 where it is compressed to a pressure of about 200 atmospheres. The compressed air is then passed through a cooling coil kept immersed in a freezing mixture so that the gas attains a temperature of about –20°C. The cooled air under a pressure of 200 atmospheres is passed through the inner pipe and suffers Joule-Thomson expansion at a throttle valve V_1 which can be operated by means of a handle. During the course of this expansion, the pressure

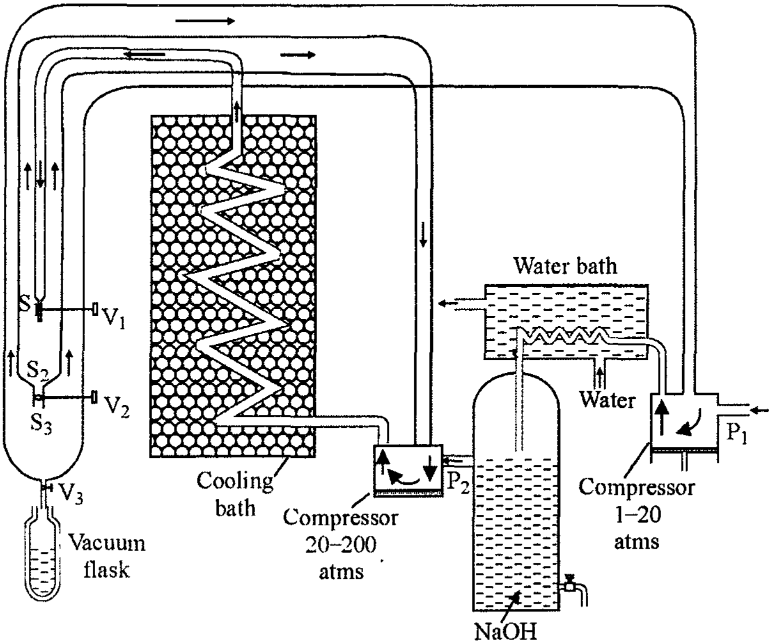


Fig. 28. Linde's apparatus.

is suddenly lowered to 20 atmospheres and this causes the temperature to fall to about –78°C. The cooled air is then made to flow through the outer coil S_1 which cools the air flowing through the inner pipe and finally returns back to the compressor P_2 where it is again compressed to a pressure of 200 atmospheres. It is again circulated through the inner pipe.

After the completion of a few cycles, the temperature of the gas falls sufficiently low and the second throttle valve V_2 is opened. The air is allowed to expand to a pressure of one atmosphere when it becomes liquid and is collected in the vacuum flask through the valve V_3. The unliquefied gas is again led back through the outermost coil S_3 back to the compressor P_1 as shown by the arrow heads. The cycle is repeated till the air begins to liquefy.

[V] Liquefaction of Hydrogen

Hydrogen at ordinary temperature shows a heating effect on throttle expansion. Its inversion temperature is –80°C, but for practical purposes a temperature below –177°C is essential to get appreciable cooling. This temperature

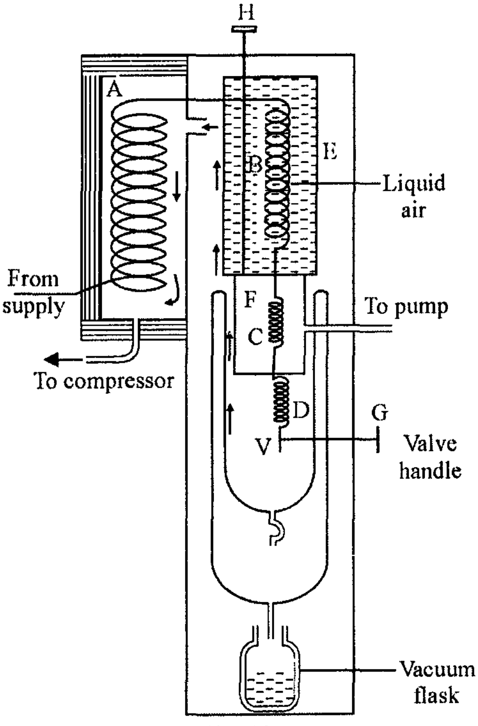


Fig. 29.

can be attained by immersing the apparatus in liquid air. The apparatus is shown in Fig. (29).

Hydrogen is compressed to about 150 atmospheres. It is then passed through coils immersed in water to get rid of the heat produced due to compression. It is freed from carbon dioxide and moisture by passing through caustic potash and anhydrous calcium chloride. The gas now enters the apparatus and is allowed to flow through the regenerative coil A which is cooled by the returning hydrogen gas from the expansion chamber. The temperature after a few cycles is about –170°C. The cooled gas then passes through the coil B (immersed in liquid air) and then through another coil C immersed in liquid air boiling at a pressure of 100 mms. This is done by a handle H which makes the liquid air from the chamber E to trickle into the chamber F which is exhausted to a pressure of 100 mms. by an exhaust pump. In this chamber, the temperature of hydrogen falls to –200°C. The gas then passes through the coil D and suffers Joule-Thomson expansion at V. The cooled gas passes round the chambers D, C, B and then A before entering the compressor where it is compressed again. After a few cycles, the temperature of a gas falls to –250°C in the coil D which on suffering Joule-Thomson expansion, is liquefied and collected in the vacuum flask as shown. Liquid hydrogen boils at –252.78°C under atmospheric pressure. By causing it to boil under reduced pressure it can be solidified to a white solid.

[VI] Liquefaction of Helium

Helium was liquefied by Onnes in 1908. The inversion temperature of helium is 35 K and for practical reasons the gas must be cooled to 17 K in order to obtain cooling by the throttle expansion. The temperature was obtained by Onnes by using liquid hydrogen in place of liquid oxygen in the apparatus discussed as in liquefaction of hydrogen. Onnes obtained the temperature of about 17 K by boiling hydrogen under a reduced pressure. In 1926, Keesom succeded in obtaining solid helium. It was found that helium solidified at 4.2 K under a pressure of 140 atmospheres and at a temperature of 1.1 K under a pressure of 23 atmospheres.

[VII] Production of Low Temperatures

A number of methods have been given for producing low temperatures, some of which are as follows :

(a) Freezing mixtures : Temperatures much below 0°C can be achieved by mixing ice with suitable salts. For example, ice and common salt in suitable proportions produce a temperature of –2°C. A mixture of ice and calcium chloride produce as low a temperature as –55°C.

When ice is mixed with common salt, some of the ice melts in cooling the salts to its own temperature and then produces a saturated solution of the salt at 0°C. Now ice cannot remain in equilibrium with this solution at 0°C and more of it melts, the temperature of which further goes down.

(b) Cooling due to evaporation : Evaporation causes cooling because when a liquid evaporates, it takes up latent heat either from the liquid itself or from the surrounding vessel. The rapid evaporation of liquid ammonia under reduced pressure has been used in the ice plants and in the refrigerators.

(c) Liquefaction of gases : The production of low temperatures by liquefaction of gases may be broadly grouped under three heads :

(i) ***By cooling and applying a high pressure*** : Whenever a gas is cooled below the critical temperature and then compressed, it liquefies. The liquefaction of chlorine and carbon dioxide has been done by this method.

(ii) ***Cascade process*** : This process utilises a series of liquids with successively lower boiling points to reach the low temperatures in stages. The liquefaction of oxygen is the best example. In this method, methyl chloride is liquefied at ordinary temperatures which is then made to evaporate under low pressure. It cools and produces a temperature as low as –90°C. This low temperature is utilised to liquefy ethylene under pressure. But when ethylene is made to boil under reduced pressure, a temperature of –160°C is produced. Oxygen under pressure liquefies at this temperature and if made to evaporate under reduced pressure gives rise to a temperature of –218°C.

(iii) ***Joule-Thomson effect and regenerative cooling*** : The English physicists James Joule and William Thomson (later Lord Kelvin) observed that when a gas under high pressure is allowed to expand into a region of low pressure, it suffers a fall in temperature. This phenomenon is known as the ***Joule-Thomson effect***.

The Joule-Thomson effect offers support to the view that attractive forces do exist between gas molecules. As the gas expands, the molecules move farther apart from each other. So, work has to be done in order to overcome the cohesive or attractive forces which tend to hold the molecules together. Therefore, work is done by the system at the expense of the kinetic energy of the gaseous molecules. Thus, the kinetic energy decreases and since this is proportional to temperature, cooling results. It is to be observed that in this case no external work has been done by the gas during expansion.

Experiments have shown that gases become cooler during the Joule-Thomson expansion only if they are below a certain temperature, known as ***inversion temperature***, T_i. The inversion temperature is characteristic of each gas. This temperature is related to vander Waals constants (a, b) of the gas by the following equation :

$$T_i = \frac{2a}{Rb}$$

At the inversion temperature, there is no Joule-Thomson effect. So, if a gas under pressure is allowed to pass through a porous plug and expands adiabatically into a region of very low pressure at the inversion temperature, there is neither a fall nor rise in temperature. If, however, the expansion occurs below the inversion temperature there is a small fall of temperature and if it occurs above the inversion temperature, there is a small rise of temperature.

In most gases, the inversion temperature lies within the range of ordinary temperatures, hence they get cooled during the Joule-Thomson expansion.

To cool air by Joule-Thomson effect, its temperature is reduced to 253 K by passing it through a freezing mixture. As the inversion temperature of hydrogen is 193 K it has to be cooled to 73 K for practical purposes. This is done by passing it through liquid air boiling under reduced pressure. The lowest temperature thus attained is 20.2 K which is the boiling point of hydrogen at atmospheric pressure.

The inversion temperature for helium is 35 K. Hence, the liquefaction of helium was achieved by first cooling it to a temperature of 17 K by allowing hydrogen to boil under reduced pressure, and then subjecting it to Joule-Thomson effect. Solid helium has a temperature of 42 K.

(d) Adiabatic expansion process : Whenever a gas is allowed to expand adiabatically, it does work at the cost of the internal heat energy and is, therefore, cooled considerably. This method was used by Cailletet (1877) to liquefy oxygen. Oxygen was compressed to a pressure of 300 atmospheres in a strong capillary tube cooled to –29°C by liquid sulphur dioxide boiling under reduced pressure. When the pressure was suddenly removed, oxygen was found to be in the liquid state. Pictet even obtained solid oxygen by the same method, *i.e.*, by compressing the gas to 5.0 atmospheres and cooling it to –130°C by liquid carbon dioxide boiling under reduced pressure. Similarly, by cooling compressed hydrogen with liquid oxygen and then suddenly removing the pressure, even hydrogen was liquefied.

The process though more efficient than Joule-Thomson cooling ($\eta = 15\%$) has not been developed on a commercial basis as it is not a continuous process. Moreover, there is difficulty in obtaining a lubricant which could be used in the moving parts of the compressor because most of the lubricants solidify at the low temperatures involved.

(e) Paramagnetic cooling : It was shown by Debye on theoretical grounds that a very close approach to absolute zero was possible by adiabatic demagnetisation of a paramagnetic salt. When a paramagnetic substance is magnetised, external work is done on it and its temperature rises. But when it is demagnetised, external work is done by it and the temperature falls. This is known as ***magnetocaloric effect***. As the paramagnetic susceptibility, κ, of a substance varies inversely as the absolute temperatrue, *i.e.*, $\kappa \propto 1/T$ (Curie's law), the value of κ becomes very large as the absolute zero is approached and the magnetocaloric effect is very much pronounced.

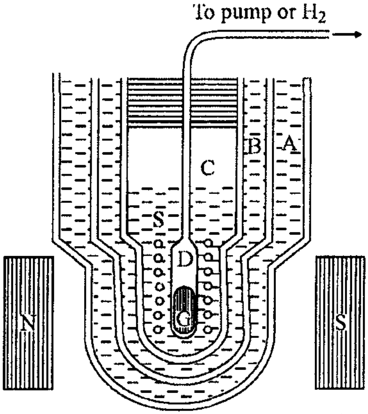


Fig. 30. Adiabatic demagnetisation.

The experimental set up for adiabatic demagnetisation is shown in figure (30). It consists of three double walled Dewar flasks. The outermost flask A contains liquid air, the middle flask B liquid hydrogen and the inner most flask C contains liquid helium placed within the pole pieces NS of an electromagnet. The paramagnetic substance gadolinium sulphate is taken in the form of a sphere or an ellipsoid of compressed power and placed within the tube D suspended in liquid helium as shown. A magnetic field of the order of 10,000 oersteds is switched on when the specimen G is magnetised. The heat produced due to magnetisation is removed by introducing hydrogen into the tube D and then pumping it out by a vacuum pump, thus thermally insulating the specimen. The specimen, therefore, attains the temperature of liquid helium in the magnetised state. The magnetic field is now switched off, the salt gets demagnetised adiabatically and the temperature falls.

The temperature can be measured by fitting a coil S round the tube D and with its help the susceptibility of the salt is measured before and after the experiment. If κ_1 and κ_2 are the susceptibilities and T_1 and T_2 the absolute temperatures, before and after the experiment, then according to Curie's law,

$$\frac{T_2}{T_1} = \frac{\kappa_1}{\kappa_2}$$

$$T_2 = \frac{\kappa_1}{\kappa_2} \cdot T_1$$

In this way, a temperature of the order of 0.002 K has been attained.

EXERCISES

[I] Long Answer or Essay Type Questions

1. Write a short account of kinetic theory of gases. Derive the kinetic equation of gases.
2. Derive the equation $PV = RT$ from kinetic considerations. Show how the various gas laws are consistent with it ?
3. From kinetic equation calculate the ratio of specific heat at constant pressure to specific heat at constant volume in case of gases. How does this ratio differ with molecular complexity of the gas ?
4. Explain the distribution of molecular velocities. How would you verify the distribution of molecular velocities experimentally ?
5. Derive the terms average velocity, root mean square velocity and most probable velocity of molecules and derive a relation for each. How is RMS velocity determined ?
6. What are the limitations of the equation $PV = RT$? Show in what aspects vander Waals equation is an improvement over the simple gas equation ? Derive the vander Waals equation and discuss it.
7. (a) What do you understand by critical constants ? How are they calculated in terms of vander Waals constants and determined experimentally ?
   (b) Explain the physical significance of vander Waals constants '*a*' and '*b*'.
   (c) What do you understand by continuity of state ? Explain with the help of isotherms of carbon dioxide.
8. Write short notes on the following :
   (i) Other equations of state
   (ii) Law of corresponding states
   (iii) Mean free path
   (iv) Collision number and collision frequency
   (v) Collision diameter.
9. Discuss vander Waals equation for real gases. Deduce the relationship between the value of critical constants of a gas and vander Waals constants.

[II] Short Answer and Very Short Answer Type Questions

1. Describe : Boyles law, Charles' law Graham's law based on the kinetic theory of gas equation.
2. State the law of corresponding states. Write the equations for the critical constant of a gas in terms of its vander Waals' constants.
3. Define the terms critical temperature, critical volume and critical pressure.

4. Deduce the critical constants of a gas in terms of vander Waals constants.
5. What is the principle of equipartition of energy ? Explain how this principle helps in estimating the energy of different types of molecules.
6. Calculate the kinetic energy of an ideal gas from kinetic equation of gases.
7. Why does value of C_p differ from C_v ?
8. Derive $C_p - C_v = R$ for an ideal gas.
9. Write the differences between a real and an ideal gas.
10. Write briefly about mean free path.
11. Write vander Waals equation in terms of reduced parameters.
12. Derive Dieterici equation of state.
13. Derive Berthelot's equation of state.
14. Derive Boyle's law from kinetic gas equation.
15. Comment on the statement, 'mean free path depends on collision frequency and molecular size'.
16. What is the cause of gas pressure ?
17. Give the law of equipartition of energies.
18. Write the law of corresponding states.
19. Define mean free path of gas molecules.
20. Explain Joule-Thomson effect.
21. Define inversion temperature.
22. What is Boyle's temperature.

[III] Numerical Problems

1. What is the average kinetic energy of one mole of nitrogen oxide at 300 K in kJ ?
2. At what temperature will the average speed of a gas molecule be double its value at 273 K ?
3. At what temperature would the hydrogen gas molecules have the same average speed as helium atoms at 300 K ?
4. A gas at 1.2 atmosphere pressure has a density 1.21 g/L. Calculate the RMS velocity of the gas molecules.
5. Calculate the critical temperature of a vander Waals gas for which $P_C = 100$ atm and $b = 50$ lit mol^{-1}.
6. Using vander Waals equation, calculate the pressure exerted by one mole of CO_2 when it occupies a volume of 0.05 litre at 100°C, given that $a = 3.593$ lit^2 atm mol^{-2}, $b = 0.04267$ lit mol^{-2} and $R = 0.0821$ lit atm K^{-1} mol^{-1}.
7. Calculate the temperature at which 10 moles of CO_2 occupies a volume of 5 litres under a pressure of 50 atm. The values of 'a' and 'b' are 3.592 lit^2 atm mol^{-2} and 0.04267 lit mol^{-1}.
8. Calculate the mean free path of O_2 gas at 25°C and 1 atm pressure. Collision diameter, $\sigma = 3.61$ Å.
9. Calculate the critical temperature of n-hexane, if its boiling point is 68.9°C.
10. Calculate the Boyle temperature, T_B for CO_2 gas assuming it to be a vander Waals gas ($a = 3.59$ lit^2 atm mol^{-2}, $b = 0.0427$ lit mol^{-1})
11. For NO gas, vander Waals constant, $b = 0.02788$ lit mol^{-1}, calculate the diameter of NO molecule.

12. For hydrogen, the vander Waals constants 'a' and 'b' are 0.246 and 2.67×10^{-2} in litre-atm units. Calculate the inversion temperature for hydrogen.

13. Calculate the ratio of rms velocities of neon (at. wt. = 20) and helium (at. wt. = 4) at 0°C.

14. The specific heat of a gas at constant volume is 0.075 cal. The molecular weight of the gas is 40. Find out the atomicity of the gas.

15. Calculate the kinetic energy of two moles of CO_2 at 300 K, assuming it to be an ideal gas.

16. Calculate the rms velocity of O_2 molecules at 27°C and 740 mm pressure.

17. At what temperature will the RMS velocity of nitrogen be the same as that of oxygen at 27°C ?

18. The specific heats of a gas at constant pressure and constant volume are 0.125 and 0.075 cal., respectively. Calculate the molecular weight of the gas.

19. One mole of NH_3 is enclosed in a five litre flask at 27°C. Calculate the pressure of NH_3, $a = 4.17$ atm. lit^2 mol^{-2} and $b = 0.0371$ lit mol^{-1}.

20. The vander Waals constants in lit. atm/mole of CO_2 are : $a = 3.6, b = 4.28 \times 10^{-2}$. Calculate T_c and V_c for the gas.

21. The specific heats of a gas at constant volume and constant pressure are 0.090 and 0.45 calories. If the atomic weight of the gas be M, calculate its molecular weight.

22. Calculate the vander Waals constants a and b, if $T_c = 31°C, P_c = 72.8$ atm. and $R = 0.0821$ lit atm/deg.

23. If vander Waals equation of a gas is given by $\left(P + \frac{0.00786}{V^2}\right)(V - 0.00224) = 0.0041$ $(273.16 + t)$ calculate the values of T_c and P_c of the gas.

24. 0.5 mole of CO_2 was filled in a vessel of volume 0.6 litre at 47°C. What pressure would be expected on the basis of vander Waals equation ? ($a = 3.36, b = 4.27 \times 10^{-2}$; $R = 0.082$, all values in lit atm units).

25. For CO_2 gas, $T_c = 304.2$ K and critical density is 0.45 g cm^{-3}. Calculate the vander Waals constants for CO_2. (**Hint** : First determine $(V_m)_C$, *i.e.*, Volume = Mass/density; molecular weight of CO_2 = 44).

26. Assuming that ethane obeys Dieterici equation of state, calculate the pressure exerted by 10 moles of this gas in a volume of 4.86 dm^3 at 300 K. The constants are : $a = 6.97$ dm^6 atm mol^{-2}, $b = 0.0694$ dm^3 mol^{-1}.

27. Calculate the Boyle's temperature for O_2, for which $a = 1.36$ dm^6 atm mol^{-2},. $b = 0.0318$ dm^3 mol^{-1}.

[IV] Multiple Choice Questions

1. The temperature at which the second virial coefficient of a real gas is zero is called :
(a) Critical temperature
(b) Eutectic point
(c) Boyle temperature
(d) Boiling point

2. The virial equation of state of a real gas is :
(a) $PV = RT + \frac{B}{V} + \frac{C}{V^2} + \ldots$
(b) $PV = RT + CP + DP^2 + \ldots$
(c) $PV = RT + RT^2 + RT^3 + \ldots$
(d) $PV = RT + B'V + C'V^2 + \ldots$

3. The compressibility factor of an ideal gas is :

(a) Zero (b) 1 (c) Infinity (d) Negative

4. The critical temperature of a liquid whose boiling point is 77°C is nearly equal to :

(a) 60°C (b) 250°C (c) 240°C (d) 290°C

5. The root mean square velocity of a certain gas at 300 K is 4×10^4 cm s^{-1}. The temperature at which the velocity will be 8×10^4 cm s^{-1} is :

(a) 1200 K (b) 600 K (c) 300 K (d) 1500 K

6. 240 g of an ideal gas of molar mass 80 g mol^{-1} is confined to a volume of 6 dm^3 at 300 K. If $R = 0.082$ dm^3 atm K^{-1} mol^{-1}, the pressure exerted by the gas is :

(a) 12.0 atm (b) 2.1 atm (c) 12.2 atm (d) 12.3 atm

7. A gas cannot be liquefied if for the gas the temperature is greater than :

(a) Critical temperature (b) Critical pressure

(c) Critical volume (d) Critical density

8. At constant pressure the specific heat of a gas ($M = 80$) is 0.125. It is :

(a) Monoatomic (b) Diatomic (c) Triatomic (d) H_2

9. The first virial coefficient of Kammerling Onnes equation at low pressure is :

(a) PV (b) RT (c) $\frac{1}{V}$ (d) $\frac{1}{RT}$

10. If the rms velocity of a gas is 100 cm s^{-1}, its average velocity is :

(a) 100 cm s^{-1} (b) 0.01 cm s^{-1}

(c) 92.13 cm s^{-1} (d) 81.64 cm s^{-1}

11. The unit of vander Waals constant (a) is :

(a) mole atm^{-1} (b) atm $mole^{-1}$

(c) lit^2 atm $mole^{-2}$ (d) atm lit^{-2} $mole^2$

12. At 27°C, the kinetic energy of 2 moles of an ideal gas is :

(a) 1800 cal (b) 900 cal (c) 600 cal (d) 300 cal

13. The following is known as a permanent gas :

(a) NH_3 (b) N_2 (c) H_2 (d) CO_2

14. The ratio of most probable, average and root mean square velocity is :

(a) 1 : 1.224 : 1.128 (b) 1 : 1.128 : 1.224

(c) 1 : 1.128 : 1.524 (d) 1 : 1.178 : 1.524

15. The vander Waals equation for n moles of a real gas is :

(a) $\left(P + \frac{a}{V^2}\right)(V - b) = nRT$ (b) $\left(P + \frac{na}{V^2}\right)(V - nb) = nRT$

(c) $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ (d) $\left(P + \frac{a}{n^2 V^2}\right)(V - nb) = nRT$

16. Which one of the following is not the characteristic of an ideal gas ?

(a) It obeys Boyle's law.

(b) The collisions between the molecules of a gas are perfectly elastic.

(c) There is no attraction between the molecules of a gas.

(d) When a gas is allowed to expand in vacuum, a cooling effect is observed.

17. Helium atom is two times heavier than a hydrogen molecule. At 300 K, the average kinetic energy of a helium atom is :

(a) Two times that of a hydrogen molecule

(b) Same as that of a hydrogen molecule (c) Half as that of a hydrogen molecule

(d) Equal to that of a hydrogen atom.

[V] Fill in the Blanks

1. In general, the more easily liquefiable gases have a .... Boyle temperature.
2. The average energy of translational motion of gas molecules is proportional only to the ....
3. Real gases behave ideally at .... temperatures and .... pressures.
4. At 274 K, rms velocity of methane molecules would be .... ms^{-1}.
5. vander Waals replaced the volume term, V in the ideal gas equation by ....
6. The intermolecular forces which exist between the neutral molecules are known as ....
7. The temperature at which the average velocity of O_2 molecules would be twice that at 20°C is .... K.
8. Average kinetic energy of gas molecules is .... to absolute temperature.
9. Gravity has .... effect on the motion of gas molecules.
10. The C_P/C_V value for a gas is 1.4. If its atomic weight is x, its molecular weight is ....
11. The unit of vander Waals constant a is .... and b is ....
12. The pressure of real gases is less than that of ideal gases because of ....
13. The velocity possessed by most of the gaseous molecules is known as ....
14. When a real gas at high pressure expands into a region of low pressure, its temperature will ....

[VI] True or False

State whether the following statements are true (T) or false (F) ?

1. $PV = \frac{1}{3} mNu^2$ is an expression for the real gases.
2. The molecules of real gases have both volume and mutual attraction.
3. Pressure depends on the number of molecules and temperature.
4. The equation $\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$ is known as the reduced equation of state.
5. The observed pressure of a real gas is less than the pressure of an ideal gas.
6. Assuming the evidence of individual particles of matter, at any temperature greater than 0K, the particles will possess kinetic energy.
7. There are large number of particles in any sample of a gas for which the average velocity must be zero, whereas the average velocity will always be final.
8. Gases which are difficult to liquefy have a low Boyle temperature.
9. Real gases obey Dalton's law exactly.
10. The vander Waals constant b is the actual volume of gas molecules.
11. Root mean square velocity of gas molecules is always greater than the average velocity under similar conditions.
12. The ratio of the average molecular kinetic energy of CO_2 to that of SF_6 both at 300 K is one.
13. The most probable velocity is that which the greatest fraction of gas molecules possess.

ANSWERS

[III] Numerical Problems

1. 3.74 kJ
2. 1092 K
3. 150 K
4. 5.49×10^5 cm s^{-1}
5. 4.87.2 K
6. 2041 atm.
7. 399 K
8. 7.02×10^{-6} cm
9. 239.8°C
10. 1026 K
11. 2.8×10^{-8} cm
12. 244.4 K
13. 0.447
14. 1
15. 7482.6 J
16. 48372.6 cm s^{-1}
17. –10.5°C
18. 40
19. 4.71 atm
20. $T_c = 303.9$ K, $V_e = 0.1284$ lit mol^{-1}
21. 28.57
22. a = 3.6 lit^2 atm mol^2, b = 0.0428 lit mol^{-1}
23. $T_c = 253.5$ K, $P_c = 58.01$ k
24. 20.34
25. $b = 0.0326$ dm^3 mol^{-1}, $a = 2.7465$ dm^6 atm mol^{-2}
26. 33 atm
27. 602.8 K

[IV] Multiple Choice Questions

1. (c)
2. (a,b)
3. (b)
4. (b)
5. (a)
6. (d)
7. (a)
8. (a)
9. (b)
10. (c)
11. (c)
12. (a)
13. (c)
14. (b)
15. (c)
16. (d)
17. (b)

[V] Fill in the Blanks

1. high
2. absolute temperature
3. high, low
4. 652
5. $(V - b)$
6. vander Waals forces
7. 586 K
8. directly
8. directly proportional
9. negligible
10. $2x$
11. lit^2 atm $mole^{-2}$, lit $mole^{-1}$
12. mutual attraction between gas molecules
13. most probable velocity
14. fall.

[VI] True or False

1. (F)
2. (T)
3. (T)
4. (T)
5. (T)
6. (T)
7. (T)
8. (T)
9. (F)
10. (F)
11. (T)
12. (T)
13. (T)

Chapter 4

LIQUID STATE

4·1. GASEOUS, LIQUID AND SOLID STATES

It is a common phenomenon that when a gas is gradually cooled, it converts into the liquid state due to the process of condensation. Further cooling will make the liquid to freeze into the solid state. However, on heating a solid, reverse changes are observed. In other words, a liquid state is an intermediate state between the gaseous and solid states but it is only qualitative in nature, because every property of a liquid is not an intermediate in value between those of solid and gaseous states. A liquid has some properties of a solid and some properties of a gas.

In gases, the molecules are free to move and except at very high pressures, they spend only a small fraction of their time sufficiently close to other molecules to exert any force upon them. In liquids, the molecules are still free to move, but are very close together and are continually within the range of the attractive and repulsive fields of forces of neighbouring molecules. Translatory motions give rise to diffusion in liquids. The rotatory and vibratory motions also occur. The cohesion due to the attractive forces imposes on the liquid a definite volume, and liquids are distinguished from gases by the possession of a well defined surface; they do not expand to fill the whole of the containing vessel, as gases do. However, in solids translatory and rotatory motions are usually absent, but the individual particles, which may be molecules, atoms, or ions, can vibrate about a fixed mean position in an orderly crystalline arrangement or space lattice.

Liquids have viscosity, which is due to the attractive forces between adjacent molecules tending to keep them in a fixed position relative to each other. Thermal agitation, increasing with increasing temperature gives the molecules of the liquid the power to slip past each other. Consequently, the viscosity of liquids almost always decreases as the temperature rises.

Molecules in a liquid diffuse in the same manner as those in a gas, but their rates of diffusion are comparatively much smaller. It is because that molecules in a liquid are much closer to one another than in a gas. Hence, they collide with one another much more frequently and the mean free path in the case of liquid molecules is less than that in gases.

The compactness and cohesion observed in the liquid suggest a structure similar to that of a solid, but the comparative ease with which the liquids flow suggests a disordered random structure like that occurring in a gas.

[I] Short Range Order and Long Range Order in Liquids

A crystal has a perfect and well ordered arrangement of the molecules throughout the whole mass, each molecule is surrounded by a set of other molecules in a special symmetrical pattern. On melting, a crystal expands about 10% in volume or about 3% in intermolecular spacing, which goes on to suggest that a molecule in the liquid state must still remain in the neighbourhood of some molecules surrounding it, The molecular rearrangement cannot be as random as that in a gas and this ordered arrangement is not completely destroyed when a solid is melted. The structure of the crystal involves a strong geometrical order. The thermal agitations introduce a disorder. An introduction of a small region of disorder into a crystal would cause disturbance in the long range and destroys the crystalline structure and so there is a sudden variation in the properties between solids and liquids. This explains the sharpness of melting points when the thermal motion causes a disorder in one region of the liquid, which spreads in all directions destroying the entire regular structure. Thus, liquids may be said to possess a structure like that of a crystal except that the well ordered pattern extends over a short range instead of over the entire mass. This has been known as ***short range order and long range order***. The short range order in the liquid structure continuously changes because of the thermal motion. X-ray diffraction of liquid reveals evidence in support of short range order. If the structure of the liquid were completely devoid of regularity, there would be a continuous scattering of X-rays without maxima or minima. But actual experiments reveal a few maxima and minima which indicate the existence of a regular pattern or order in the liquid. But the small number of maxima and minima suggests the existence of the short-range order only.

[II] Vacancy Theory of Liquids

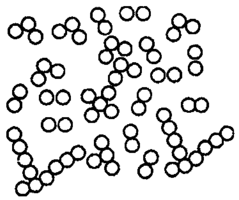


Fig. 1. The liquid as a random congregation of molecules and holes.

A liquid is generally less dense than the corresponding liquid which means that the intermolecular space in a liquid is more than that in a solid. Eyring and Ree (1961) proposed a simple theory that the intermolecular space in a liquid is not randomly distributed but contains molecular sized *holes* or *vacancies*. The liquid may be taken as a random congregation of molecules and holes [Fig. (1)]. It is supposed that the molecules surrounding a given vacancy can easily jump into it and are thus *gas like*, whereas those in immediate contact with the vacancy are *solid like*. If V_l and V_s are the respective molar volumes of the liquid and the solid, then

$$\frac{\text{Number of vacancies}}{\text{Number of molecules}} = \frac{V_l - V_s}{V_s}$$

The probability that a vacancy confers gas like properties on its neighbouring molecules is proportional to the fraction of the neighbouring positions occupied by the molecules. For a random distribution of vacancies this ratio is given by V_s/V_l. Therefore,

$$x_g = \left(\frac{V_l - V_s}{V_s}\right)\left(\frac{V_s}{V_l}\right) = \left(\frac{V_l - V_s}{V_l}\right)$$

Similarly, $$x_s = \frac{V_s}{V_l}$$

where x_s and x_g are the mole fractions of the solid like and gas like molecules, respectively. On this basis, Eyring and Ree determined the boiling point, melting point, critical constants and some thermodynamic properties of argon. The experimental results obtained were in good agreement with the proposed theory.

[III] Free Volume in a Liquid

Eyring showed that in a gas the molecules freely move about the entire space and the volume which is physically occupied by the molecules is negligible. However, in the case of a liquid, the position is reverse, the space occupied by the liquid is mostly occupied by the molecules and a comparatively small space is ***void.*** The void space in which the centres of molecules execute motion is known as ***free volume.***

In a liquid, the molecules move over an infinitesimally small distances before colliding with one another unlike a gas in which the molecules travel considerable distances before colliding with each other. This is due to the fact that each molecule in a liquid is tightly surrounded by almost 10 to 12 neighbours forming a spherical cage which can be approximated to a spherical box of radius r_f which is only slightly bigger than the enclosed molecule of radius r_m [Fig. (2)]. It is clear that the centre of the caged molecule can move about in a very small volume. Actually, the volume for a mole of molecules is known as ***free volume.***

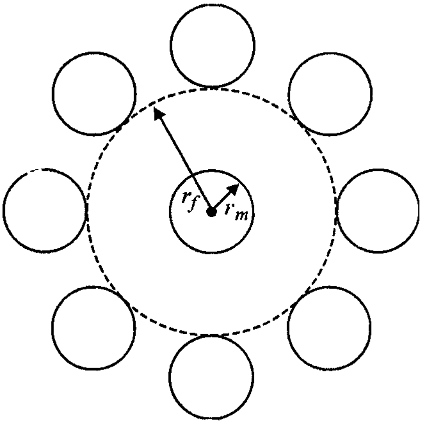


Fig. 2. The free volume in a liquid.

With the help of Trouton's rule, it can be shown thermodynamically that the magnitude of the free volume is nearly 0.37 cm^3. The free volume per molecule is thus equal to 0.61 A^3. If we equate this value to the volume of a sphere of radius r_f, we have

$$\frac{4}{3}\pi (r_f)^3 = 0.61\ \text{A}^3 \quad \text{or} \quad r_f = 0.54\text{Å}$$

The radius r_f shows the average distance travelled by a molecule between collisions with the walls of the spherical cage. Assuming the average speed of the molecules of the liquid to be 3×10^4 cm s^{-1}, we can show that the molecule would make 5.6×10^{12} collisions per second with the spherical cage.

4.2. STRUCTURAL DIFFERENCES BETWEEN SOLIDS, LIQUIDS AND GASES

Of the three states of matter, the solid state in crystalline form shows a complete ordered arrangement of molecules, atoms or ions as the case may be and the gaseous state at high temperature and low pressure shows complete randomness or disorder. The liquid state lies in between these two extremes of order and disorder. Fig (3) shows a two dimensional picture of the three states of matter.

In solids, there is a close packing of molecules, atoms or ions. This arrangement exists to some extent in the liquid state. In gases, there is no such arrangement of close packing of molecules or atoms which are taken to be like spheres.

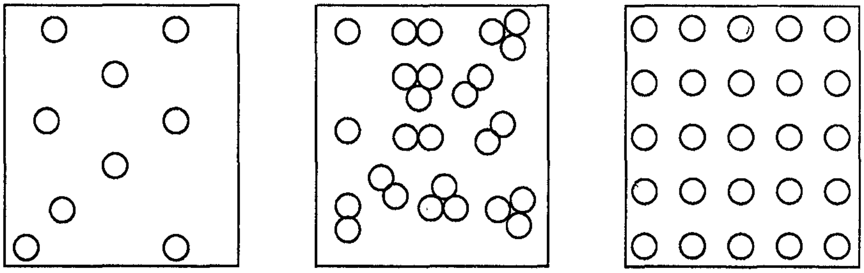

Gaseous state Liquid state Solid state

Fig. 3. Two dimensional arrangement of molecules in gases, liquids and crystalline solids.

The definite and ordered arrangement of the constituents of a solid extends over a large distance. This is known as **long range order.** The liquids show only a **short range order**, while gases show no order at all.

A liquid may be taken to be a condensed gas or a molten solid. In solids, the molecules are rigidly fixed and so it has a definite shape and a definite volume. In a gas, the molecules have random motion and so it has neither a definite shape nor a definite volume. In a liquid, the molecules are not as rigidly fixed as in solids. The molecules in liquid state have some freedom of motion which, however, is much more restricted than that in gases. Therefore, a liquid has a definite volume but indefinite shape. It is much less compressible and far denser than a gas.

The molecules in a solid are rigidly fixed and are very close to each other. However, the molecules in a liquid are not far apart from one another, so the inter-molecular forces are fairly strong. The characteristic properties of liquids arise from the nature and magnitude of these intermolecular forces. In gases, the inter-molecular distance is quite large.

Due to close packing of particles, solids have very low compressibility and can be compressed only under very high pressures. The liquids are more compressible as compared to solids. However, in gases, the compressibility is quite appreciable due to the large spaces between the constituent gaseous molecules.

Due to the lack of translational motion of the constituent particles, the solids have practically no tendency to diffuse. The constituent particles in a liquid move within the boundary of the liquid. The liquids have thus a tendency to diffuse although their rates of diffusion are much less than those of gases. The gases possess a great tendency to diffuse due to the free movement of constituent particles.

4·3 CHARACTERISTIC PROPERTIES OF LIQUIDS

Most of the characteristic properties of liquid states arise from (i) the nature and (ii) the magnitude of intermolecular forces of attraction existing between the molecules. The important properties of liquids which we shall study in this chapter are:

(i) Vapour pressure. (ii) Surface tension, (iii) Viscosity.

(1) VAPOUR PRESSURE

Consider a liquid contained in an evacuated vessel connected to a manometer, so that any pressure that is developed in the free space above the liquid can be measured. The entire system may be placed in a thermostat at a constant temperature. The vapour molecules confined in the space above the liquid strike against the walls of the vessel and thus exert pressure which can be read from the manometer. This pressure is seen to be constant at a given temperature and is known as the vapour pressure of the liquid. Therefore, ***vapour pressure*** of a liquid is defined as *the pressure of the vapour in equilibrium with the liquid at any given temperature.*

The vapour prossure measures the ease with which a liquid can be converted into vapour, *i.e.*, it is a measure of the volatility of the liquid. In other words, *vapour pressure is a measure of the escaping tendency of the molecules from the surface of the liquid.* On increasing the temperature, the number of molecules escaping from the liquid surface increases and there is an increase in the number of vapour molecules in the space above the liquid when equilibrium is attained. Hence, the *vapour pressure of a liquid increases with the rise in temperature.*

[I] Measurement of Vapour Pressure

There are generally two methods for determining the vapour pressure of a liquid, *viz.*,

(a) Static method (b) Dynamic method.

(a) Static method. In this method, the barometirc process of measurements is the simplest one. It involves the use of two barometer tubes filled with mercury and inverted in a dish containing mercury. The tubes are enclosed in a constant temperature jacket. A small amount of the liquid under examination is introduced into one of the tubes. It evaporates as it rises into the vacuum above the mercury. The heat required for the evaporation is supplied by the surroundings. Some more of the liquid is introduced in a similar way and this process is continued till a small quantity of the liquid remains as such on the surface of the mercury. The difference in the mercury levels of the two barometer tubes gives the vapour pressure of the liquid at the prevailing temperature.

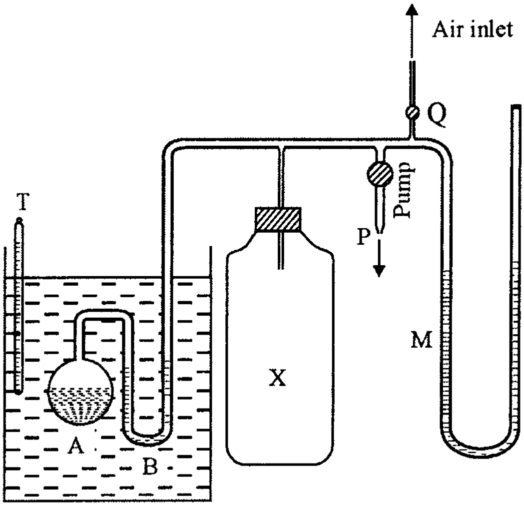


Fig. 4. Isoteniscope method.

(b) Dynamic method. In this method we shall discuss the following two methods :

(i) Smith-Menzies isoteniscope method. The apparatus (Fig. 4) consists of a small glass bulb A connected to a small U-tube B. This isoteniscope is kept in a thermostat and the outer limb of the U-tube is connected to a large bottle X to stabilise the pressure. A manometer and a pressure regulator (pump P and air inlet Q) are also attached.

Two thirds of the bulb A and the U-tube are filled up with the experimental liquid. The pressure is reduced by the pump until the liquid in A bulk boils and the air in the isoteniscope is displaced. The pressure is now gradually increased by the admission of air through Q, until the liquid levels in the U-tube are the same. The manometer and barometer readings are noted.

∴ Vapour pressure of the liquid = Barometric pressure – Pressure recorded in manometer.

(ii) Ramsay-Young method. This method gives results of very high accuracy. The apparatus used is shown in figure (5). A strong-walled boiling tube (B) provided with a side tube is employed. Its mouth is closed by means of a rubber cork carrying a thermometer and a dropping funnel with a narrow bent stem. The bulb of the thermometer is kept covered with a thin cotton wool which is always kept moist. The boiling tube is kept in a bath and the film of the liquid in the cotton wool evaporates by heat of radiation. The side tube is attached to an empty vessel, for pressure stabilisation and finally to a manometer and pressure regulator.

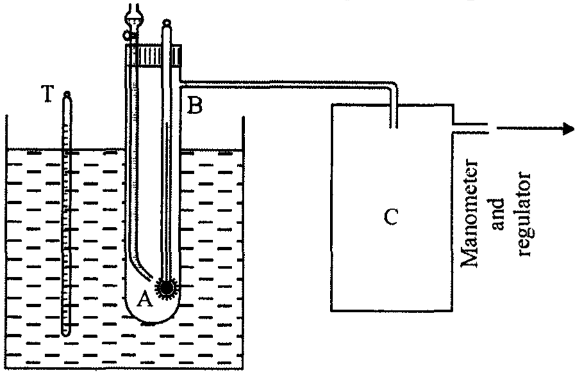


Fig. 5. Ramsay-Young apparatus.

The pressure is first reduced and evaporation of liquid from the cotton wool occurs. At a given pressure, a steady state is reached when the thermometer shows a constant reading and distillation from the surface of the thermometer bulb proceeds smoothly. The manometer reading gives the vapour pressure at that temperature. By regulating the pressure, it is possible to determine the vapour pressure at different temperatures.

(2) SURFACE TENSION

Surface tension is the most significant of the characteristic properties of liquids. Consider a liquid in contact with its vapour. A molecule in the interior of the liquid is subjected to forces of attraction from all possible directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed. In other words, it means that the molecules at the surface are pulled inwards. The result is that liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this pseudo-membrane tends to contract. It explains why a small amount of liquid, left freely, always takes a spherical shape. This is because the sphere, for a given volume, has the least surface area. *Therefore, the unbalanced attractive force acting dowanwards tends to draw the surface molecules into the body of the liquid and, therefore, reduces the surface to a minimum.* This liquid then behaves as if it were under a strain or tension. It is this force which is called *surface tension.* It may, therefore, be defined as, ***'the force in dynes acting on the surface of a liquid at right angles to one centimetre length of the surface'.***

[I] Surface Energy

Due to the phenomenon of surface tension, the natural tendency of a liquid is to occupy as little area as possible. Let us consider that it is desired to extend the area of a surface by 1 cm^2. Then some work will have to be performed against the force of surface tension. The work required to be done is given by the surface tension, γ, *i.e.*, the force in dynes per cm which tends to oppose the increase, multiplied by 1 cm, *i.e.*, the distance through which the point of application of force is moved. Thus,

$$\text{Work done} = \gamma \times 1 \text{ erg.}$$

The work done in order to increase the area of surface by 1 cm^2 is known as ***surface energy***. Therefore.

$$\text{Surface energy} = \gamma \times 1 \text{ erg.}$$

Hence, we conclude that *surface tension and surface energy are numerically equal to one another*. But surface energy has the units of work, *i.e.*, erg per cm^2 while surface tension, being a force, is expressed in dyne per cm.

[II] Interfacial Tension

Consider that two immiscible liquids are present one above the other in a vessel. The force acting per unit length along the interface is called the *interfacial tension.* Its value is less than the surface tension of the liquid with a higher value because the unbalanced forces acting along the surface of each liquid are partly compensated by the forces of mutual attraction between the molecules of the two liquids.

It has been observed that surface tension and interfacial tension involve the same type of forces. In surface tension of a liquid, the force acts along the surface of separation between the liquid and its vapour. In the case of interfacial tension, however, the force acts along the surface of separation of the two liquids concerned.

[III] Angle of Contact

The surface of contact near its point of contact with a solid is generally a curved one. The angle between the tangent to the liquid surface at the point of contact and the solid surface inside the liquid, is called the *angle of contact* for that pair of liquid and solid. The angle of contact which depends upon the nature of the solid and the liquid, may obviously have values between 0° and 180°. For water and glass it is approximately 18°, while for mercury and glass it is nearly 140°.

[IV] Measurement of Surface Tension

There are a number of methods for determining the surface tension of liquids. These are as follows :

(i) Capillary rise method : It is a common phenomenon that when a capillary tube is lowered in a liquid that wets its surface, the liquid rises in the tube. For example, when a capillary tube is dipped in water, it rises to a certain height against the force of gravity. Most of the liquids exhibit the same tendency. The height to which the liquid rises depends upon the surface tension and density of the liquid.

Suppose a liquid of density, d, rises in a capillary tube of radius r, to a height h. Let γ be the surface tension of the liquid in dyne per cm.

The total force due to surface tension, raising the liquid column upward

$$= \gamma \times \text{ inside circumference of the capillary}$$

$$= \gamma \times 2\pi r = 2\pi r.\gamma \text{ dynes.}$$

Force of gravity pulling the liquid column downward

$$= \text{ Weight of the liquid column}$$

The weight of the liquid in the column = Vdg dynes

where v is the volume of the liquid in the tube and is equal to $\pi r^2 h$.

$\therefore$ At equilibrium, $2\pi r.\gamma = \pi r^2 hdg$

$$\therefore \quad \gamma = \frac{rhd\,g}{2} \text{ dyne per cm.} \qquad \dots (1)$$

Thus, in order to measure the surface tension of a liquid, it is necessary to measure the values of r and h in cms. The height to which a liquid rises is measured by means of a *cathetometer*, while the radius of the capillary tube is measured by a *travelling microscope.*

In the derivation of equation (1), it has been assumed that the angle of contact (θ) between the glass and the liquid is zero, *i.e.*, the wetting is perfect. If this is not so then it can be shown that,

$$\gamma = \frac{rhd\,g}{2\cos\theta} \qquad \dots (2)$$

(ii) Drop weight method. This method is based on the fact that the weight (W) of a drop of a liquid falling from a given capillary tube held vertically is approximately proportional to the surface tension (γ) of the liquid. If the surface tensions of the two liquids 1 and 2 are γ_1 and γ_2, then

$$\frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2}$$

where W is the mean weight of a drop of liquid falling from a vertical capillary tube.

It is, however, more convenient to count the number of drops formed by a given volume of a liquid than to find the weight of a drop. Let equal volumes (V) of two liquids when allowed to fall through the same capillary tube form n_1 and n_2 drops. So, the mean weights of such drops, W_1 and W_2 are given by

$$W_1 = \frac{V}{n_1} \cdot d_1 \qquad \dots (3)$$

$$W_2 = \frac{V}{n_2} \cdot d_2 \qquad \text{(where } d = \text{ density of the liquid)} \qquad \dots (4)$$

$$\therefore \quad \frac{\gamma_1}{\gamma_2} = \frac{W_1}{W_2} = \frac{\frac{V}{n_1} \cdot d_1}{\frac{V}{n_2} \cdot d_2}$$

or

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2} \qquad \dots (5)$$

If the surface tension of one liquid is known, then that of the other can be calculated from equation (5).

The above expression is generally used to compare the relative surface tensions of two or more liquids. A pipette like tube called the ***stalagmometer***, shown in figure (6) having a very smooth capillary end is used for the purpose. The stalagmometer is first thoroughly cleaned with chromic acid and water and finally dried. It is kept in a vertical position in an enclosure free from disturbances or air currents. The liquid is then filled upto a certain mark by sucking. The liquid is then allowed to drop very slowly ensuring that every drop is fully formed. A definite volume of the liquid, say V ml. determined by marks in the stalagmometer is allowed to come out and the number of drops (n) counted. The number of drops per minute should not exceed 20, as otherwise they will not be properly formed. This rate can be controlled with the help of a pinch cock attached to a rubber tube at the upper end of the stalagmometer. The density of the liquid is separately determined by means of a pyknometer. The surface tension is calculated from equation (5).

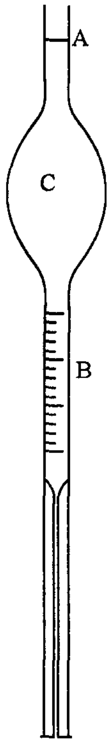


Fig. 6. Stalagmometer.

(iii) du Nouy's method. This method is now commonly used for quick determination of surface tension with great accuracy. This method, also known as *ring detachment method,* is based on measurement of the force P, required to detach a horizontal platinum ring (radius r) from the surfaces of the experimental liquid. The force will be required to overcome the pull due to surface tension. Thus,

$$P = 4\pi r\gamma \quad \text{or} \quad \gamma = \frac{P}{4\pi r} \qquad \dots (6)$$

The appratus consists of du Nouy's torsion balance shown in figure (7). The platinum ring (R) is well cleaned and suspended from the hook (H) of the beam (B), balanced at the other end by a torsion wire (W). One end of the latter carries a pointer (P) on a circular scale (S) and is previously calibrated with known weights taken by the beam. In a flat dish (D), the liquid is taken and placed in such a way that the platinum ring just touches the surface. The knob of the torsion wire is slowly turned until the ring is just detached from the surface, keeping the beam always in a horizontal position. The reading of the pointer gives the force P just at the moment of detachment of the ring from the liquid surface. The value of γ is then calculated from equation (6).

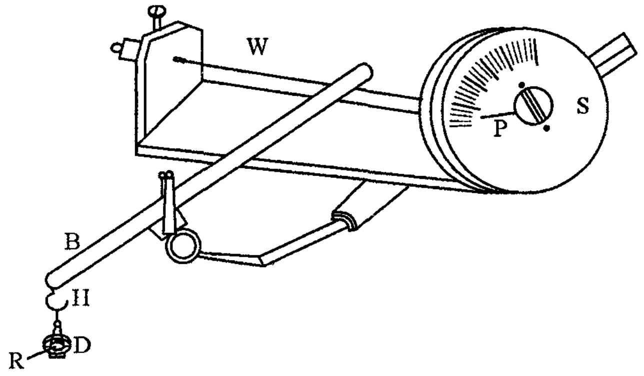


Fig. 7. due Nouy's torsion balance

[V] Surface Tension and Vapour Pressure

Surface tension is intimately connected with the attraction between the molecules. The process of evaporation in which the molecules escape from the surface depends upon the intermolecular attraction. Thus, a relation exists between the surface tension and vapour pressure, which can be arrived at as follows :

Suppose a capillary tube is dipped in a liquid and x and y represent the final and initial levels of the liquid in the tube, respectively. We then have,

$$\gamma = \frac{hdr}{2}$$

where r is the radius of the tube and d is the density of the liquid. Further, imagine that the system is enclosed in a chamber and is in equilibrium. There is a vapour pressure difference at x and y. If p be the vapour pressure at y then the vapour pressure at x is $p—h\rho g$, where ρ is the density of the vapour. This must be the maximum pressure in contact with the curved surface at x. If it were not so, then there would have been condensation or evaporation at x and a circulation would be set up without any supply of energy which is contrary to our experience. The difference of vapour pressure,

$$dp = h\rho g$$

But, we know that $$h = \frac{2\gamma}{rdg}$$

$$\therefore \quad dp = \frac{2\gamma \, . \, \rho g}{rdg} = \frac{2\gamma\rho}{rd}$$

Assuming the vapour to behave as an ideal gas, we have

$$\rho = \frac{Mp}{RT}$$

Thus, $$dp = \frac{2\gamma \, . \, Mp}{rdRT}$$

or $$\frac{dp}{p} = \frac{2\gamma \, . \, M}{rdRT}$$

The above equation gives the relation between the surface tension and vapour pressure.

[VI] Variation of Surface Tension with Temperature

Surface tension is not, whole of energy associated with a liquid or solid surface. It is only the free energy, the part of which can be recovered as mechanical work, when the surface contracts. When a surface is extended heat is absorbed, and so the surface tension decreases as the temperature rises. Qualitatively, we may regard the absorption of heat during extension of a surface as due to the inward attractive force, slowing the molecules on their way to the nearly formed surface, and lowering their temperature unless heat is supplied. Similarly, we can regard the lowering of surface tension with rise in temperature as due to the increased thermal agitation assisting the molecules to the surface, so that less work is required to form the new surface. Quantitatively, the total energy in 1 cm^2 is given by

$$E_s = \gamma - T\frac{d\gamma}{dT} \qquad \text{... (7)}$$

Equation (6) is a special case of Gibbs-Helmholtz equation, and gives the relation between the free and total changes in any process. The term $-T\,(\partial\gamma/\partial T)$ is the heat absorbed in forming 1 cm^2 of new surface.

As a rough approximation, the surface tension decreases linearly with temperature, E_s being nearly constant; consequently the total surface energy varies only slightly with temperature. The surface tension vanishes at the critical temperature, when the visible surface between the liquid and vapour disappears.

A rather better approximation to the actual relation between surface tension and temperature was given by Eotvos. If M and v represent the molecular weight and specific volume of a liquid, respectively, then molecular surface of a liquid, assuming it to be a spherical mass, is proportional to $(Mv)^{2/3}$. The molar surface energy is then given by $k_1(Mv)^{2/3}\gamma$, where k_1 is an appropriate constant and γ is the surface tension of the liquid. Eotvos suggested that molar surface energy and temperature are related to one another by a linear relationship, *i.e.*,

$$k_1\,(Mv)^{2/3}.\,\gamma = -\,k_2t + x_1 \text{ (constant)}$$

or $$(Mv)^{2/3}\,\gamma = -\,kt + x \text{ (constant)}$$

At critical temperature t_c, the surface tension (γ) is zero, so that we have

$$x = kt_c$$

$\therefore$ $$(Mv)^{2/3}.\,\gamma = k\,(t_c - t) \qquad \dots (8)$$

If $(Mv)^{2/3}.\,\gamma$ is plotted against temperature, we get a straight line which meets the temperature axis at the critical temperature. Ramsay and Shields showed that in actual practice the line cuts the temperature axis approximately six degrees before the critical temperature. Therefore, Eotvos equation was modified to the following form to conform to the experimental results.

$$(Mv)^{2/3}.\,\gamma = k\,(t_c - t - 6) \qquad \dots (9)$$

For most of the liquids which might be presumed to have the molecular weight equal to the formula weight, the constant k often called *Eotvos-Ramsay-Shields coefficient* has the same value of 2.12. Other *'associated'* liquids had smaller values of k. It was hoped that the value of k could be employed as an indication of the extent to which the molecules of the liquid were associated into group of higher molecular weight, but it is now clear that many other factors besides molecular association influence k. The non-validity of the claim that small values of k indicates molecular association is shown by the very small values of k (sometimes less than 0.5). This value of k is found for some fused salts which are certainly dissociated into ions. The very high values of k (upto nearly 6) given by triglycerides, suggest that they are certainly not dissociated.

The value of k can be evaluated by measuring the surface tension and specific volume (from density) at two temperatures, for

$$k = -\frac{\gamma_1\,(Mv_1)^{2/3} - \gamma_2\,(Mv_2)^{2/3}}{t_1 - t_2}$$

Problem 1 : ***A drop of water, 0.4 cm in radius is split up into 125 tiny drops. Find the increase in surface energy.*** **(γ_{H_2O} = 72 *dynes/cm*).**

Solution : If r be the radius of the tiny drops, then

$$\frac{4}{3}\pi\,(0.4)^3 = \frac{4}{3}\pi r^3 \times n = \frac{4}{3}\pi\, r^3 \times 125$$

or $$r = 0.08 \text{ cm.}$$

The increase in surface area

$$= 4\pi\,(0.08)^2 \times 125 - 4\pi\,(0.4)^2 = 4\pi\,(0.64) \text{ sq. cm.}$$

The increase in surface energy

= Surface tension × Area

= 72 × 4π × 0.64 = **578.76 ergs.**

Problem 2 : ***In a surface tension measurement, water was found to rise to a height of 2.88 cm. in a capillary tube of 1 mm. diameter. Calculate the surface tension of water.***

Solution : Neglecting curvature and assuming the angle of contact to be zero,

$$\gamma = \frac{rhdg}{2} = \frac{0.05 \times 2.88 \times 1 \times 980}{2}$$

$$= \mathbf{70.56\ dynes/cm.}$$

[VII] Trouton's Rule

The molecules in a liquid are much closer to one another than those in a gas. Intermolecular forces of attraction are, therefore, much stronger in liquids than in gases. When a liquid converts into vapour state, these intermolecular forces have to be overcome. So, a certain amount of energy has to be supplied to the liquid in the form of heat. *The amount of heat which has to be supplied to one mole of a liqiid at its boiling point to convert it into vapour state at the same temperature, is called the* ***molar heat of vaporisation*** (ΔH_v) *of the liquid at that temperature.*

The molar heat of vaporisation of water is 40.67kJ at 100°C. The same amount of heat is evolved when one mole of steam condenses into liquid water at 100°C. The molar heats of vaporisation of water is much higher than that of ether, benzene carbon tetrachloride etc., which shows that the intermolecular forces of attraction operating in water are much stronger than those operating in most of the organic liquids.

The molar heat of vaporisation of a liquid expresed in joules divided by the boiling point of the liquid on the absolute scale is approximately equal to 88. This statement is known is ***Trouton's rule***. It may be represented as,

$$\frac{\Delta H_v}{T_b} \approx 88\ \text{J mol}^{-1}\ \text{K}^{-1}$$

The values of $\Delta H_v/T_b$ are seen to vary over a wide range, *viz.*, from nearly 60 to 112 J mol^{-1} K^{-1}. These deviations from Trouton's rule occur in both directions. The quantity $\Delta H_v/T_b$ is known as ***entropy of vaporisation*** (ΔS_v). Trouton's rule helps us in calculating the heat of vaporisation of a liquid if its boiling point is known.

Problem 1. ***The boiling point of n-heptane is 36°C. If it obeys Trouton's rule, calculate the molar heat of vaporisation of n-heptane.***

Solution. According to Trouton's rule,

$$\frac{\Delta H_v}{T_b} = 88\ \text{J mol}^{-1}\ \text{K}^{-1}$$

or

$$\Delta H_v = (88\ \text{J mol}^{-1}\ \text{K}^{-1})\ (T_b) = (88\ \text{J mol}^{-1}\ \text{K}^{-1})\ (309\ \text{K})$$

$$= \mathbf{27.192\ kJ\ mol^{-1}}$$

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(3) VISCOSITY

Viscosity implies resistance to flow. It is a well known fact that all liquids do not flow equally readily. Those liquids which flow readily, *e.g.*, water are said to possess low viscosity and those liquids which flow slowly, *e.g.*, glycerine, honey etc., are said to possess high viscosity.

Consider the flow of a liquid through a narrow pipe. All parts of the liquid do not flow with the same velocity. A thin layer, immediately in contact with the walls of the tube, is almost stationary. Each succeeding thin layer of the liquid moves with gradually increasing velocity which becomes maximum as the centre of the tube is approached. *The resistance that one part of a liquid flowing with a certain velocity offers to another part of the liquid flowing with a different velocity is known as* ***viscosity.*** In other words, **viscosity** may be defined as ***the force of friction between two layers of a liquid moving past one another with different velocities.***

Consider a cylindrical liquid layer of area A sq cm., which moves over another similar layer at a distance of s cm with a velocity difference of v cm per sec. The tangential force of friction (F) required to maintain a constant difference of velocity, is given by

$$F \propto \frac{Av}{s}$$

or

$$F = \frac{\eta Av}{s} \qquad \dots (1)$$

where η is a constant at a given temperature and is known as coefficient of viscosity, which depends upon the nature of the liquid.

If $A = 1$ cm^2 and $v = 1$ cm per sec and $s = 1$ cm, then

$$\eta = F$$

Hence, coefficient of viscosity of a liquid may be defined as the ***force in dynes per square centimeter required to maintain a difference of velocity of 1 cm per sec between two parallel layers of liquid held at a distance of 1 cm from one another.***

[I] Fluidity (ϕ)

Fluidity is the reciprocal of coefficient of viscosity, *i.e.*,

$$\phi = \frac{1}{\eta}$$

[II] Units of Viscosity

From equation (1), it follows that

$$\eta = \frac{Fs}{Av}$$

If F is measured in dynes, s in cm, A in cm^2 and v in cm sec^{-1}, then the units of η are $\frac{\text{dyne} \times \text{cm}}{\text{cm}^2 \times \text{cm sec}^{-1}} = \text{dyne cm}^{-2}$ sec. For simplicity, the units of viscosity, *viz.*, dyne cm^{-2} sec is called ***poise***. Still more convenient units of viscosity are centipoise and millipoise (one millipoise = 0.001 poise and 1 centipoise = 0.01 poise).

If F is measured in newtons, s in meters, A in square meters and v in meter sec^{-1}, then the coefficient of viscorty in SI system will have the units of kg m^{-1} s^{-1}, as shown below :

$$\eta = \frac{Fs}{Av} = \frac{\text{kg m s}^{-2}\text{ m}}{\text{m}^2 \,.\, \text{m s}^{-1}} = \text{kg m}^{-1}\text{ s}^{-1}$$

It can be shown that 1 poise = 10^{-1} kg m^{-1} s^{-1}.

[III] Reynolds Number

The flow of a liquid through a pipe of radius R is seen to be associated with a number called Reynolds number, N_R, defined as

$$N_R = \frac{2R\bar{v}\rho}{\eta}$$

where $\bar{v}$ is the average bulk velocity of the fluid, ρ is the density and η is the coefficient of viscosity. If $N_R > 4000$, the flow is turbulent and if $N_R < 2100$, the flow of liquid is laminar. In the laminar flow, a velocity profile given by,

$$\bar{v} = \frac{\Delta P\,(R^2 - r^2)}{4\eta l}$$

is seen in a pipe where ΔP is the pressure drop over a length l and r is the distance from the axis of the pipe of radius, R. The volume of liquid flowing in time t through a pipe of radius R is given by,

$$V = \frac{\pi R^4\,(\Delta P)\,t}{8\,\eta\,l}.$$

[IV] Determination of Viscosity

(1) Principle. There area number of methods for measuring the viscosity of liquids. Poiseuille's equation (2) is the basis of most of the methods employed for the determination of coefficient of viscosity, *i.e.*,

$$\eta = \frac{\pi r^4 t P}{8Vl} \qquad \text{... (2)}$$

where V is the volume in c.c. of the liquid flowing in t sec through a narrow tube of radius r cm and length l cm under a hydrostatic pressure of P dyne per sq cm and η is the coefficient of viscosity in dyne per square cm (poise).

The hydrostatic pressure (P) of a liquid column is given by

$$P = hdg$$

where h is the height of the column and d is the density of the liquid. Equation (2) can now be written as,

$$\eta = \frac{\pi r^4 t\,h\,d\,g}{8Vl} \qquad \text{... (3)}$$

(i) Ostwald viscometer method. It is not necessary to find all the factors on the right hand side of equation (3), but the usual procedure is to determine the viscosity of a liquid with reference to that of water, whose viscosity has been measured quite accurately. This value is termed as *relative viscosity.*

The relative viscosity for ordinary liquids is commonly determind with the help of Ostwald viscometer (figure 8). It consists of a special U-tube with bulbs in each limb. There are markings in one of the limbs. All we do to measure the reltive viscosity is to measure the times of flow for equal volumes of water and the liquid under examination through the same capillary. If t_1 and t_2 are the times of flow of same volume of water and liquid, respectively and η_1 and η_2 are their respective coefficients of viscosity, then

$$\frac{\eta_1}{\eta_2}=\frac{\pi r^4 t_1 h d_1 g}{8Vl}\times\frac{8Vl}{\pi r^4 t_2 h d_2 g}$$

The value of h is the same in both the cases, as equal to volumes of both liquids are taken and they stand at the same height. Thus,

$$\frac{\eta_1}{\eta_2}=\frac{t_1 d_1}{t_2 d_2}$$

or

$$\eta_2=\eta_1\times\frac{t_2 d_2}{t_1 d_1} \qquad \dots (12)$$

The density of water can be separately determined by means of a pyknometer. Adequate precautions must be taken to maintain constant temperature and the tube must be thoroughly cleaned before use.

(ii) Falling sphere viscometer method : When a body moves through a viscous medium, its motion is opposed by frictional resistance. In order to maintain a uniform velocity, a driving force is applied to overcome the viscous drag.Stokes showed that when a spherical body of radius R cm. moves with a constant terminal velocity of v cm. per sec. through a medium having coefficient of viscosity η, the driving force (F) which just balances the frictional resistance is given by the relation

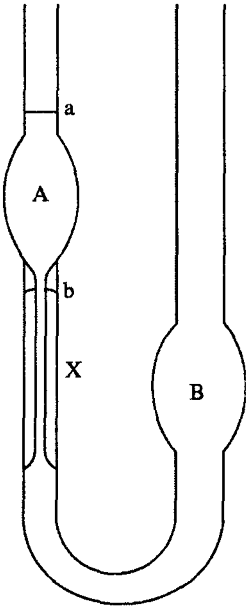


Fig. 8.

$$F = 6\pi\,\eta\,Rv$$

If a spherical body of density, D, falls under gravity, then it attains its limiting velocity, in a liquid of density, d where the viscous resistance is equal to its weight, mg, then

$$mg=\frac{4}{3}\pi\,{}^3g\,(D-d)=6\pi\eta\,Rv$$

or

$$\eta=\frac{2}{9}\frac{R^2g\,(D-d)}{v} \qquad \dots (12.1)$$

The viscosity can, therefore, be found by measuring the limiting rate of fall of a solid sphere in the liquid. When R is smaller than the distance between the molecules there is a tendency for the falling body to *'drop'* or *'channel'* and the equation is no longer applicable.

Stokes' law is the basis of the falling sphere viscometer shown in figure (9). The viscometer consists of a vertical cylindrical tube filled temperature. A steel ball, of density D and a diameter suitable to give a slow rate of fall, is now dropped through the neck of the tube, and the time of fall between two marks is determined with a stop watch. If the process is repeated with a liquid of known density and viscosity, then equation (12.1) gives the ratio of the two viscosities as,

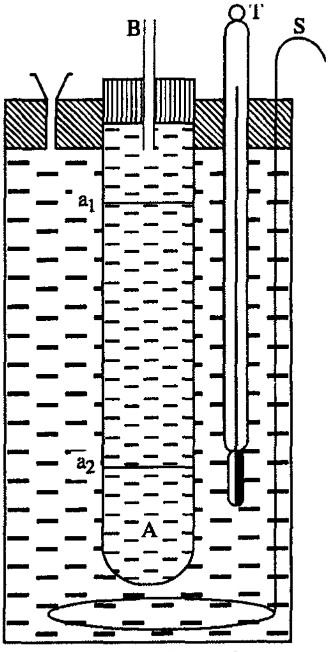


Fig. 9. Falling sphere viscometer

$$\frac{\eta_1}{\eta_2} = \frac{(D - d_1)\, t_1}{(D - d_2)\, t_2} \qquad \text{... (12.2)}$$

Therefore, knowing one of the viscosities, the density of the ball, and the densities of the two liquids, the viscosity of the liquid under study can be calculated by means of equation (12.2) from the observed values of t_1 and t_2.

Problem 1. ***A steel ball of density 7.9 and diameter 4 mm. took 50 seconds to fall a distance of 1 meter through an oil of density 1.1. Calculate the viscosity of oil.***

Solution : From equation (12.1), we have

$$\eta = \frac{2}{9} \cdot \frac{R^2 (D - d)}{v} g$$

$$= \frac{2}{9} \cdot \frac{(0.2)^2 (7.9 - 1.1) \times 980}{100/50} = \mathbf{29.64\ poise.}$$

[V] Variation of Viscosity with Temperature

It has been observed that viscosity of liquids decreases with rise in temperature. A number of empirical relations have been given between viscosity and temperature, but the following expression holds good for a larger number of liquids

$$\log \eta = \frac{A}{T} + B$$

where A and B are constants for the given liquid.

Rise of temperature decreases the viscosity of liquids, indicating that the mechanism of viscosity in liquids differ fundamentally from that in gases, whose viscosity is increased by rising temperature. Approximately, the effect of temperature on viscosity of liquids is given by

$$\eta = Ae^{E/RT} \qquad \text{... (13)}$$

However, Andrade (1932) showed that a more accurate expression is given as follows :

$$\eta v^{1/3} = Be^{E/RT} \qquad \text{... (14)}$$

where v is the specific volume of liquid. (14) may be regarded as a correction of (13) for the thermal expansion of the liquid.

The following table gives the coefficients of viscosity (in centripoises) of several liquids at various temperatures.

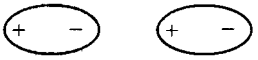
Liquid	0°C	20°C	40°C	60°C	80°C
Benzene	0.912	0.652	0.503	0.392	0.392
Carbon tetrachloride	0.329	0.969	0.739	0.585	0.488
Ethyl alcohol	1.773	1.200	0.834	0.592	–
Ethyl ether	0.240	0.233	0.197	0.140	0.118
Mercury	1.685	1.554	14.500	1.367	1.298
Water	1.792	1.002	0.656	0.469	0.357

4·4. INTERMOLECULAR FORCES IN LIQUIDS

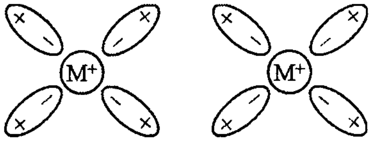
The forces of attraction between molecules are known as intermolecular forces or vander Waals forces. These are short range forces and are weak in comparison to chemical bonds. They are responsible for several important attractions between electrically neutral molecules. These forces are responsible for holding the molecules of the liquid in a given space. In liquids, the following main intermolecular forces work :

(1) Dipole-dipole forces. Polar molecules align themselves so that the positive end of one molecule attracts the negative end of another molecule and so on. Such interactions are known as dipole-dipole interactions [Fig. 10(a)] and the forces causing these interactions are known as **dipole-dipole forces**. These are also called **Keesom forces**. If these forces are considerable, the liquid has a high boiling point and in case of a solid, it has a high melting point.

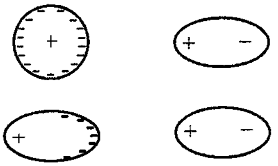
(2) Ion-dipole forces. We know that ions have great tendency to attract polar molecules. The positive ion attracts the negative pole and the negative ion attracts the positive pole of the polar molecule. Such an interaction is known as ion-dipole interaction and the forces causing these interactions are known as **ion-dipole forces** [Fig. 10(b)].



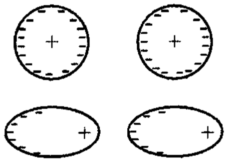
(a) Dipole-dipole interaction



(b) Ion-dipole interaction



(c) Dipole-induced dipole interaction



(d) Instantaneous dipole-induced dipole interaction

Fig. 10. Principal intermolecular forces.

(3) Dipole-induced dipole forces. When permanent polar molecules approach neutral molecules their positive poles attract the electron cloud of the neutral molecules causing distortion. The neutral molecules become polarised and are said to have induced dipoles. The forces causing these interactions are known as **dipole-induced dipole forces.** These are also called ***debye forces*** [Fig. 10(c)].

(4) Temporary dipole-induced dipole forces. The electrons are in constant motion and so the charge distribution of a neutral molecule fluctuates. At any given time, a molecule may act as an instantaneous dipole, inducing a dipole effect in a nearby molecule. This generates an attraction between the instantaneous dipole and the induced dipole [Fig. 10(d)]. These attractions are also known as ***London forces*** (given by Fritz London, 1930). They occur in all atoms and molecules, both polar and non-polar. London forces are weaker than dipole-dipole forces and their strength increases as the number of electrons in the atom or molecule increases.

London forces are short-range forces as the attraction energy, known as London energy varies inversely as the sixth power of distance between the molecules. (The intermolecular energy of attraction involved in continuous generation of dipoles and their subsequent decay is known as London energy).

$$\text{London energy} = -\frac{d}{r^6}$$

where r = distance between the molecules and d = constant.

(5) Hydrogen bonding. When a hydrogen atom is covalently bonded to a small strongly electronegative atom, a highly polar molecule is formed. A sufficient positive charge is acquired by the hydrogen end of such a molecule to attract and form a hydrogen bond with a nearby electronegative atom. The hydrogen atom may not be involved in such bonding, there may be any other atom capable of attracting bonded electrons towards itself to produce dipole. The strongest bonds are formed between H and F, N or O. Intermolecular hydrogen bonding occurs between two different molecules, whereas intramolecular hydrogen bonding occurs between atoms or groups within the same molecule. Hydrogen bonding is stronger than dipole-dipole forces and contributes mainly to the intermolecular forces in liquids. It is the characteristic property of several liquids.

4·5. STRUCTURE OF LIQUIDS

On cooling a gas sufficiently, it condenses into liquid state, which when further cooled turns into solid state. The volume occupied by a liquid is much less (upto nearly 0.001) than that in the gaseous state. So, liquids and solids are regarded as condensed states of matter.

A liquid state lies between the gaseous and the solid states, because there is neither the complete disorder and free random motion as in gases nor the rigid and well-ordered arrangement and total absence of free translational motion of molecules as in solids.

In liquids, the average inter-molecular distance is much smaller than in case of gases, so that the intermolecular forces of attraction is upto 10^6 times as strong as in gases. The intermolecular force between liquid molecules are strong enough to prevent free random motion but not strong enough to prevent the displacement within the boundaries of the liquid surface, *i.e.*, the position of molecules in liquids are not rigidly fixed.

The molecules of liquid are in a state of constant random motion, but the motion is much smaller as compared to gaseous molecules. Much of the space in a liquid is occupied by molecules with only a small fraction of space being available for free motion. This leads to higher density, little compressibility and slower rate of diffusion than that of gases.

The average kinetic energy of liquid molecules is proportional to absolute temperature. An increase of temperature increases the kinetic energy and the distance between the molecules. This lowers the intermolecular forces of attraction. When the kinetic energy of molecules, due to rise in temperature is sufficient enough to overcome the attractive forces completely, the liquid structure breaks down to free the molecules which assumes the gaseous form. This temperature is known as ***boiling point of the liquid.***

In a solid, the molecules are arranged in a highly ordered state throughout the entire mass. Each molecule is surrounded by several other molecules in a definite pattern. When a solid melts, it changes into a liquid and the volume increases by nearly 10%. This suggests that the liquids possess a *quasi-crystalline or pseudo-crystalline structure* and may be regarded as *imperfect or modified solid* as shown in figure (11). This confirms the assumption that a liquid has basically the structure similar to a solid with *holes* in its lattice.

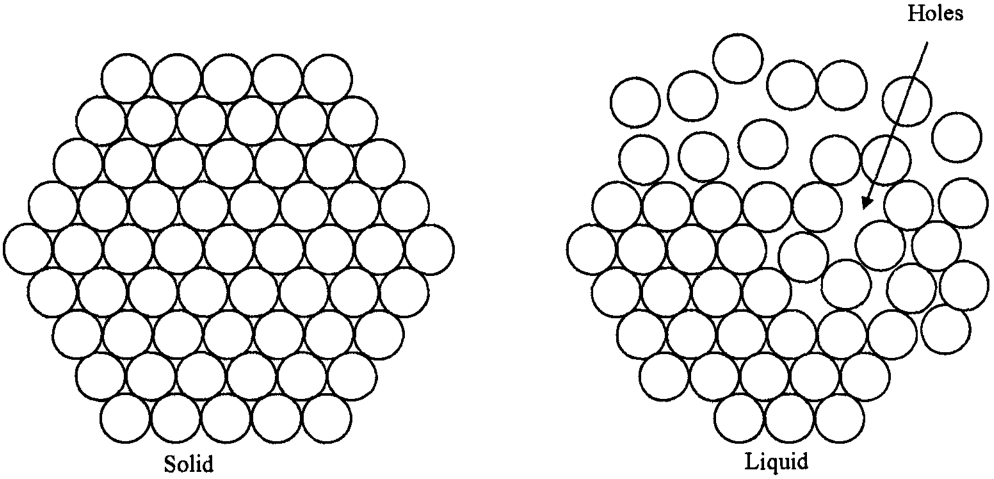


Fig. 11. Two dimensional representation of the highly ordered structure of a solid and quasi-crystalline structure of a liquid..

Bernal and Scott suggested that the structure of liquid has a random packing of liquid molecules. A liquid although possesses a random structure, yet some sort of close packing is present in it. According to Bernal, random packing gives rise to the formation of polyhedra of different irregular shapes. Polyhedra with 13 faces having number of sides to number of faces ratio equal to 5 are more common.

Stewart (1927) suggested that the liquids possess a micro-crystalline structure and contains a large number of clusters known as ***cybotactic groups*** (Greek : cybotactic = space arrangement). In such a group about hundred or more molecules are arranged in a relatively ordered pattern. The molecules which are present between the cybotactic groups are distributed randomly. Cybotactic groups are not permanent and do not possess sharp boundaries. Molecules on account of their mobility come out of these groups and pass into the region of random molecules. Similarly, the molecules from the random region move into cybotactic groups, as shown in figure (12).

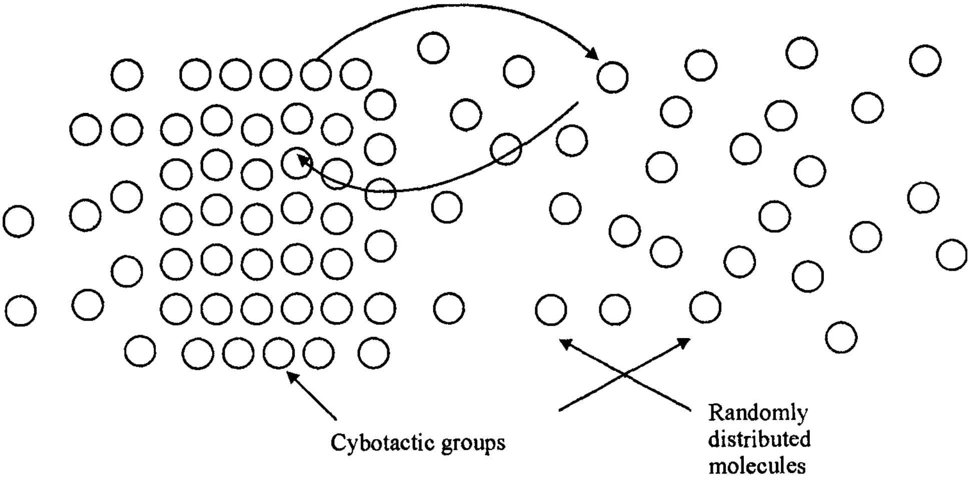


Fig. 12. Micro-crystalline structure of liquids.

[I] Radial Distribution Function

X-ray diffraction, electron diffraction and neutron diffraction methods revealed the structure of simple liquids such as liquid metals and simple monoatomic liquefied gases like argon. These methods show the existence of short-range order and long-range disorder in the liquid state. The short-rangeorder gives a definite structure, while the long-range disorder gives rise to the fluidity of the liquid. For studying the monoatomic liquids, the electron diffraction and neutron diffraction methods are mainly useful. The liquid diffraction patterns characteristically indicate one or two well formed small-range diffraction maxima that correspond to the short-range order. They also show diffuse diffraction rings that correspond to the farther removed molecules.

In theoretical chemistry, the theory of the liquid state is a very difficult problem. However, some advances have been made in the *computer simulation of liquids*. The well known ***radial distribution function*** characterises the average structure of a liquid, or more accurately, the average distribution of its molecules relative to one another. For a complete uniform distribution of molecules, the number $N(r)$ of them lying within a spherical shell of radius r and thickness dr is given by,

$$N(r) = 4\pi r^2 \rho \, . \, dr$$

where ρ is the number density of the species. The radial distribution function $g(r)$ measures the variation with r in the probability of noticing one species at a distance r from another and is defined by,

$$g(r) = \frac{N(r)}{(4\pi^2\rho)\, dr}$$

Now consider a system of n atoms and consider any one of them as an origin. For a sequence of values of r, count the number $N(r)$ of other atoms whose centres lie within spherical shells of volume $4\pi r^2 dr$. This method is repeated with each of the other $(n - 1)$ atoms as centre and finally an average is taken of the results for each value of r. Thus, one gets a radial distribution function $g(r)\, dr$ as a function of the parameter r.

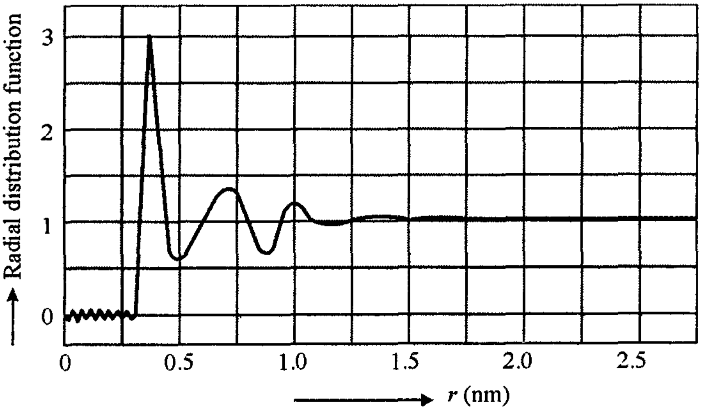


Fig. 13. Radial distribution function for liquid argon at 85 K.

The molar internal energy E_m for a simple liquid consists of the kinetic energy (which is $\frac{3}{2}RT$) and the potential energy, given by Lennard Jones potential energy $V(r)$. It may be written as

$$E_m = \frac{3}{2} RT + \left(4\pi\rho \frac{N}{2} \right) \int_0^r r^2 V(r) g(r)\, dr$$

The factor $\frac{1}{2}$ arises because each pair of interactions in $V(r)$ must be included only once. The radial distribution function $g(r)$ can be obtained from X-ray diffraction or neutron diffraction or by computer simulation methods. The radial distribution function for liquid argon at 85K calculated using neutron scattering method is shown in fig.(13). We observe that the layer of mearest neighbours clearly shows up, as does the diffuseness of the large-range structure.

The radial distribution method for deciding the structure of liquids is applicable to those liquids whose molecules contain only one important scattering element or to those in which the scattering powers of the element, *i.e.*, atomic numbers do not differ much.

4·6. LIQUID CRYSTALS

On heating, certain solids undergo two sharp phase changes one after the other. Firstly, they fuse sharply giving turbid liquids and then again equally sharply at a higher temperature giving clear liquids. These changes get reversed on cooling at the same temperatures. The transluscent or turbid liquid exhibit anisotropy, *i.e.*, they have different physical properties in different directions. Anisotropy is particularly seen in the optical behaviour of liquids. They show double refraction and give interference patterns in polarised light. On the other hand, true liquids are isotropic, *i.e.*, same physical properties in different directions. As anisotropic properties like double refraction are associated with crystalline state, the turbid liquids are known as ***liquid crystals.*** The usage of this term is not satisfactory because the substances in this state do not possess properties of crystalline state. Actually, they are more like liquids in showing properties like mobility, viscosity, surface tension etc. The other names suggested are ***crystalline liquids*** and ***anisotropic liquids*** but these are also not satisfactory. Therefore, the term ***mesomorphic state*** (Greek : mesomorphic = intermediate form) is the most suited term. However, at present the term liquid crystals continue to be used.

Substances which show the above behaviour are usually some long chain organic molecules either terminating in groups, *e.g.*, – OR, – COOR or having groups like $-C \equiv N\_$, $N = NO -$, $- C = C-$ in the middle. The first solid showing this peculiar property which was discovered in 1888 was cholesteryl benzoate, $C_6H_5COOC_{27}H_{45}$. It fuses sharply at 145°C to form a turbid liquid and on further heating changes into a clear liquid at 178°C. If we cool, the above changes are reversed, *i.e.*, the clear liquid when cooled first changes into turbid state at 178°C and then into the solid state at 145°C.

Later on, *p*-azoxyanisole and *p*-azoxyphenetole were found to exhibit properties like cholesteryl benzoate. In 1991, P. G. de Gennes, a French physicist, got the Nobel Prize in Physics for his contributions to liquid crystals and polymers.

An essential pre-requisite for the mesomorphism to occur is that the molecule must be anisotropic in shape like a disc or a rod. Industrial lubricants generally exist in liquid crystalline, *i.e.*, mesomorphic state. Depending on the detailed molecular structure, the system may pass through one or more mesophases before it is converted into the isotropic liquid. Conversion into the intermediate states may by carried out either by ***thermotropic mesomorphism*** (*i.e.*, by thermal processes) or by ***lyotropic mesoprophism*** (*i.e.*, by the intervention of the solvent). The first temperature at which a solid changes into a turbid liquid is known as ***transition temperature.*** The second temperature when the turbid liquid changes into a clear liquid is known as ***melting point.*** For *p*-cholesteryl benzoate, the changes may be expressed as :

$$\underset{\text{(Solid)}}{p\text{-Cholesteryl benzoate}} \xrightleftharpoons{145^\circ\text{C}} \underset{\text{(Liquid crystal)}}{p\text{-Cholesteryl benzoate}} \xrightleftharpoons{178^\circ\text{C}} \underset{\text{benzoate (Liquid)}}{p\text{-Cholesteryl}}$$

Those substances which exhibit liquid crystal behaviour are highly stable and do not decompose on heating.

[I] Other Examples of Liquid Crystals

A few examples of substances showing liquid crystal behaviour are given in table-1.

Table–1. Different liquid crystals

S. No.	Name	Formula	Transition temp. (°C)	Melting point (°C)
1.	*p*-Azoxyanisole	$CH_3OC_6H_4.NONC_6H_4OCH_3$	116	135
2.	*p*-Azoxyphenetole	$C_2H_5OC_6H_4NONC_6H_4OC_2H_5$	137	167
3.	*p*-Methoxy cinnamic acid	$CH_3OC_6H_4CH = CHCOOH$	170	185
4.	Anisaldazine	$CH_3OC_6H_4CH = NN = CHC_6H_4OCH_3$	165	180
5.	Diethyl benzidine	$C_2H_5\ NHC_6H_4.C_6H_4.NHC_2H_5$	116	121
6.	Mercury di-(*p*-ethoxybenzal-aminophenyl)	$Hg(C_6H_4N = CHC_6H_4OC_2H_5)_2$	205	272

[II] Vapour Pressure-Temperature Curves

The phase changes occurring during the conversion of an ordinary solid into liquid and gaseous state is represented as

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

However, the phase changes involved in the case of a solid showing mesomorphic behaviour is represented as :

$$\text{Solid} \rightleftharpoons \underset{\text{(Mesomorphic state)}}{\text{Liquid crystal}} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Vapour}$$

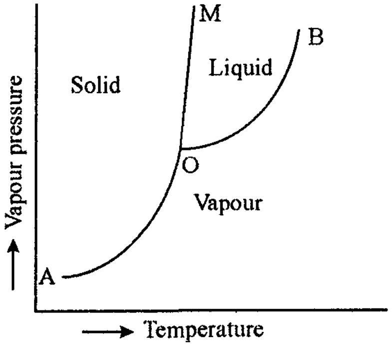


Fig. 14. Vapur pressure-temperature curves for an ordinary substance.

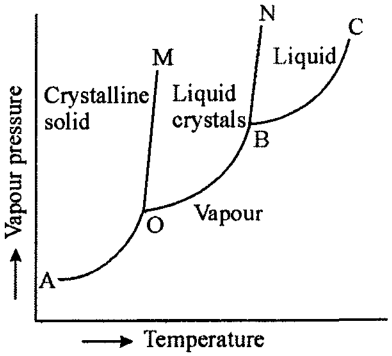


Fig. 15. Vapour pressure-temperature curves for a substance undergoing mesomorphic change.

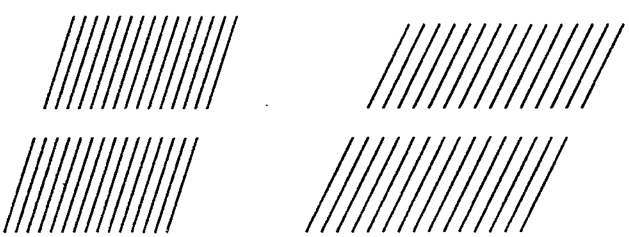
The above phase changes are represented by pressure-temperature ($p - t$) curves as shown in figure. (14) and (15). In fig (10), AO is the vapour pressure curve of the substance in the solid (crystal) state and OB is the vapour pressure curve of the same substance in the liquid state. So, along AO, the solid (crystal) phase is in equilibrium with the vapour phase. Along OB, the liquid phase is in equilibrium with the vapour phase. At O, all the three phases, *viz.*, solid (crystal), liquid and vapour exist in equilibrium with each other. The point O is thus known as ***triple point.*** It is also the melting point of the solid or the freezing point of the liquid. The curve OM indicates the effect of varying pressure on the melting point (or freezing point) of the substance. The solid, liquid and vapour phases exist singly in areas shown in figure (14).

In figure (15), AO is the vapour pressure curve of the solid crystal, OB is the vapour pressure curve of the liquid (*i.e.*, liquid crystal) and BC is the vapour pressure curve of the isotropic liquid. At O known as transition point, solid crystal changes into liquid crystal and at B, known as melting point, the liquid crystal changes into clear liquid. Thus, points O and B are the two triple points of the system. At O, the three phases namely solid crystal, liquid crystal and vapour coexist in equilibrium with one another. At B, the three phases namely liquid crystal, liquid and vapour coexist in equilibrium with one another. The curve OM shows the effect of pressure on the transition temperature, while the curve BN shows the effect of pressure on the melting point of the substance. The solid crystal, liquid crystal, liquid and vapour phases exist singly in areas shown in figure (15).

[III] Classification of Thermotropic Liquid Crystals

Friedel introduced the terms *mesomorphic state, mesoform* or *mesophase* to show that liquid crystals are intermediate between solid crystals and isotropic liquids. He showed that they fall into three categories : (i) *Nematic* (ii) *Smectic* (iii) *Cholesteric.*

(1) Nematic liquid crystals. Nematic or thread like liquids were given the name because mobile threads are often visible in them. X-ray diffraction shows diffuse halos very similar to those found in the isotropic liquids and in the same positions but somewhat sharper, indicating that the ordered regions are larger, or better ordered or both. There is no sign of a layer like structure, but it is assumed that the molecules are aggregated into swarms with the long axes of the molecules parallel or nearly so, as shown in figure (17). The anisotropy involves a pronounced tendency for the molecules to be parallel in group swarms. The application of quite small electric or magnetic fields orients the swarms in the same direction. The electric dipole moment of a nematic swarm is about 10^{15} times that of a single molecule, indicating that the number of molecules in the swarm is of the order of



Solid crystalline Smectic

Fig. 16.

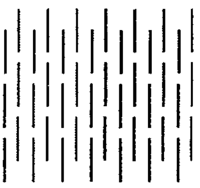
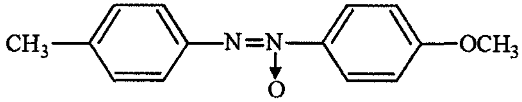


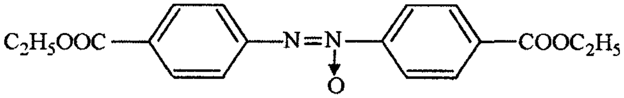
Fig. 17.

10^5. The nematic liquids lose their turbidity, becoming clear, when the swarms are oriented in an electric or magnetic field. Near the solid surface, the swarms tend to orient themselves at the same angle to the surface, producing an oriented layer of molecules in the liquid.

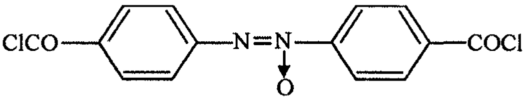
The anomalous viscosity is found in nematic liquids. The flow of nematic liquids is very similar to that of isotropic liquids. The examples of nematic liquid crystals are a number of rather elongated aromatic molecules, especially those containing the azoxy group, *e.g.*, *p*-azoxyanisole,



and ethyl p-azoxybenzoate,



are isotropic but the corresponding acid chloride,



is not a liquid crystal, showing that quite fine details of arrangement of attractive groups are important in deciding whether the liquid is isotropic or doubly refracting.

(2) Smectic liquid crystals. Smectic state is shown by common soaps at high temperatures (≈ 200° C) or in presence of water and so the name given to this phase, *i.e.*, smectic means soap like.

Smectic liquid crystals do not flow as normal liquids but they flow in layers. The layers can slide over one another, because of weak forces of attraction. The smectic state is more ordered than the nematic type, because it has an additional one-dimensional translational order. In compounds where both states exist, smectic state occurs at a lower temperature.

Certain cases are known in which the crystalline solid passes through one smectic phase before being changed into the liquid. The temperature of transition from one phase to another is also fixed. For example, cholesteryl myristate has two mesomorphic phases, before it is changed into the liquid.

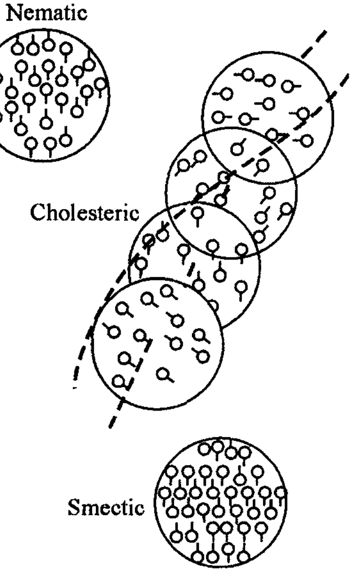


Fig. 18.

$$\text{Crystal} \xrightleftharpoons{78^\circ\text{C}} \text{Mesophase I} \xrightleftharpoons{78^\circ\text{C}} \text{Mesophase II} \xrightleftharpoons{83^\circ\text{C}} \text{Liquid}$$

On cooling, the above changes are exactly reversed.

(3) Cholesteric liquid crystals. Some liquid crystals, such as chloresteryl esters show in addition to nematic behaviour, some colour effect under polarised light. So, a special name *cholesteric* phase is given.

Because of optically active molecules, the cholesteric state has a spontaneous twist about an axis normal to the director. The helical arrangement is left or right handed. This state has an appreciable optical rotatory power. The plane of polarised light is rotated by a few thousand degree per mm which is thousand times greater than the rotatory power of a solid crystal, *e.g.*, quartz. The pitch of the helix decreases with rise of temperature and wavelength of reflection falls out.

Only a few types of chemical constitution favour the formation of liquid crystals. It is desirable that the molecules should be long and that some strongly attractive groups should be present to promote adhesion between adjacent molecules. Several esters and esters of cholesterol form smectic liquid crystals, also a few soaps including thallous soaps and ammonium oleate. (Most of the soaps do not form liquid crystals).

[IV] Uses of Liquid Crystals

(i) They are used in electronic display instruments because of their electrical and optical properties. For example, they are used in gas-liquid chromatography and in digital displays like digital wrist watches, pocket calculators.

Seven segment cell. The substances used for liquid crystal displays in pocket calculators and wrist watches are nematic type liquid crystals. Their optical characteristics are affected by an electric field. A thin film of liquid crystal is put between transparent electrodes that are arranged on glass in special patterns. When a particular electrode segment is energised, the orientations of the molecules in the liquid crystal vary and so the substance becomes opaque. By activating appropriate segments in this fashion, different letters or numbers can be formed. An important advantage of these displays is that they consume very little energy and so the battery lasts longer.

(ii) They are used for detecting tumours in the body by using a method called *thermography*.

(iii) They are used as solvents for studying the structure of anisotropic molecules spectroscopically.

(iv) They are used as commercial lubricants.

(v) They are most suited to biological functions. As the colour of liquid crystals depend sensitively on temperatures, these are, therefore, used in measuring skin temperature. The proteins and fats, which are important constitutents of food, also exist or get changed into liquid crystal state before digestion and are, therefore, easily assimilated in the body. The state also plays an important role in nutritional and other processes.

[V] Theory of Liquid Crystals

At one time urbid liquids were considered to be heterogeneous systems, consisting of minute particles in suspension. However, this suggestion was

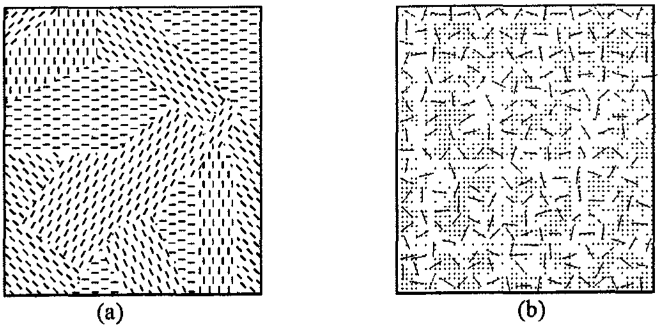

(a) (b)

Fig. 19. Arrangement of molecules in anisotropic liquid crystals and isotropic liquid.

discarded, as neither any particles could be detected microscopically nor any could be separated by filtration. Lehmann showed that turbid liquids are homogeneous and that turbidity is in reality, a simple optical effect.

Bose proposed ***swarm theory*** to explain the turbidity. According to him, since mesomophic behaviour is exhibited by substances having long chains, their free rotation is restricted and they tend to arrange themselves in parallel formations. So, a number of groups or swarms are obtained. The molecules in any one swarm are parallel to one another but may not be parallel to those present in any other swarm. [figure 19 (a)].

Each swarm which consists of several molecules arranged parallel to one another, is considered as a small crystal. So, a turbid liquid is viewed as consisting of a series of small crystals distributed randomly in the body of the liquid. Lehmann actually observed that each particular swarm appears as a transparent liquid crystal when seen under a microscope. The turbidity of the liquid crystals is simply due to the scattering of light at the boundaries between the various swarms. This effect is similar to that observed when glass (transparent substance) is finely powdered. Each piece is transparent but when they come together, the mass appears opaque.

On increasing the temperature of liquid crystals, the molecular motion increases and an interchange between the swarms occurs. The swarms become smaller and smaller with rise in temperature and at a certain temperature, the swarms become smaller than half the wavelength of light. They are then too small to scatter light. Thus, the turbidity disappears and the liquid becomes clear. The anisotropic properties and double refraction due to orientation of molecules within the swarms disappear. The liquid becomes singly refracting and isotropic. This temperature is the melting point of the substance. In an isotropic liquid, the arrangement of molecules is as shown in [figure 17 (b)].

According to swarm theory, the clearance of turbidity should be gradual as the swarms become smaller and smaller with rise in temperature. But it is actually observed that the turbidity of the liquid crystals clears off all of a sudden at one particular temperature, *viz.*, melting point is the weakness of this theory.

On the basis of thermodynamics, it can be shown that if the swarms decrease in size suddenly at a particular temperature, then the vapour pressure curve of the liquid crystals should also rise rapidly at that temperature. However, the rise in the vapour pressure of the liquid crystals with rise in temperature is gradual and not sudden as shown in figure (14). This observation is in accordance with the theory.

This theory has not been finally accepted, as it cannot explain many facts. For example, it is not clear why certain long chain molecules do form liquid crystals while several others do not do so.

[VI] Molecular Arrangement in Various States of Liquid Crystals

In nematic state, the arrangement of the molecules is parallel but now there are no layers. The arrangement is irregular and the molecules now have greater freedom of motion [figure 20 (ii)]. This arrangement would still lead to difference in properties in different directions, *i.e.*, lead to anisotropic character.

In smectic state, the molecules are arranged in nearly parallel layers as shown in [figure 20 (i)]. The layers are held at regular distances from one another but the molecules within each layer are not regularly spaced. The anisotropic properties, *e.g.*, double refraction can be easily understood.

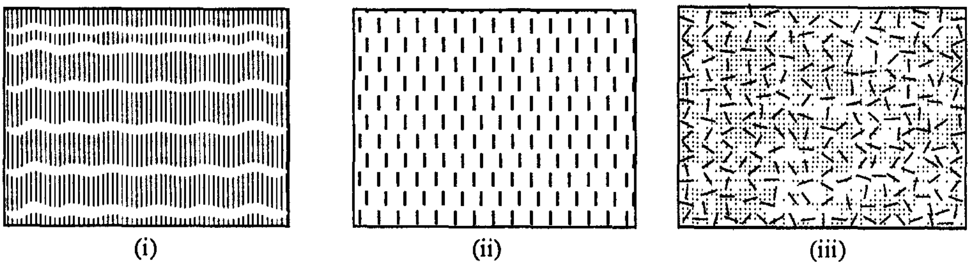

(i) (ii) (iii)

Fig. 20.

In case of normal clear/liquid, the mlecular arrangement is as shown in [figure 20 (iii). The molecules are now moving completely at random and so there is no scope for double refraction or any anisotropy. The substance is fully isotropic like a true liquid.

[VII] Differences Between Liquid Crystal, Solid and Liquid

(1) The liquid crystals possess a structure between that of a liquid and a crystalline solid.

(2) In a liquid, the molecules have disordered arrangement and they are able to move relative to each other. In a solid crystal, the molecules have fixed ordered arrangement in fixed positions. In liquid crystals, the molecules have an ordered internal arrangement, *i.e.*, are arranged parallel to each other but can flow together like a liquid. Therefore, the liquid crystals have fluidity of liquids and a laterally ordered arrangement of crystals.

(3) True liquids in pure state, except mercury and other molten metals are generally transparent, but liquid crystals show turbidity, *i.e.*, are translucent.

(4) True liquids and crystals having a symmetrical arrangement in all directions are *isotropic, i.e.*, they possess same physical properties in all directions, but liquid crystals are *anisotropic*, *i.e.*, they exhibit different physical properties in different directions.

(5) The anisotropicity of liquid crystals is seen particularly in their optical behaviour, *e.g.*, they show double refraction (*i.e.* splitting unpolarised light into two beams of polarised light having polarisation perpendicular to one another) and give interference patterns in polarised light.

4·7. THERMOGRAPHY

The phase changes seen on heating a solid showing mesomorphic behaviour are sometimes represented in the form of time-temperature curve as shown in figure (21). This is known as ***thermography***. When a solid is heated, its temperature starts rising along the curve AB. This process continues till the solid starts changing into the liquid crystals. This occurs at point B. The temperature then remains constant till both the phases, *viz.*, solid and liquid crystals are present. This process is represented by the curve BC. At C, when the solid completely changes into liquid crystals, the temperature again starts rising along CD. This continues till the liquid crystals start converting into the liquid at point D. The temperature again remains constant as long as both the phases, *viz.*, liquid crystals and the liquid are present together. This is shown by the curve DE. When the liquid crystals completely change into liquid, at E, the temperature again starts rising along EF. This continues as long as liquid starts changing into vapour phase at F. The temperature again becomes constant and remains so as long as the liquid and vapour phases are present together along the curve FG. When vapour phase is present, the curve would again begin to rise from the point G. Figure (22) shows the thermographic behaviour of an ordinary solid.

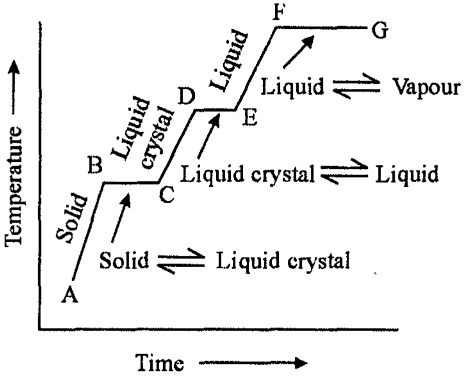


Fig. 21. Thermographic behaviour of a solid showing mesomorphism.

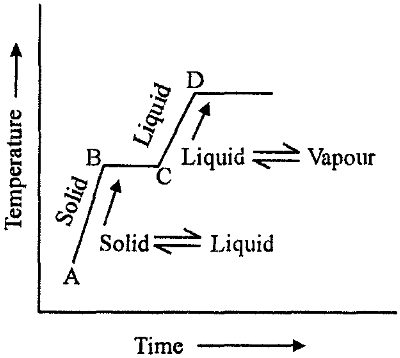


Fig. 22. Thermographic behaviour of an ordinary solid.

EXERCISES

[I] Long Answer or Essay Type Questions

1. Discuss briefly the general properties of liquids.
2. State and explain vapour pressure of a liquid. What is the effect of temperature on vapour pressure of a liquid ?
3. Define the terms viscosity, coefficient of viscosity and fluidity. Discuss the effect of temperature on viscosity of a liquid.
4. Define surface tension. What are its units? Write the Ramsay and Shield's equation and explain the terms used in it.
5. Define viscosity. How will you measure the coefficient of viscosity? What is the effect of temperature on viscosity?
6. What are liquid crystals? How are they classified? Differentiate clearly between smectic liquid crystals and nematic liquid crystals. What are cholesteric liquid crystals?

[II] Short Answer and Very Short Answer Type Questions

1. Define surface tension. What is its unit?
2. What is the effect of temperature on surface tension?
3. How does vapour pressure vary with temperature?
4. Write a short note on vapour pressure of a liquid.
5. Explain why :
   (i) Melting point of ice is lowered on increasing the pressure while that of monoclinic sulphur is raised with increase of pressure ?
   (ii) At the boiling point, the temperature of liquid does not rise although it is being heated?
   (iii) Drops of liquids are spherical in shape ?
   (iv) The boiling point of liquid rises on increasing the pressure?

(v) Glycerol is more viscous than water?

(vi) Water wets the glass surface while mercury does not?

[**Ans**.

(i) Density of ice is lower than that of water, while the density of monoclinic sulphur is greater than that of liquid sulphur.

(ii) Heat is used up in overcoming forces of attraction and making up the loss of energy due to evaporation.

(iii) Due to surface tension, the liquids tend to decrease the area to a minimum and the area of a sphere is minimum.

(iv) The boiling point is the temperature at which the vapour pressure of the liquid is equal to the pressure above it. On increasing the pressure above the liquid, the boiling point thus rises.

(v) Hydrogen bonding is more predominant in glycerol than in water.

(vi) Because the forces of adhesion between water and glass are greater than the forces of cohesion between water molecules but Hg-Hg intermolecular forces are greater than the forces of adhesion between mercury and glass.]

5. Explain the following terms :

(a) Thermography (b) Seven segment cell (c) Free volume in a liquid.

6. Give a brief account of the molecular arrangements which exist in different states of liquid crystals.

7. How would you account for the turbidity observed in liquid crystals?

8. What do you understand by mesomorphic state ?

9. Write a note on intermolecular attractions which exist in liquids.

10. Write short notes on the following :

(i) Dipole-dipole interactions (ii) London forces

(iii) Hydrogen bonding (iv) Radial distribution function

11. Mention the main structural differences between smectic and nematic liquid crystals.

12. Mention the differences between solid, liquid crystal and a liquid.

13. Explain thermography.

[III] Multiple Choice Questions

1. Surface energy is defined as :

(a) Work done to decrease the surface area by 1 cm^2

(b) Work done to increase the surface area by 1 cm^2

(c) Work done to keep the surface area constant

(d) Work done to increase the surface length by 1 cm.

2. Vapour pressure is related to surface tension according to :

(a) $d\log p = \frac{2\gamma M}{rdRT}$ (b) $\log p = \frac{2\gamma M}{RT}$ (c) $d\log p = \frac{\gamma}{D-d}$ (d) $\log p = \frac{M\gamma^{1/4}}{D}$

3. The reciprocal of viscosity is known as :

(a) Anti-viscosity (b) Intrinsic viscosity

(c) Reduced viscosity (d) Fluidity

4. p-Azoxyanisole is :

(a) Nematic liquid crystal (b) Smectic liquid crystal

(c) Cholesteryl liquid crystal (d) Solid crystal

5. The unit of coefficient of viscosity in SI unit is :

(a) $kg\ m^{-1}\ s^{-1}$ (b) $kg\ m^{-2}\ s^{-1}$

(c) $kg^{-1}\ m^{-1}\ s^{-1}$ (d) $kg\ m^{-1}\ s^{-2}$

6. With rise in temperature, the surface tension of the liquid :
   (a) Increases
   (b) Decreases
   (c) Remains constant
   (d) Sometimes increases and sometimes decreases
7. The vapour pressure of water at 100°C is :
   (a) 76 cm (b) 0 cm (c) 760 cm (d) 0.1 atm
8. A relation between vapour pressure and temperature is known as :
   (a) Gas equation (b) Clapeyron equation
   (c) Clausius equation (d) Clausius-Clapeyron equation
9. Liquid crystal exhibits :
   (a) Isotropy (b) Anisotropy (c) Monotropy (d) Azeotropy
10. Debye forces involve.
    (a) Dipole-dipole interactions
    (b) Dipole-induced dipole interactions
    (c) Temporary dipole-induced dipole interactions
    (d) Hydrogen bonding

[IV] Fill in the Blanks

1. The arrangement of molecules in a liquid is .... range order.
2. The quasi-crystalline model considers a liquid as a .... solid.
3. Water exists in the liquid state at ordinary temperature. This is due to the presence of ....
4. A liquid has a very high value of molar heat of vaporisation. The intermolecular forces present in the liquid are ....
5. p-Azoxyanisole forms liquid crystals of .... type.
6. The liquid crystals possessing limiting mobility and flowing in layers are of ....type.
7. Dipole-dipole interactions in liquid are also called .... forces.
8. The concept of free volume in liquids was given by ....
9. The forces developed due to interactions between a dipole and an induced dipole are called .... forces.
10. In hydrogen bonding, a hydrogen atom is bonded to a highly .... atom through a covalent bond.

[V] True or False

State whether the following statements are true (T) or false (F) ?

1. In the smectic phase, the molecules are arranged in parallel layers.
2. London forces include temporary dipole-induced dipole interactions in liquid.
3. Cybotactic groups mean large number of clusters of molecules of liquid.
4. Hydrogen bonding involves strong forces of attraction.
5. Turbid liquids or liquid crystals exhibit anisotropy.
6. Transition point is always less than melting point of a liquid crystal.
7. Nematic liquid crystals are thread like mesomorphic substances.
8. The property of cholesteric liquid crystals is used in monitoring the body temperature.
9. Cholesteryl benzoate is a smectic type liquid crystal.

10. Liquids which have high magnitude of vander Waals forces have both higher melting and boiling points.

ANSWERS

[III] Multiple Choice Questions

1. (b) **2.** (a) **3.** (d) **4.** (a) **5.** (a)
6. (b) **7.** (a) **8.** (d) **9.** (a) **10.** (b).

[IV] Fill in the Blanks

1. Short **2.** modified **3.** hydrogen bonding **4.** strong **5.** nematic
6. smectic **7.** Keesom **8.** Eyring **9.** Debye **10.** electronegative

[V] True or False

1. (T) **2.** (T) **3.** (T) **4.** (F) **5.** (T)
6. (T) **7.** (T) **8.** (T) **9.** (F) **10.** (T).

❑❑❑

Chapter 5

SOLID STATE

5·1 CLASSIFICATION OF SOLIDS

Out of different states of matter, gas is *characterised only by high degree of compressibility and fluidity.* The molecules have a zig-zag random motion and do not exert any appreciable attraction on one another. On the contrary, solids are *characterised by incompressibility, rigidity and mechanical strength.* The molecules, atoms or ions in solids are closely packed. Thus, we can conclude that while in gases we have a chaotic motion, in solids there is an orderly molecular arrangement. Solids are of the following types :

(a) Crystalline solids, (b) Amorphous solids, (c) Poly-crystalline or micro-crystalline solids.

[I] Crystalline Solids

The solids in which atoms, ions or molecules are arranged in a definite pattern, constantly repeated, giving a definite geometrical shape, characteristic of the substance and independent of the sources from which they have been obtained are called ***crystals***. A ***crystalline solid*** is an aggregate of minute crystals, packed together in a well-defined order.

Properties of crystals. (i) In a crystal, there is perfect and well-ordered arrangement of molecules throughout the entire body, each molecule is surrounded by a set of other molecules in a definite symmetrical way.

(ii) A crystal when melted expands only about 10% in volume or about 3% in inter-molecular spacing.

(iii) The crystals are bounded by surfaces which are planar and arranged on a definite plan.

(iv) The crystals have a rigorous geometrical order. Thermal motions cause disorder. It is clear that if a small region of disorder is introduced into a crystal, it would cause disturbance in the long range and destroys the crystalline arrangement. This explains the reason of sharp melting points of crystalline substances.

(v) When subjected to a mechanical stress, a crystal tends to fracture along a perfectly definite direction.

(vi) The important feature of crystal is the periodicity of arrangement along with regularity.

(vii) A crystalline substance is anisotropic, *i.e.*, its physical properties like mechanical, electrical and optical properties are different in different directions. For example, the velocity of light passing through a crystal changes with the direction in which it is measured. Moreover, in silver iodide crystal, the coefficient of thermal expansion is positive in one direction and negative in another direction. Anisotropy offers a strong evidence for the presence of well ordered molecular arrangement in crystals.

[II] Amorphous Solids

The solids which do not have any definite geometrical shape are called ***amorphous solids,*** *e.g.,* glass, rubber, plastic etc.

Physical properties of amorphous solids. (i) Amorphous solids are considered to be super-cooled liquids in which the force of attraction holding the molecules together is so great that the substance is rigid and there is no regularity of structure.

(ii) Amorphous solids do not have sharp melting points. They gradually soften on heating. Absence of sharp melting point suggests the absence of long-range order in amorphous solids.

On increasing the temperature, the viscosity of amorphous substances decreases and gradually changes into the liquid state.

(iii) In amorphous solids, there is non-periodicity of the arrangement alongwith no regularity.

(iv) Amorphous solids are isotropic, *i.e.*, their physical properties like mechanical, thermal, electrical properties are same in all directions. In amorphous substances, the particles are randomly arranged and disordered. Due to this, all directions are equivalent and so all the properties remain the same in all directions.

[III] Micro-crystalline or Poly-crystalline Solids

In many solids, we may not clearly see the shape of the crystals, because several small or micro-sized crystals are tightly packed together without any specific order. Therefore, a substance, which in fact is crystalline, but is superfine to be seen as crystal, is called a ***micro-crystalline*** or ***poly-crystalline solid,*** *e.g.*, several metals and alloys. A copper wire does not look to be a crystalline substance, but on examining its surface by a microscope, its crystalline nature appears. So, copper wire is said to have a micro-crystalline structure. In micro-crystalline solids, the micro-crystals are randomly oriented, so the former will appear to be isotropic, even when each single crystal is anisotropic.

5·2 WHAT IS A CRYSTAL ?

A crystal is a solid which is composed of atoms arranged in an orderly repetitive array. This is the shortest but complete definition of a crystal.

In other words, a crystal may also be defined as, ***"a homogeneous anisotropic substance (substance whose physical properties such as refractive index, electrical conductivity, magnetic susceptibility etc. are different in different directions) having a definite geometrical shape with surfaces that are usually planar and have sharp edges."***

To study a crystal, one has to examine its external form as well as its internal form. Hauy suggested that the external form of a crystal is not its main characteristic. It is only the internal form which gives the true picture of a crystal. External form of a crystal depends upon the condition of growth which may suppress the growth of faces and angles, but the angles between the faces will always remain the same whatever the external conditions may be.

5·3 EXTERNAL FEATURES OF A CRYSTAL

The external features of a crystal are as follows :

(1) Faces : The crystals are bounded by surfaces which are usually planar and arranged in definite pattern. These surfaces are called ***faces*** of the crystal.

Faces are of two types, *viz.*, *like faces* and *unlike faces*. For example, fluorspar is generally obtained in cubes, alum in regular octahedron, all of which have *like faces.* On the other hand, galena crystals are a combination of cubical and octahedral faces, *i.e.*, galena has *unlike faces*. The faces with larger areas have a slower rate of deposition of atoms or ions.

(2) Forms : All the faces corresponding to a crystal are said to constitute a ***form***. The like faces constitute the form called *simple* form of crystal, whereas a crystal consisting of two or more simple forms is called a combination.

(3) Edge : When two adjacent faces intersect, we get an ***edge.***

(4) Solid angle : When three or more edges intersect, we get a ***solid angle.***

(5) Interfacial angle : The angle between the normals to the two intersecting faces is called an interfacial angle. In figure (1), there are two intersecting faces A and B. The angle between the normals to these faces is the interfacial angle C.

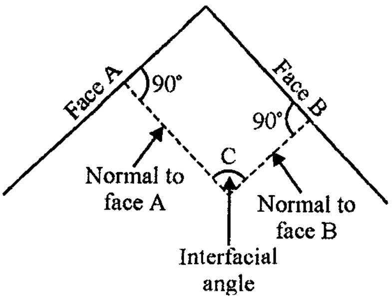


Fig. 1. Interfacial angle.

(6) Relationship between faces, edges and interfacial angles : A crystal is bounded by three external elements which are plane faces, straight edges and interfacial angles. These are inter-related by the following equation,

$$f + c = e + 2$$

where f = Number of faces,
c = Number of interfacial angles,
e = Number of edges.

(7) Zone and zone-axis : The faces of a crystal occur in sets. These sets are known as ***zones***. These zones meet in parallel edges or would do so if the planes of faces were extended. Each zone forms a complete belt around a crystal. A line drawn through the centre of a crystal in a direction parallel to the edges of a zone is known as ***zone axis.***

5·4 LAWS OF CRYSTALLOGRAPHY

That branch of science which deals with geometry, structure and properties of crystals and crystalline bodies is known as ***crystallography.*** There are three fundamental laws of crystallography, *viz.*,

(i) Law of constancy of angle,
(ii) Law of constancy of symmetry and
(iii) Hauy's law of rational intercepts.

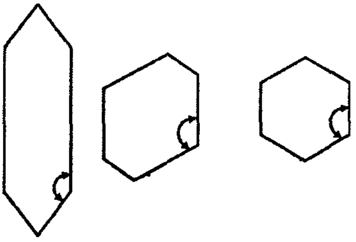


Fig. 2. Constancy of angles.

[I] Steno's Law of Constancy of Angle

According to this law, ***"under the same physical conditions, the angle between the corresponding faces on various crystals of the same substance is constant."***

Steno (1669) gave this law after performing a number of measurements on rock crystal specimens obtained from various places. In figure (2), the three crystals of the substance are shown in two dimensions, their shapes are different, but the angles of intersection of two corresponding faces remain the same.

[II] Law of Constancy of Symmetry

According to this law, ***"all crystals of one and the same substance have the same symmetry."***

On rotating a crystal about an axis or reflection across a plane, the appearance of a crystal remains the same, *i.e.*, a crystal shows a geometrical symmetry which may be about a centre, an axis or a plane. The total number of planes (axes) and centres of symmetry of a crystal are known as its ***elements of symmetry***. So, the elements of symmetry are :

(a) *centre of symmetry*, (b) *axis of symmetry*, (c) *plane of symmetry.*

(a) Centre of Symmetry : *Centre of symmetry of a crystal is such a point that any line drawn through this point intersects the surface of the crystal at equal distances in both directions.*

(b) Axis of Symmetry : *An axis of symmetry is an imaginary line, about which the crystal may be rotated such that it presents the same appearance more than once during one complete revolution.*

If the crystal presents the same appearance *n* times in one complete revolution, the axis is said to be one of **n-fold axis.** The only values of *n* can be 2, 3, 4 and 6, when the axis is known as **two-fold** (or **diad-axis**), **three-fold** (or **triad-axis**), **four-fold** (or **tetrad-axis**) and **six-fold** (or **hexad-axis**), respectively. The angles between pairs of axes of symmetry are 30°, 45°, 60°, and 90°. The axis of symmetry is always perpendicular to a possible crystal face and parallel to a possible interfacial crystal edge.

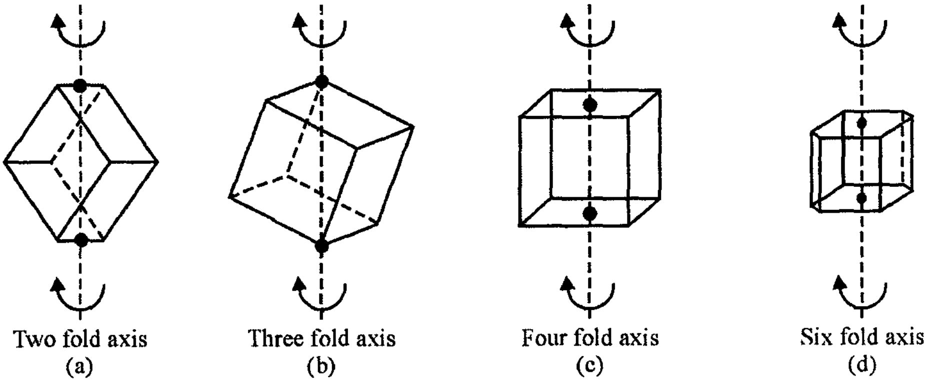

Two fold axis (a) Three fold axis (b) Four fold axis (c) Six fold axis (d)

Fig. 3. Axis of symmetry.

(c) Plane of Symmetry : *If a crystal can be divided by an imaginary plane passing through its centre into two equal portions each of which is a mirror image of the other, the crystal is said to possess a plane of symmetry.*

It must be noted that plane and axis of symmetry constitute the elements of symmetry, while the centre of symmetry is not an element of symmetry. Furthermore, a crystal may have one or more than one plane or axis of symmetry, but it cannot have more than one centre of symmetry.

[III] Hauy's Law of Rational Intercepts

See §5.14.

5·5 POINT GROUPS

Any crystal or any molecule of the crystal will have some combinations of symmetry elements. These combinations of symmetry elements are known as ***point groups***. The general theory of groups is applicable to symmetry operations. These point groups are called ***classes*** or ***systems***. We have 32 theoretically possible different combinations of the symmetry elements. In other words, maximum number of point groups or classes for any symmetrical body is 32.

Symmetry operations generated by symmetry of elements

A symmetry operation is defined as a movement of a body, such that afer the movement has been carried out, every point of the body is coincident with an equivalent point of the body in its original orientation. We have four principal symmetry operations for repeating a figure. These are : (a) translation operation. (b) rotation operation (c) reflection operation and (d) inversion through a point.

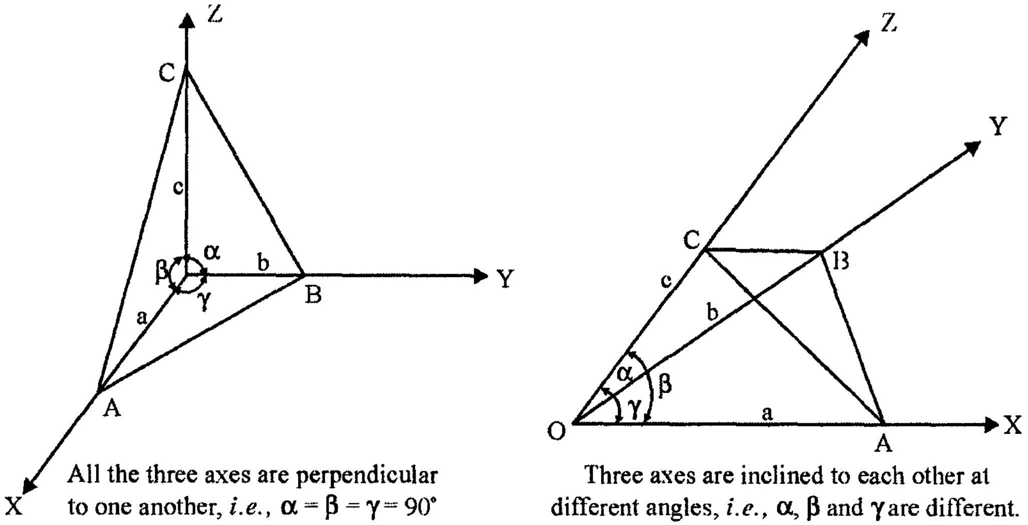
So, 230 forms of crystals fall into 32 point groups or classes, each class having same elements of symmetry, *i.e.*, same axes, planes and centre of symmetry. These 32 classes are grouped into seven different classes. These are : cubic, tetragonal, monoclinic, triclinic, hexagonal, rhombohedral (or trigonal) and orthorhombic (or rhombic).

5·6 CRYSTALLOGRAPHIC TERMS

In order to describe the geometry of a crystal, we should know the following terms called elements of a crystal.

(a) Crystallographic axes : The geometry of a crystal can be best described in terms of three (See fig.4) non-co-planar coordinate axes, called crystallographic axes. The three axes called X, Y and Z, may coincide or be parallel to the lines of intersection, *i.e.*, edges of any three faces which do not lie in the same plane. These axes may be mutually at right angles to each other or may be inclined to each other at different angles. As per convention, the angle between axes in Y and Z directions is represented by α, angle between Z and X directions by β and the angle between X and Y direction by γ.

(b) Standard or unit plane : Any face of the crystal may cut one or more of the crystallographic axes. The face which cuts all the three axes is called ***standard or unit plane***. The distances of the points where the standard plane cuts the three axes from the origin are called ***intercepts***. The intercepts a, b and c on X, Y and Z axis are called ***crystal parameters*** (See figure 4).



All the three axes are perpendicular to one another, *i.e.*, $\alpha = \beta = \gamma = 90°$

Three axes are inclined to each other at different angles, *i.e.*, α, β and γ are different.

Fig. 4. Crystalligraphic axes and intercepts.

(c) Axial ratio : The actual values of unit intercepts a, b and c on X, Y and Z axes, respectively depend on the point O, where all the three axes meet. In practice, the ratio $a : b : c$ on different axes will be the same for all crystals of the same substance. The ratio $a/b : 1 : c/b$ or $a : b : c$ is called the ***axial ratio***.

5·7 CRYSTAL SYSTEMS

As discussed above, there are 230 crystal forms possible, and practically all have been observed. On the basis of their symmetry, these 230 crystal forms may be grouped into 32 classes and these in turn may be referred to seven crystal systems. All the crystals belonging to a particular system are characterised by the fact that though they may not all have the same elements of symmetry they can all be referred to a particular set of crystallographic axes which differ from system to system in terms of length of the various axes and angles of inclination between the axes. The following table lists the seven crystal systems, their axial characteristics, minimum symmetry necessary for each system and some examples of each system.

Table–1. Crystal systems and their characteristics

System	Axial characteristics	Minimum symmetry	Examples
1. Cubic	Three axes at right angles. Unit distances : $a = b = c$	Four three-fold axes	NaCl, KCl, Diamond, CaF_2 (fluorspar)
2. Tetragonal	Three axes at right angles, only two of equal length. Unit distances : $a = b \neq c$	One four-fold axis	SnO_2 (cassiterite), TiO_2 (rutile)
3. Monoclinic	Three axes, all unequal. Two axes at right angles, the third inclined to these at an angle other than 90°.	One two-fold axis	$Na_2SO_4.10H_2O$, $Na_2B_4O_7.10H_2O$, S (monoclinic)

4. Triclinic	Three axes of unequal length, all inclined at angles other than 90°.	None	$K_2Cr_2O_7$, H_3BO_3, $CuSO_4.5H_2O$
5. Hexagonal	Two axes of equal length in one plane making an angle 120° with each other, and a third axis at right angles to these and of unequal length. Unit distances : $a = b \neq c$	One six-fold axis	PbI_2, Mg, Beryl, ZnO (zincite)
6. Rhombohedral (Trigonal)	Three axes of equal length, with all angles equal but other than 90°. Unit distances : $a = b = c$.	One three-fold axis	$NaNO_3$, $CaCO_3$ (calcite)
7. Orthorhombic (Rhombic)	Three axes at right angles but all of different length. Unit distances : $a \neq b \neq c$	Three two-fold axes	Sulphur (rhombic), $BaSO_4$ (baryta), $PbCO_3$ (cerrusite).

Problem 1. ***Classify the following unit cells into proper systems.***

(i) $a = 10.8Å$, $b = 9.47Å$, $c = 5.2Å$.

$\alpha = 41°, \beta = 83°$ and $\gamma = 93°$.

(ii) $a = b = 10.73Å$, $c = 14.3Å$

$\alpha = \beta = 90°, \gamma = 120°$.

Solution. (i) In this case, $a \neq b \neq c$ and no two axes are at right angles to each other. This is characteristic of a triclinic structure. Hence, the unit cell belongs to *triclinic crystal system.*

(ii) As $a = b \neq c$ and $\alpha = \beta = 90°$, it is characteristic of a hexagonal structure and so the unit cell belongs to hexagonal crystal system.

5·8 SPACE LATTICE

The position of atoms, molecules or ions in a crystal, relative to one other in space, are usually designated by points. Such a representation is called ***space lattice.*** A space lattice is thus defined as ***an array of points showing how molecules, atoms or ions are arranged at different sites in three dimensional space.***

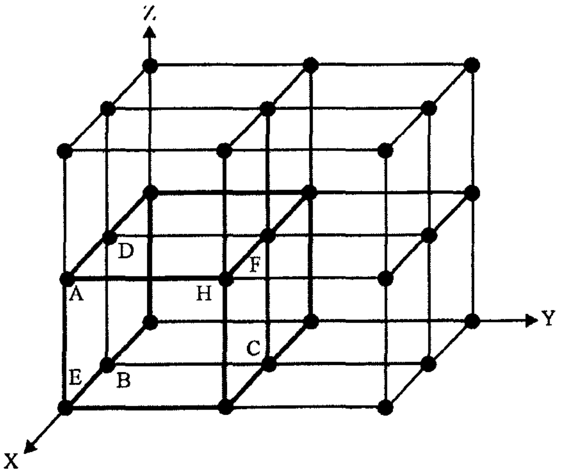


Fig. 5. Space lattice.

An example of array of points in a three-dimensional space lattice is shown in figure (5). Each point represents an identical atom or group of atoms. The points signify only the position of centres of the constitutent particles, *i.e.*, atoms, ions or molecules, but not their actual size. The most important characteristic of a space lattice is that each point in the space lattice is identical with any other such point and that the distance between any two points must be an integral multiple of the distance between consecutive points.

To gain insight of the internal structure of the crystals, crystallography postulates that any macroscopic crystal of a substance is built up by repetition and extension in all directions of a fundamental structural unit known as ***unit cell.***

5·9 UNIT CELL

It is defined as ***"the smallest geometrical portion of the crystal, which when repeated in three dimensions, would generate the complete crystal."*** Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be, and arranged to give the particular geometrical configuration of the crystal.

The unit cells are of the following types :

(a) Simple or primitive unit cell (P) : The simplest unit cell which has the lattice points at the corners is called a simple or primitive unit cell. It is denoted by *P*.

(b) Non-primitive or multiple unit cell : When a unit cell contains more than one lattice point, it is called a non-primitive or multiple unit cell. It is further sub-divided into the following three categories :

(i) Face-centred unit cell (F) : When in a unit cell, besides the points present at the corners of the unit cell, there is one point at the centre of each face, it is called *face-centred arrangement* or *face-centred unit cell.* It is denoted by *F*.

(ii) Body-centred unit cell (I) : When in a unit cell, besides the points at the corners of the cell, there is one point at the centre within its body, it is called *body-centred arrangement* or *body-centred unit cell.* It is denoted by *I*.

(iii) Side-centre or end face unit cell (C) : When in a unit cell, besides the points at the corners of the cell, the points are located at the centre of any two parallel faces of the unit cell, it is called *side-centred or end face unit cell.* It is denoted by *C*.

Lattice Planes or Net Planes

In a space lattice, all points may be situated in a set of parallel and equally spaced planes, called the lattice planes. If each plane of the set is densely occupied by points, the planes will be widely spaced and if they are sparsely occupied, they will closely spaced. Widely spaced planes form the natural boundaries to the collection of unit cells in a space lattice, *i.e.*, the faces of the crystals. Sparsely spaced planes have not much physical reality. It is observed that law of indices hold good only for planes which contain a large number of lattice points per unit.

5·10 COORDINATION NUMBER

The coordination number of any given sphere in a crystalline structure is defined as the number of spheres by which it is immediately surrounded. The coordination number in a hexagonal and face centred cubical closed packed structures is 12, while in a body centred cubical structure, the coordination number is 8. Greater the coordination number, the more closely packed is the structure. For three types of cubic lattices, the coordination number may be determined as follows :

(a) Simple cubic lattice : In it, one atom is situated at each of the eight corners of the unit cell. According to the geometry of the structure, if we consider an atom at one corner as the centre, it will be surrounded by six equidistant neighbours. So, the coordination number will be six. If a be the side of the unit cell, the distance between the nearest neighbours will be a.

In most types of simple cubic lattices, the coordination number is 6, but in caesium chloride (an exception), the value is 8, because each chlorine atom is surrounded by eight nearest neighbouring ions of caesium. Another difference is that the nearest distances between two neighbouring ions of opposite charges is $\frac{a\sqrt{3}}{2}$ and not a, as in other cases.

(b) Face centred cubic lattice : In it, atoms are situated at the corners and one each at the centre of each face of the unit cell. The nearest neighbour to any atom is situated at a distance of $\frac{a}{\sqrt{2}}$ from it. From the geometry, of arrangement, it can be seen that there are 12 such atoms at a distance of $\frac{a}{\sqrt{2}}$ from any atom. So, the coordination number will be 12.

(c) Body centred cubic lattice : In it, the atoms are situated at the corners of the unit cell and one at the centre of the body. The nearest neighbour to any atom is placed at a distance of $\frac{a\sqrt{3}}{2}$. From the geometry, of arrangement, it can be seen that there are 8 such atoms at a distance of a $\frac{a\sqrt{3}}{2}$ from any atom. So, the coordination number will be 8.

5·11 CALCULATION OF NUMBER OF PARTICLES IN A UNIT CELL

There are two methods for determining the number of particles (atoms, ions or molecules) in a unit cell.

[I] First Method

This method is based on the fact that we should be familiar with the shapes and structures of crystal lattices. This can be further explained as follows :

(i) In simple cubic unit cell, one atom is situated at each corner. So, each atom is shared by 8 unit cells, *i.e.*, its one-eighth part belongs to each cube. Thus, number of atoms, $z = 1/8 \times 8 = 1$ **atom.**

(ii) In body centred cubic unit cell, 8 atoms are situated at 8 corners and 1 atom at the centre of the cube. As each corner atom is shared by 8 unit cells, so sharing of 8 corners $= 8 \times 1/8 = 1$ atom. One atom is placed at the centre and so, $z = 1 + 1 = 2$ **atoms.**

(iii) In face centred cubic unit cell, 8 atoms are situated at 8 corners. So, their share is $8 \times 1/8 = 1$ atom. One atom is situated at the centre of each of the 6 faces which is shared by 2 unit cells. So, the share of 6 faces $= 6 \times 1/2 = 3$ atoms. So, $z = 1 + 3 = 4$ **atoms.**

(iv) In diamond unit cell, 8 atoms are situated at 8 corners of the cube and each atom is shared by 8 unit cells. 6 atoms are present in 6 faces and each atom is shared by 2 unit cells. 4 atoms are also present inside the unit cell.

$$\therefore \qquad z = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 1 + 3 + 4 = \mathbf{8\ atoms.}$$

[II] Second Method

The number of atoms per unit cell can be determined from the knowledge of volume density and molecular weight of the constituent atoms of the cell.

Suppose the edge length of the cubic unit cell be a pm. Then,

Volume of unit cell, $V = a^3\ (\text{pm})^3 = a^3 \times 10^{-36}\ \text{m}^3 = a^3 \times 10^{-30}\ \text{cm}^3$

Mass of crystal in a unit cell

$$= (\text{No. of particles in a unit cell}) \times (\text{Mass of each particle})$$

$$= (z \times m)\ \text{g}$$

$$\text{Density of crystal} = \text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{z \times m}{a^3 \times 10^{-30}}\ \text{g cm}^{-3}$$

If M is the molecular weight of the solid, then $m = \frac{M}{N}$, where N is Avogadro's number.

$$\therefore \qquad \text{Density of unit cell, } \rho = \frac{z \times M}{(z^3 \times 10^{-30}) \times N}\ \text{g cm}^{-3}$$

$$\text{or} \qquad z = \frac{\rho \times N \times (a^3 \times 10^{-30})}{M} = \frac{\rho \times N \times V}{M} \qquad \ldots (1)$$

Thus, z can be calculated.

The volume (V) of a unit cell for different lattices is given below :

Cubic = a^3, hexagonal = $abc \sin 60°$, orthorhombic = abc,

rhombohedral = $\frac{1}{2} a^2 \ \sin^2 \alpha / \cos \frac{\alpha}{2}$.

Therefore, we can calculate the lattice dimensions from equation (1), provided the density of the crystal and the number of molecules per unit cell are known.

Problem 1. ***A substance crystalises in a form like NaCl. If its density is 1.984 and molecular weight 74.56, calculate the length of the edge of a simple cell.***

Solution. Molecular volume = 74.56/1.984 ml.

$$\text{Volume occupied by one molecule} = \frac{74.56}{1.984 \times 6.023 \times 10^{23}\ \text{ml}}$$

As one unit contains four molecules, hence

$$\text{Volume of each unit} = \frac{4 \times 74.56}{1.984 \times 6.023 \times 10^{23}}$$

Volume of a single cell = $(2a)^3 = 8a^3$, where a = side of the cube.

$$\therefore \qquad 8a = \frac{4 \times 74.56}{1.984 \times 6.023 \times 10^{23}}$$

$$\text{or} \qquad a = d_{100} = 3.148\ \text{Å}$$

So, the edge of a single cell = $2d_{100} = 2 \times 3.148$ Å

$$= \mathbf{6.296\ Å}$$

Problem 2. ***Molybdenum forms bcc lattice whose density is 12.96 gm cm^{-3}. Calculate :***

(a) edge length of unit cube and (b) distance between (100) and (111) planes.

Solution. (a) Let the edge length of the unit cube be a Å.

$\therefore$ Volume of unit cell $= a^3 \times 10^{-24}$ cm^{-3}.

In bcc, the number of atoms per unit cell $= 2$

$\therefore$ Volume occupied by one mole of Mo atoms

$$= \frac{a^3 \times 10^{-24} \times 6.023 \times 10^{23}}{2}$$

$$\text{Density of Mo} = \frac{\text{Mass of one molecule}}{\text{Volume of one molecule}}$$

$$12.96 = \frac{95.94 \times 2}{a^3 \times 10^{-24} \times 6.023 \times 10^{23}}$$

($\because$ Mass of molecule = 95.94)

$$\therefore \quad a^3 = \frac{95.\ 94 \times 2}{12.96 \times 6.023 \times 10^{-1}} \quad \text{or } a = 2.458 \text{ Å}$$

(b) For bcc lattice : $d_{(110)} = a/\sqrt{2} : d_{(111)} = a/2\sqrt{3}$.

$$\therefore \quad d_{(110)} = \frac{2.458}{\sqrt{2}} = \frac{2.458}{1.414} = 1.7383 \text{ Å}$$

$$d_{(111)} = \frac{2.458}{2\sqrt{3}} = \mathbf{0.7104 \text{ Å}}.$$

5·12 HAUY'S LAW OF RATIONAL INTERCEPTS OR INDICES

According to Hauy's law, ***'the intercepts of planes of various faces of a crystal are small integrals, multiples of the intercepts made by the unit or standard plane'.*** In other words, ***'the intercepts of any plane of a crystal, along the crystallographic axes, are either equal to the unit intercept (i.e., the intercepts made by unit plane, which are denoted by a, b, c) or some small whole number multiples of them.*** Such a ratio of three intercepts of any plane is given by $la : mb : nc$, where l, m and n are small whole numbers and a, b and c are the intercepts made by unit plane along crystallographic axes.

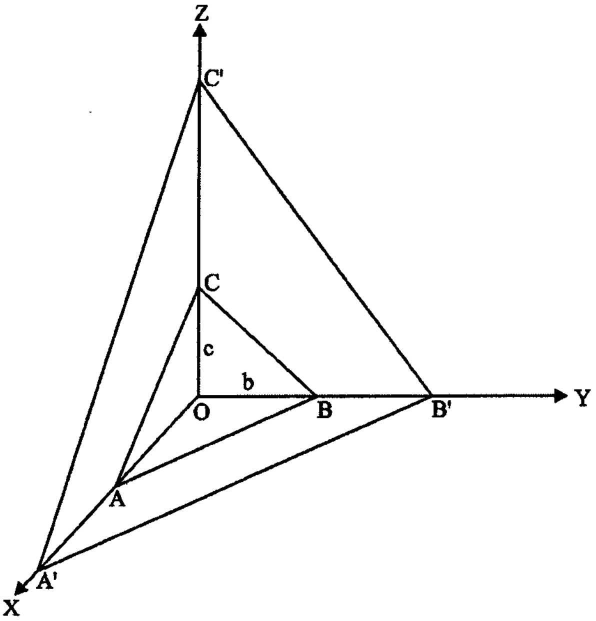


Fig. 11. Rational intercepts.

Let OX, OY and OZ represent the three crystallographic axes and ABC be a unit or standard plane. The unit intercepts will then be a, b and c, as shown in figure (11). If any plane A′B′C′ cuts the three axes with intercepts x, y and z then according to law of rational intercepts,

$$OA' = x = la;\ OB' = y = mb;\ OC' = z = nc$$

$$\therefore \qquad x : y : z = la : mb : nc$$

where the multiples l, m and n are small whole numbers. But this is not always true. These may also be fractional as well as infinity.

5·13 WEISS INDICES

The intercepts of the unit or standard plane along crystallographic axes OX, OY and OZ are a, b and c, respectively. These are known as ***unit*** or ***standard intercepts.*** If a plane or face parallel to the standard plane or face cuts the above three axes with intercepts x, y and z, respectively, then according to the law of rational intercepts,

$$x = la\ ;\ y = mb;\ z = nc$$

The coefficients or multiples l, m and n are called ***Weiss indices*** of the plane. These numbers characterise and represent any plane of the crystal. The corresponding plane is designated as (lmn) plane. Weiss indices are generally small whole numbers and may be fractions of whole numbers as well as infinity.

If, however, the plane is parallel to one axis, say X-axis, then the plane will cut the X-axis at ∞ and the ratio of intercepts would then be

$$x : y : z = \infty a : mb : nc.$$

In such cases, the use of Weiss indices is rather awkward and so these indices have now been universally replaced by Miller indices.

5·14 MILLER INDICES

Another way of representing a crystal face in terms of crystallographic axes and axial ratios is based on the method given by Miller (1839). Each face is represented by a set of 3 integers, h, k and l, called the ***Miller indices***. Then the plane or face whose Miller indices are (h, k, l) will be denoted by (hkl). In other words, such lattice plane is said to (hkl) plane. In general, Miller indices of crystal faces are small integers as well as zero.

The Miller indices of a plane are obtained by taking the reciprocals of Weiss indices, i.e., coefficients of unit intercepts a, b and c and if found necessary, the reciprocals are to be multiplied by the smallest number, i.e., least common multiple, to make all reciprocals as simple small integers.

Thus, in figure (11) for the face A′B′C′ the intercepts, OA′, OB′ and OC′ and $2a$, $2b$ and $3c$, respectively. The reciprocals of the intercepts are 1/2, 1/2 and 1/3. The reciprocals are in the ratio 3 : 3 : 2. These numbers, *i.e.*, 3, 3 and 2 are known as Miller indices of the face A′B′C′ and is designated as (332) face. Now for the unit plane ABC, the intercepts a, b and c are all units, therefore, the reciprocals are in the ratio 1 : 1 : 1. So, the Miller indices of the ABC face are (111). Suppose a face cuts only two axes OY and OZ, intercepts being $2b$ and $2c$ and it does not cut the axis OX at all, being parallel to it. The reciprocals are 0, 1/2, 1/3. The ratio is thus

0 : 3 : 2. The Miller indices are thus (032). So, the Miller indices of any crystal face are inversely proportional to the intercepts of the face on the different axes. In general, planes designated in terms of Miller indices are termed (*hkl*) planes. For example, in (011) plane, $h = 0$, $k = 1$ and $l = 1$.

If a plane makes an intercept on the negative side of the axes, say $a, -b, \infty c$, then Weiss indices are $1, -1, \infty$ and so Miller indices will be $1, -1, 0$ or $1, \bar{1}, 0$. The bar above the Miller index indicates the intersection of the plane on the negative side of the axis. This plane is indexed as $(1\bar{1}0)$.

The Miller indices do not define merely a particular plane but a set of parallel planes. It is only the ratio of the Miller indices which is of importance, *e.g.*, (242) plane is the same as (121) plane; the (200) plane is the same as (100) plane and (222) plane is the same as (111) plane. It is also important to note that parallel crystal planes, containing large concentration of particles (ions, atoms, molecules) are usually represented by Miller indices.

Problem 1. ***Calculate the Miller indices of crystal planes which cut through the crystal axes at the following :***

(i) **(2*a*, 3*b*, *c*)** ***(ii)*** **(*a*, ∞, ∞)**

(iii) **(6*a*, 3*b*, 2*c*)** ***(iv)*** **(2*a*, – 3*b*, – 4*c*)**

Solution.

(i)	*a*	*b*	*c*	
	2	3	1	Intercepts
	1/2	1/3	1/1	Reciprocals
	3	2	6	Clear fractions

∴ Miller indices are **(326)**.

(ii)	*a*	*b*	*c*	
	1	∞	∞	Intercepts
	1	1/∞	1/∞	Reciprocals
	1	0	0	Clear fractions

∴ Miller indices are **(100)**.

(iii)	*a*	*b*	*c*	
	6	3	2	Intercepts
	1/6	1/3	1/2	Reciprocals
	1	2	3	Clear fractions

∴ Miller indices are **(123)**.

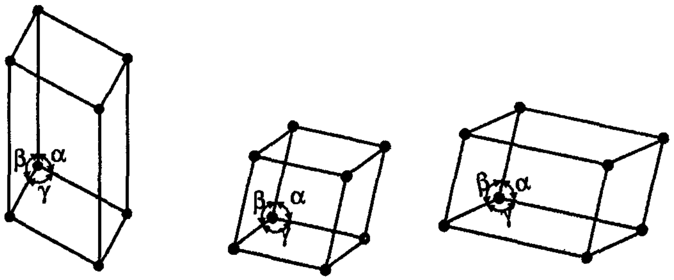
(iv)	*a*	*b*	*c*	
	2	–3	–4	Intercepts
	1/2	1/–3	1/–4	Reciprocals
	6	–4	–3	Clear fractions

∴ Miller indices are $(\mathbf{6\,\bar{4}\,\bar{3}})$.

(The negative sign in Miller indices is indicated by placing a bar in the integer).

5·15 BRAVAIS SPACE LATTICES

Bravais (1848) established that there are fourteen unique and basic ways in which points can be arranged in three dimensional point lattices. These fourteen

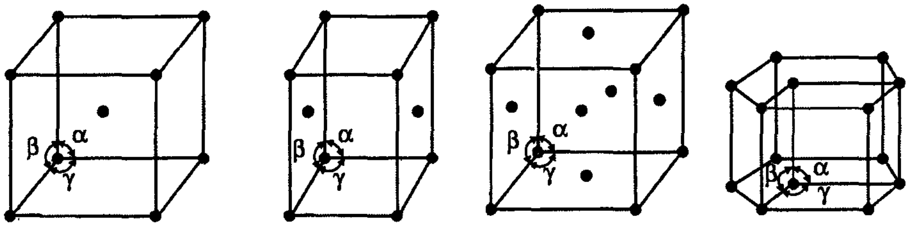


1. Simple triclinic Bravais lattice

2. Simple monoclinic Bravais lattice

3. Side (end) centred monoclinic Bravais lattice

4. Simple (primitive) orthorhombic Bravais lattice

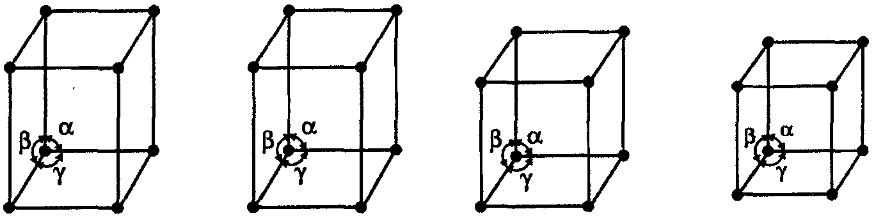


5. Body centred orthorhombic Bravais lattice

6. End centred orthorhombic Bravais lattice

7. Face centred orthorhombic Bravais lattice

8. Hexagonal Bravais lattice

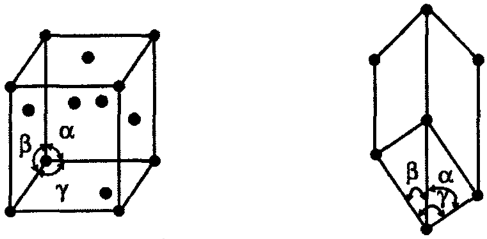


9. Simple tetragonal Bravais lattice

10. Body centred tetragonal Bravais lattice

11. Simple (primitive) cubic Bravais lattice

12. Body centred cubic Bravais lattice



13. Face centred cubic Bravais lattice

14. Rhombohedral Bravais lattice

Fig. 6. Bravais lattices.

basic arrangements, known as Bravais space lattices are shown in figure (6), where the black circles indicate the location and number of lattice points involved.

5·16 INTERPLANAR DISTANCES OR SEPARATION BETWEEN LATTICE PLANES

The separation between two successive lattice planes of a cubic, tetragonal and orthorhombic crystal system, in which edges are mutually perpendicular, is calculated as follows :

Consider a two dimensional space lattice [Fig. (7)] with O as origin of coordinate system at one of the lattice points. Suppose a plane AB cuts intercepts $3a$ and $2b$ on X- and Y-axis, respectively. The entire lattice is considered to be made up of lattice planes which are parallel to AB. Draw a perpendicular OD from O on AB. The triangles AOD and AOB are similar, we have

$$\frac{\mathrm{OD}}{\mathrm{OA}} = \frac{\mathrm{OB}}{\mathrm{AB}} \quad \text{or} \quad \mathrm{OD} = \frac{\mathrm{OB}}{\mathrm{AB}} \times \mathrm{OA}$$

or
$$\mathrm{OD} = \frac{2b \times 3a}{\sqrt{(3a)^2 + (2b)^2}} = \left[\frac{1}{(3a)^2} + \frac{1}{(2b)^2}\right]^{-1/2}$$

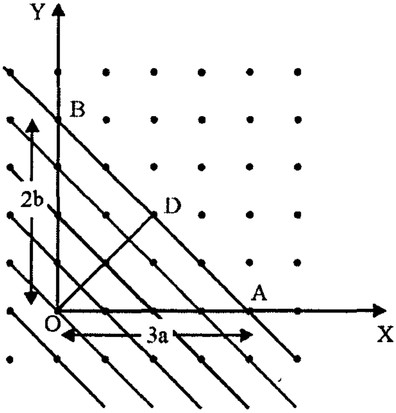


Fig. 7.

From the figure we see that there are five more planes between O and AB. Thus, there are six planes between O and AB. So, the separation between successive lattice planes is given by

$$d = \frac{\mathrm{OD}}{6} = \frac{1}{6}\left[\frac{1}{(3a)^2} + \frac{1}{(2b)^2}\right]^{-1/2} = \left[\frac{36}{(3a)^2} + \frac{36}{(2b)^2}\right]^{-1/2} \quad d = \left[\frac{1}{(a/2)^2} + \frac{1}{(b/3)^2}\right]^{-1/2}$$

The separation ratio of the plane AB with OX and OY axes is 1/3 : 1/2, the Miller indices h, k of this plane will be 2 : 3. The value of d becomes,

$$d_{hk} = \left[\frac{1}{(a/h)^2} + \frac{1}{(b/k)^2}\right]^{-1/2} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2}\right)^{-1/2}$$

If we consider the three dimensional lattice with Miller indices h, k and l, we may similarly prove that the separation between successive planes is given by

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{-1/2} \qquad \text{...(1)}$$

(i) For a **cubic lattice,** $a = b = c$ and so, equation (1) becomes

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{a^2} + \frac{l^2}{a^2}\right)^{-1/2} = \left(\frac{h^2 + k^2 + l^2}{a^2}\right)^{-1/2}$$

or
$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \qquad \text{... (2)}$$

(ii) For a **tetragonal lattice,** $a = b \neq c$, so equation (1) becomes

$$\frac{1}{(d_{hkl})^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \qquad \text{...(3)}$$

(iii) For **orthorhombic lattice,** $a \neq b \neq c$, so equation (1) becomes

$$\frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad \text{...(4)}$$

Problem 1. ***The parameters of an orthorhombic unit cell are a = 50 pm, b = 100 pm, and c = 150 pm. Determine the spacing between the (123) planes.***

Solution. For an orthorhombic unit cell, the interplanar distance is given by,

$$\frac{1}{(d_{hkl})^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\frac{1}{(d_{hkl})^2} = \frac{1}{(d_{123})^2} = \left(\frac{1}{50\text{ pm}}\right)^2 + \left(\frac{2}{100\text{ pm}}\right)^2 + \left(\frac{3}{150\text{ pm}}\right)^2 = 3\ (1/50\text{ pm})^2$$

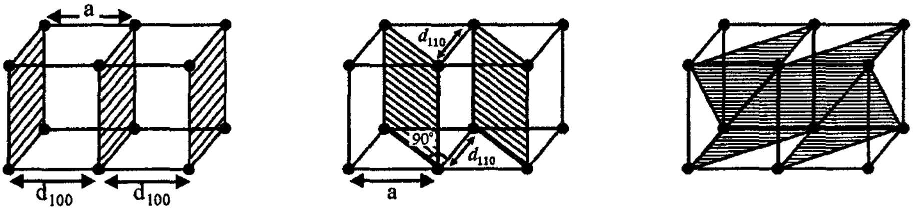
$$\frac{1}{d_{123}} = \frac{\sqrt{3}}{50\text{ pm}}$$

$$\therefore \qquad d_{123} = \frac{50\text{ pm}}{\sqrt{3}} = \mathbf{29\ pm}$$

[I] Calculation of Inter-Planar Separations of Various Cubic Lattices

1. *Simple or Primitive Cubic Lattice.*

In figure (8) various planes of a simple cubic lattice are shown. If a is the side of the unit cube, the separation between two successive lattice planes are calculated as follows :



(i) The shaded lattice planes are (100) planes in the simple cubic lattice (*i.e.*, points are situated at the corners).
$\therefore\ d_{100} = a.$

(ii) The shaded lattice planes are (100) planes in the simple cubic lattice and the points are situated at the corners.
$\therefore\ d_{110} = a/\sqrt{2}$

(iii) The shaded lattice planes are (100) planes in simple cubic lattice, the points are situated at the corners.
$\therefore\ d_{111} = a$

Fig. 8.

(i) Between two successive (100) lattice planes : In it, the (100) planes cut the X-axis and are parallel to the Y and Z axes [fig. 8(i)]. The perpendicular distance between two successive (100) lattice planes is denoted by d_{100} and is calculated by putting $h = 1$, $k = 0$ and $l = 0$, in equation (1), so,

$$d_{100} = \frac{a}{(1^2 + 0^2 + 0^2)^{1/2}} \quad \text{or} \quad d_{100} = a \qquad \text{... (5)}$$

(ii) Between two successive (110) lattice planes : In it, the (110) planes cut obliquely across the X- and Y-axis but cut the Z-axis at infinity, *i.e.*, parallel to Z-axis [fig. 8 (ii)]. The perpendicular distance between two successive (110) lattice planes is denoted by d_{110} and is calculated by putting $h = 1$, $k = 1$ and $l = 0$. So,

$$d_{110} = \frac{a}{(1^2 + 1^2 + 0^2)^{1/2}} \quad \text{or} \quad d_{110} = \frac{a}{\sqrt{2}} \qquad \ldots (6)$$

(iii) Between two successive (111) lattice planes : In it, the (111) planes cut all the three axes obliquely and intercept each axis at the same distance from the origin [Fig. 8 (iii)]. The perpendicular distance between two successive (111) lattice planes is denoted by d_{111} and is calculated by putting $h = 1$, $k = 1$ and $l = 1$ in equation (1) so,

$$d_{111} = \frac{a}{(1^2 + 1^2 + 1^2)^{1/2}} \quad \text{or} \quad d_{111} = \frac{a}{\sqrt{3}} \qquad \ldots (7)$$

The ratio of separation between successive (100), (110) and (111) lattice planes will be :

$$d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}}$$

or

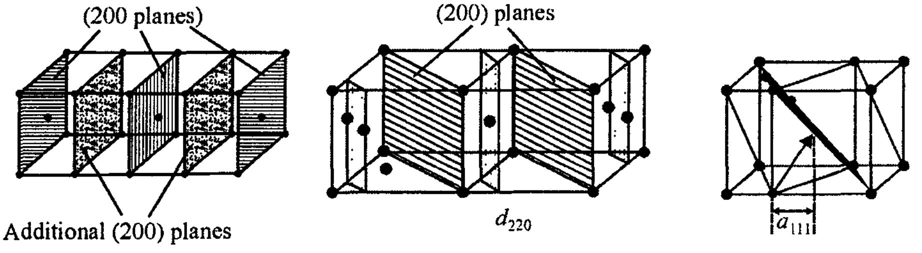
$$d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577 \qquad \ldots (8)$$

2. *Face Centred Cubic Lattice.*

In face centred cubic lattice, one unit is placed at each corner and one at the centre of each of the faces. So, in this case, additional planes can be passed through black dots. They pass through the centre of front and back faces vertically. The inter-planar distances are calculated as follows :

(i) Between two successive (100) lattice planes : In this case, d_{100} the distance between successive (100) planes is $a/2$, [fig. 9 (i)], if d_{100} for simple cubic lattice is assumed to be a.

(ii) Between two successive (110) lattice planes : It is assumed that an additional set of (110) planes parallel to the first set can be passed through this type of lattice, these additional planes include the units in the centre of the front and the side faces and are midway between the planes of simple cubic lattice (Fig. 9-(ii)).



(i) The dark shaded lattice planes are (200) planes in face-centred cubic lattice. The dotted lattice planes, are additional (200) planes. Thus, $d_{200} = a/2$.

(ii) The dark shaded lattice planes are additional (220) planes. Thus, $d_{220} = a$.

(iii) Showing the (111) planes and d_{111} between two successive planes in face-centred cubic lattice. Thus, $d_{111} = a/\sqrt{3}$

Fig. 9.

$\therefore$ d_{100} for face centred cubic lattice = 1/2 of d_{110} for simple cubic lattice $= \frac{1}{2} \times \frac{a}{\sqrt{2}} = \frac{a}{2\sqrt{2}}$.

(iii) Between two successive (111) planes : In this case, d_{111} remains the same as that for a simple cubic lattice, as (111) planes of the simple cubic lattice already pass through the centre of all the faces of the face centred cubic lattice (fig. 9 (iii)). Therefore,

$$d_{111} = \frac{a}{\sqrt{3}}$$

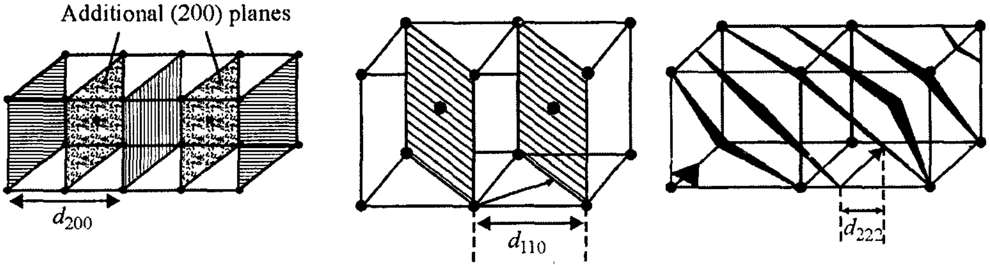
The ratio of separation between successive (100), (110) and (111) planes will be

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$$

$$= 1 : 0.707 : 1.154 \qquad \dots (9)$$

3. *Body Centred Cubic Lattice.*

In such a lattice, one unit is situated at each corner and one at the centre of the cube. In it, the additional planes can be passed through the structural units. The inter-planar distances are calculated as follows :



(i) Showing (200) planes and d_{200} between two successive planes in body-centred cubic lattice. The dark shaded planes are (200) and dotted planes are additional (200) planes.

(ii) Showing (110) planes in body-centred cubic lattice and inter-planar distance (d_{110})

(iii) Showing (222) planes and inter-planar distance d_{222} in body-centred cubic lattice.

Fig. 10.

(i) Between two successive (100) planes : In this case [Fig. 10(i)], d_{100} will be half of the distance d_{100} for simple cubic lattice, as new planes lie midway between the planes of the latter lattice [Fig. 10 (i)].

$$d_{100} = \frac{a}{2}$$

(ii) Between two successive (110) planes : The (110) planes of simple cubic lattice already pass through the structural units in the centre of the cube, so in this case, the value of d_{100} will be the same as that for a simple cubic lattice. Therefore,

$$d_{110} = \frac{a}{\sqrt{2}}.$$

(iii) Between two successive (111) planes : In simple cubic lattice, the (111) planes do not pass through the structural units in the centre of the cube and so in body centred lattice, another set of planes can be inserted through these units which lie midway between (111) planes of the simple cubic lattice. Therefore,

$$d_{111} = \frac{a}{2\sqrt{3}}$$

The ratio of separation between successive (100), (110) and (111) planes will be

$$d_{100} : d_{110} : d_{111} = \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}}$$

$$= 1 : 1.404 : 0.577 \qquad \text{... (10)}$$

5·17 INTERNAL STRUCTURE OF CRYSTALS

When X-rays were first investigated, the problem arose of measuring their wavelength. It is a well known fact that, if light is allowed to strike a surface consisting either of a series of edges or of lines spaced closely enough to be of the same order of magnitude as that of the wavelength of light, the beam of light is diffracted, and the various radiations are dispersed into a series of spectra known as first, second, third etc. order spectra. Further, there is a definite relation between the angle of diffraction, the wavelength of radiation and the spacing of the lines on the ruled grating. Since X-rays are of the same nature as light, it should be theoretically possible to determine the wavelength of this radiation in the same way. However, it is impossible by any mechanical means to rule a grating as fine as that required, namely one with about 10^8 lines per centimeter. To overcome this difficulty, Max von Laue (1912) made the suggestion that if a crystal consists actually of an orderly arrangement of atoms, then the atomic planes in the crystal should be spaced at intervals of about 10^{-8} cm and the crystal should act then as a natural and very fine three-dimensional diffraction grating for X-rays.

Furher advance in this connection was made by Braggs due to the suggestion of W.L. Bragg. *viz.*, to use the crystal as a reflection grating, the resulting spectra being much simpler and amenable to theoretical treatment. Following methods have been developed for the study of X-ray diffraction for ascertaining the internal structure of crystals.

(1) Laue's photographic method,

(2) Bragg's spectrophotometer method,

(3) Rotating crystal method,

(4) Oscillating crystal method,

(5) Powder method.

[I] Laue's Photographic Method

von Laue showed by mathematical analysis that if a beam of X-rays were directed against a crystal, the beam should be diffracted and transmitted through the crystal in such a way that the image caught on a photographic plate behind the crystal should show a series of spots arranged in some geometrical way about the centre of the beam. The Laue method of examining the diffraction of X-rays by a

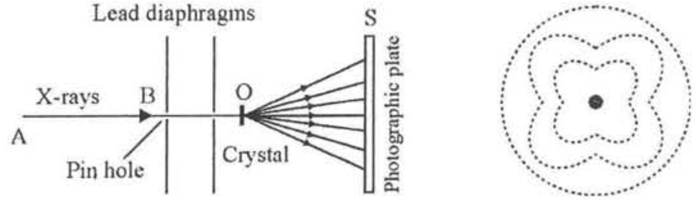


Fig. 12. Laue's method.

crystal differs from other methods, in that a homogeneous beam of X-rays is used. The beam falls upon a small crystal, or thin crystal section, and the diffracted beams are recorded on a photographic plate placed at a distance of a few centimeters from the crystal. The rays are limited to a narrow pencil by the slit system A, the crystal is set at O on a holder which permits the adjustment of its orientation, and the photgraphic plate is placed at S (Fig. 12). A beam with a continuous range of wavelengths is conveniently obtained by using a bulb with a tungsten anticathode and a tension of about 65,000 volts.

A feature of the Laue photograph is the arrangement of the spots on ellipses which, one end of their major axis at the central spot. The same feature is shown more or less distinctly by all Laue photographs, the spots occurring where the ellipses intersect. All the spots which lie on any one ellipse are due to reflections by planes parallel to a common zone axis, as will be clear from the construction in (Fig. 13). Incident rays fall upon a crystal at C, which has a zone axis parallel to ZC, and we consider rays which are reflected by a plane of the corresponding zone. Suppose a reflecting plane to be rotated about ZC, the reflected beam will trace out a curve EE′ on the plate. If the incident rays make an angle θ with the zone axis, the reflected rays will always make the same angle with it, so that they lie on a cone of semi-vertical angle, θ around the zone axis. The ellipses in the Laue photograph are the intersections of such cones with the photographic plate. Each spot is at an intersection of ellipses, since a plane parallel to two zone axes is a crystal plane and can reflect the X-ray beam.

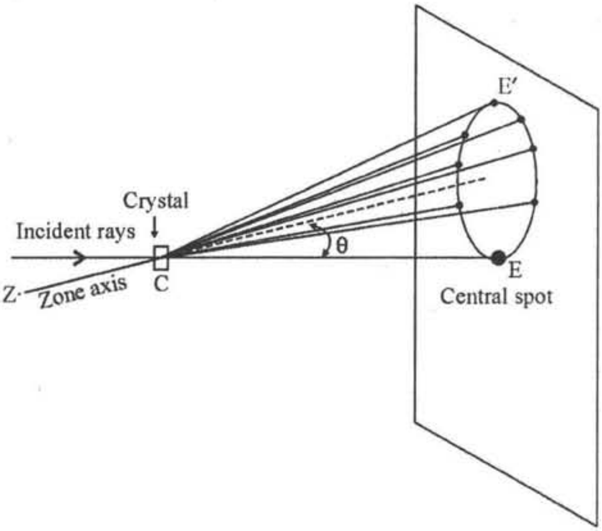


Fig. 13. Laue's photographs.

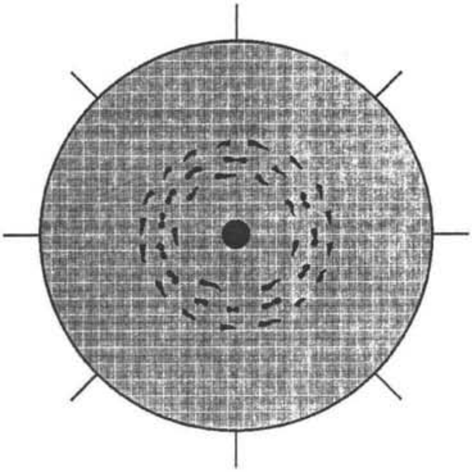


Fig. 14. Laue diffraction pattern of zinc blende.

If a cylindrical rod of brightly polished metal is placed in an inclined position in a narrow beam of light from a lantern, its surface will reflect radiation so as to trace out the complete curve EE′ in figure (13), as it represents all orientations of a plane round the axis of the cylinder or zone axis. One of the Lalue's diagrams the crystal of zinc blende (ZnS) is shown in figure (14).

[II] Bragg's Spectrophotometer Method

Bragg pointed out that scattering of X-rays by crystals could be taken to be equivalent to reflection from successive planes of atoms in the crystal. However, unlike reflection of ordinary light, the reflection of X-rays can take place only at certain angles which are dependent on wavelength of the X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wavlength of X-rays, the interplanar distance in the crystal and the angle of reflection is known as ***Bragg's equation.*** It can be derived as follows.

The horizontal lines represent parallel planes in the crystal structure separated from one another by a distance, d. Suppose a beam of X-rays incident at an angle θ falls on the crystal. Some of them will be reflected from the uppermost plane at the same angle, θ, while others will be absorbed and get reflected from successive planes as shown in figure (15). Let the two wavefronts be drawn perpendicular to the incident and reflected beams, respectively. The waves reflected from different layer planes will be in phase with one another only if the difference in the path lengths of the waves reflected from the successive planes is equal to an integral number of wavelengths. Drawing perpendiculars OL and OM to the incident and reflected beams, it will be seen that the difference in the wavelengths, say δ of the waves reflected from the first two planes is given by,

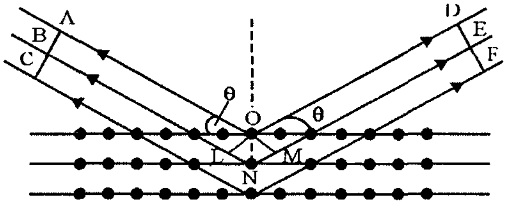


Fig. 15. X-ray diffraction by crystals.

$$\delta = \text{LN} + \text{MN}$$

This should be equal to a whole number multiple of wavelength λ, *i.e.*,

$$n\,\lambda = \text{LN} + \text{MN}$$

Since the triangles OLN and ONM are congruent, LN = MN

$$\therefore \qquad n\,\lambda = 2\text{LN} = 2d \sin\theta \qquad \ldots (1)$$

Equation (1) is known as ***Bragg's equation.***

If homogeneous X-rays are used, λ has a certain definite value. For a given set of lattice planes, d will also have a fixed value. Thus,x the possibility of getting maximum reflection (*i.e.*, possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be obtained at which the reflections will be maximum. At these positions, n will have several values equal to 1, 2, 3, ... etc.

On the above basis, there are different orders of reflection, given by different values of n. The diffraction maxima are called first, second, third, fourth etc. order when n = 1, 2, 3, 4, ... etc., respectively.

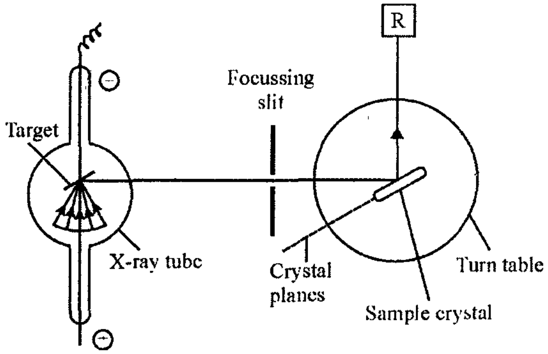


Fig. 16. Bragg's spectrometer.

The study of the intensity of the X-ray spectrum will furnish the information as regards the arrangement of planes of different atoms in the given space lattice. Bragg obtained the positions of maximum reflection intensity by means of an *X-ray spectrometer* whose construction is shown in figure (16).

The spectrometer consists of an X-ray tube enclosed in a box coated with lead. The X-rays pass through the slit and apertures and finally fall on the crystal. The crystal is placed on a table having a revolving arm. At the end of this arm is fitted a vernier, working in conjunction with a graduated circular scale. The reflected X-rays then pass through the first slit of an ionisation chamber, which is mounted in such a manner, as to be rotated about the same vertical axis as the crystal table. The ionisation chamber is filled with an easily ionisable gas like SO_3 or CH_3Br. Two electrodes raised to a high voltage are fitted in the chamber. These electrodes are then connected to an accurate electrometer. This whole assembly constitutes the ***Bragg's ionisation spectrometer.***

The X-rays reflected from the crystal pass through an aluminium window and then enter the ionisation chamber, and ionise the gas inside it. A flow of current is registered on the electrometer. The strength of this current is proportional to the intensity of the entering reflected X-rays. In some cases, a photographic plate is used instead of the ionisation chamber. In such a case, the crystal is rotated so that the X-rays fall at different angles. Thus, a clear spectrum or photograph is obtained. Such an instrument is known as ***spectragroph***. In actual practice, the crystal and the ionisation chamber are rotated about their common axis. The chamber is rotated through twice the angle through which the crystal is rotated, so that all reflected rays enter the chamber, whatever the position of the crystal may be.

In the beginning, we start with a small glancing angle between the X-rays and the crystal. Then we slowly increase the angle by rotating the crystal and measure the intensity of the current in the chamber in each case. This procedure is repeated for all important planes of the crystal.

The values of θ for the first order reflection from the three faces of a crystal (say NaCl) were found to be 5.9°, 8.4° and 5.2°, respectively. Using Bragg's equation (*viz.*, $d = n\,\lambda/2\sin\theta$), and knowing that n and λ are the same in each case, the distance, d between the successive planes in the three faces will be in the ratio of

$$\frac{1}{\sin 5.9^\circ} : \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} = \frac{1}{0.103} : \frac{1}{0146} : \frac{1}{0.091}$$

$$= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.704 : 1.155$$

This ratio is very close to that expected for inter-planar spacing of a face centered cube. We thus conclude that sodium chloride has a face centered cubic lattice.

Determination of wavelength of X-rays

By means of Bragg's equation $n\lambda = 2d \sin \theta$, we can find out the distance between two successive planes, provided the wavelength of X-rays is known. But if the spacing between the planes is known, we can calculate the wavelength of X-rays.

The interplanar distance can be determined even from physical dimensions of the crystal and knowledge of the number of ions associated with each unit cell of the crystal lattice, without the application of Bragg's equation. Let us take the example of sodium chloride.

$$\text{Density } (\rho) \text{ of NaCl} = 2.163 \text{ g/c.c.}$$

$$\text{Molecular weight of NaCl} = 58.45.$$

$$\therefore \quad \text{Molecular volume} = \frac{58.45}{2.163} = 27.02 \text{ c.c.}$$

$$\text{Volume occupied by each unit} = \frac{27.02}{N} = \frac{27.02}{6.023 \times 10^{23}}$$

$$= 44.88 \times 10^{-24} \text{ c.c.}$$

As already discussed, in the unit cell of NaCl, there are fourteen points representing Na ions and thirteen representing Cl ions. Eight Na ions are arranged in the eight corners, one at each corner. The remaining six are arranged in the faces, one each at the centre of each face.

From geometrical considerations it can be shown that each sodium ion at the corner is shared between eight cubes meeting at each corner. Hence, there is only one sodium ion per unit cell. Six sodium ions at the face centres are each shared between the two cubes. This gives an average of three sodium ions for each cell, therefore, total average number of sodium ions per unit cell is 1 + 3 = 4.

In the case of chloride ions, twelve are shared between four cubes meeting at each of the edges and one in the centre, and belongs exclusively to the unit cell. Hence, each unit cell is associated with four chloride ions. Therefore, four molecules of sodium chloride are associated per unit cell–four sodium ions and four chloride ions.

Since the volume of each unit is 44.88×10^{-24} c.c. as deduced above, the volume of each unit cell is given by

$$4 \times 44.88 \times 10^{-24} = 179.52 \times 10^{-24} \text{ c.c.}$$

$$= 179.52 \times (\text{Å})^3$$

$$\text{Therefore, each edge of the cube} = [179.52\ (\text{Å})^3]^{1/3}$$

$$= 5.64 \text{ Å}.$$

From figure (15), it is clear that each edge of the cube is equal to twice the interplanar spacing, so

$$d_{100} = \frac{1}{2} \times 5.64 \text{ Å} = 2.82 \text{ Å}.$$

Hence, the distance between two successive planes in a sodium chloride crystal is 2.82 Å.

In the case of NaCl, the angle of ***first order reflection*** for (100) planes is 5.9°. Hence, from Bragg's equation we have

$$n\lambda = 2d_{100} \sin \theta$$

$$1.\lambda = 2 \times 2.82 \times 10^{-8} \times \sin 5.9°$$

or $$\lambda = 2 \times 2.82 \times 10^{-8} \times 0.103 = 0.581 \times 10^{-8} \text{ cm.}$$

or $$\lambda = \mathbf{0.581\ Å}$$

Once the wavelength of X-rays has been calculated, we can determine the distance between the planes of any other crystal for which maximum reflected angle has been experimentally determined.

Problem 1. ***In case of sodium chloride the first order reflections from (100), (110) and (111) faces using monochromatic X-rays are 5.9°, 8.4° and 5.2°, respectively. What is the crystal structure of sodium chloride ?***

Sodium. Using Bragg's equation $n\lambda = 2d \sin \theta$

$$d = \frac{n\lambda}{2 \sin \theta}$$

Since the reflection is of first order, $n = 1$, so

$$d_{(100)} : d_{(110)} : d_{(111)} = \frac{\lambda}{2 \sin 5.9°} : \frac{\lambda}{2 \sin 8.4°} : \frac{\lambda}{2 \sin 5.2°}$$

$$= \frac{1}{\sin 5.9°} : \frac{1}{\sin 8.4°} : \frac{1}{\sin 5.2°}$$

$$= \frac{1}{1.103} : \frac{1}{0.146} : \frac{1}{0.0906}$$

$$= 1 : 0.705 : 1.154$$

As the ratio corresponds to a face centered cubic (fcc) lattice, *i.e.*, 1 : 0.747 : 1.154, the sodium chloride has a fcc structure.

Probelm 2. ***At what angle (θ) will X-rays of wavelength* 1.542×10^{-10} *m be reflected by planes separated by* 3.5×10^{-10} *m ? What is an alternative interpretation of these reflections ?***

Solution. From Braggs' equation, $n\lambda = 2d \sin \theta$,

$$\theta = \sin^{-1} \frac{n\,\lambda}{2d}$$

For $n = 1$, $$\theta = \sin^{-1} \frac{(1)\,(1.542 \times 10^{-10}\text{ m})}{(2)\,(3.5 \times 10^{-10}\text{ m})} = 12.73°$$

For $n = 2$, $\theta = 26.14°$ and for $n = 3$, $\theta = 41.37°$. These reflections can also be interpreted as being due to first order reflections from (100), (200) and (300) planes, which have interplanar spacings of d_{hkl} of 3.5×10^{-10}m, 1.75×10^{-10} m and 1.17×10^{-10} m.

[III] Powder Method

Powder method is the simplest technique for obtaining X-ray diffraction, It was first used by P.J.W. Debye and P. Scherrer. Instead of taking a single crystal having a definite orientation to the impinging X-rays, we can take a mass of finely divided crystal with random orientations. This method is better adapted due to its simplicity and versatility. In this method, the crystal sample need not be taken in large quantity but as little as 1 milligram of the material is sufficient for study.

Moreover, the substance present reveals the true state of chemical combination and the interpretation of patterns is simple and straightforward.

Figure (17) shows the experimental arrangement of the method. The crystalline powder is contained in a thin walled glass capillary. Polycrystalline metals (*Polycrystalline solids are those solids in which the crystals are so small that they can be recognised only under a powerful microscope*) are studied in the form of fine wires. A beam of monochromatic X-rays falls on the powdered specimen through the slit system. The function of these slits is to obtain a narrow pencil of X-rays. Fine powdered specimen stuck on a hair by means of gum is suspended vertically in the axis of a cylindrical camera. This helps sharp lines to be obtained on the photographic film which is bent in the form of a circular arc surrounding the powder crystal. The X-rays after falling on the powder pass out of the camera through a cut in the film so as to minimise the fogging produced by the scattering of the direct beam. The observed pattern on a photographic plate consists of traces as shown in figure (18).

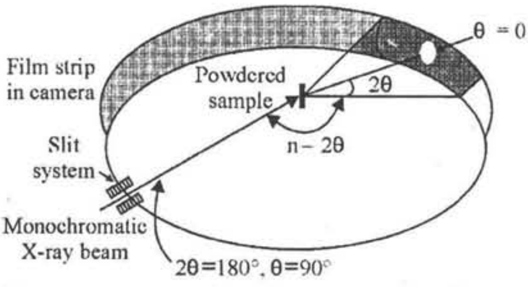


Fig. 17 Powder method for X-ray diffraction.

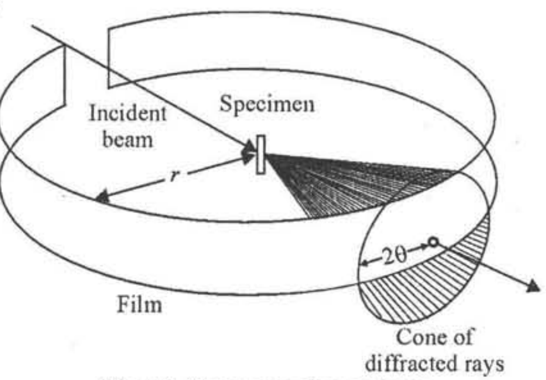
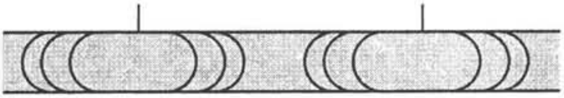


Fig. 18. X-ray powder camera.

Theory and calculation : When a monochromatic beam of X-rays is allowed to fall on a powdered crystal then there will be some particles out of the random orientation of small crystals in the fine powder, which lie with a given set of lattice planes (marking the correct angle with the incident beam) for reflection to occur. There will be another fraction of the powdered particles which will have another set of planes in the correct position for the reflection to occur and so on. So, reflections are possible in different orders for each set.

All the like orientations of the particles due to reflection for each set of planes and for each order will constitute a diffraction cone whose intersection with a photographic plate gives rise to a trace as shown in figure (18). The crystal structure can be obtained from the arrangement of the traces and their relative intensities.

If the angle of incidence is θ, then the angle of reflection will be 2θ, as shown in figure (19). If the film radius is r, the circumference $2\pi r$ corresponds to scattering angle of 360°. Then we can write,



Unrolled film strip

Fig. 19.

$$\frac{l}{2\pi r} = \frac{2\theta}{360^\circ} \text{ or } \theta = \frac{l}{4\pi r} \times 360^\circ$$

From the above equation, the value of θ can be calculated and substituting this value in Bragg's equation, we can calculate '*d*'.

This method is most suitable for cubic crystals several metals and alloys. It can also be used for analytical and identification purposes. An interesting application of powder method is that many substances which were considered to be amorphous are now considered as microcrystalline. As substances like rubber, cellulose, asbestos etc. give definite diffraction patterns, it can be concluded that they possess a definite structure. Rubber has been seen to crystallise on stretching and decrystallise on slackening.

5·18 STRUCTURE OF CRYSTALS

[I] Structure of Rock-Salt (NaCl)

The rock-salt crystal was studied by Bragg's spectrometer and the intensity of the current in the ionisation chamber was determined for different angles of rotation of the crystal. By plotting a curve between the current intensity (Y-axis) and glancing angles (X-axis), the nature of the curves for (100), (110) and (111) faces is shown in figure (20). This gives a diagrammatic view of the actual positions of the spectra.

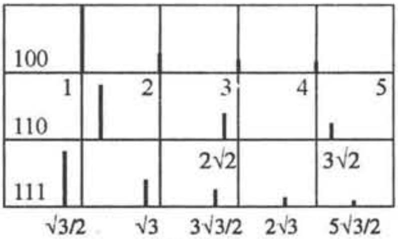


Fig. 20.

Furthermore, when rock-salt crystal is analysed by Bragg's method, it is observed from the X-ray spectra consisting of the curves obtained by drawing the intensity of reflected X-rays as ordinate and 2θ as abscissa, where θ, is the glancing angle, that the maximum intensity of reflections occurs at the glancing angles of 5.9°, 8.4° and 5.2° for (100), (110) and (111) faces, respectively for first order reflections.

We know that,
$$n\lambda = 2d \sin\theta$$
or
$$\frac{1}{d} = \frac{2}{n\lambda} \cdot \sin\theta$$

Therefore, for a particular order of reflection,
$$d \propto \frac{1}{\sin\theta}$$

If only first order reflections are considered, then
$$\begin{aligned} d_{100} : d_{110} : d_{111} &= \frac{1}{\sin 5.9^\circ} \ \frac{1}{\sin 8.4^\circ} : \frac{1}{\sin 5.2^\circ} \\ &= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.091} \\ &= 9.731 : 6.844 : 11.04 \\ &= 1 : 0.704 : 1.155 \end{aligned}$$

But we know that for a face centered cubic lattice,
$$d_{100} : d_{110} : d_{111} = 1 : 0.704 : 1.154.$$

Therefore, we may safely conclude that the crystal of NaCl has a face centred cubic lattice.

Now, the problem is to decide about the structural units (molecules, atoms or ions) of the crystal. The problem can be solved by considering the plane (III). In planes (III), the first order spectrum is abnormally weak, the second abnormally strong, the third abnormally weak and fourth abnormally strong. The alternation of these intensities are due to alternate layers or planes of chlorine atoms separated by layers of sodium atoms. From the alternations in these intensities we can say that the real unit of matter in crystal lattice is the atoms are neither molecules nor ions.

Bragg gave the structure of NaCl as shown in figure (21). From the structure it follows that :

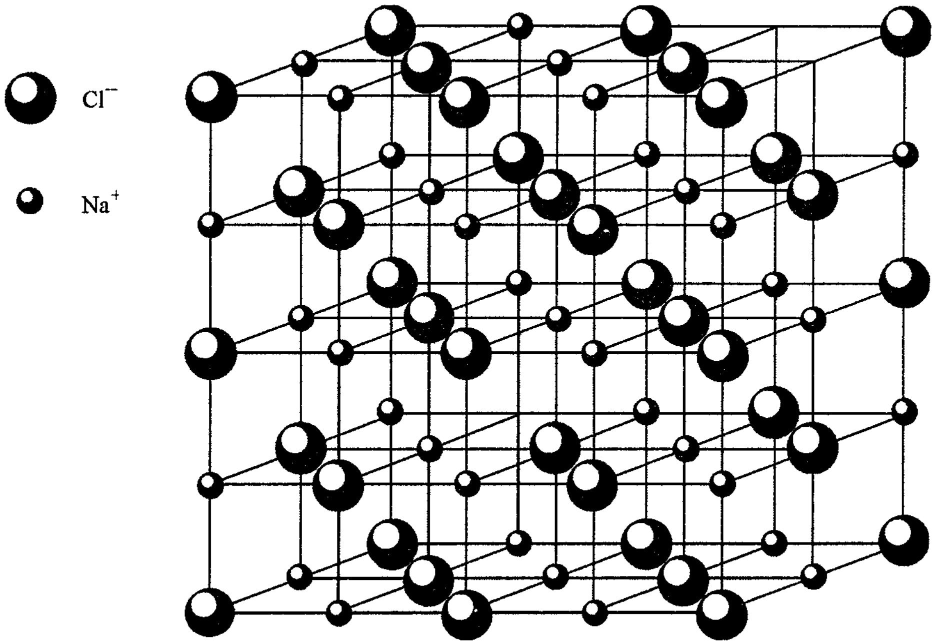


Fig. 21. A model showing the arrangements of Na^+ and Cl^- ions in NaCl crystal.

(i) NaCl crystal has a face centred cubic lattices with sodium and chlorine atoms arranged alternately in all directions parallel to the three rectangular axes.

(ii) Each unit cell of the crystal consists of 14 sodium atoms and 13 chlorine atoms.

(iii) Each chlorine atom is surrounded by 6 sodium atoms and each sodium atom is surrounded by 6 chlorine atoms.

[II] Structure of Sylvine (KCl)

On investigating the sylvine (KCl) crystal, the intensity order of reflection diagram was obtained and is shown in figure (22). In this case, the maximum reflections of X-rays, corresponding to first order reflections are observed to occur at the glancing angles 5.38°, 7.61° and 9.38° for (100), (110) and (111) faces, respectively. Therefore,

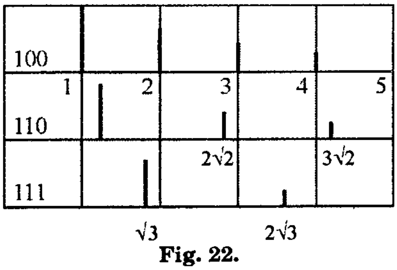


Fig. 22.

$$d_{100} : d_{110} : d_{111} = \frac{1}{\sin 5.38^\circ} \quad \frac{1}{\sin 7.61^\circ} : \frac{1}{\sin 9.38^\circ}$$

$$= \frac{1}{0.0938} : \frac{1}{0.1326} : \frac{1}{0.1630}$$

$$= 1 : 0.704 : 0.575$$

But for a simple cubic lattice

$$d_{100} : d_{110} : d_{111} = 1 : 0.707 : 0.577$$

Therefore, KCl crystal has a simple cubic lattice, Potassium chloride is isomorphous with sodium chloride. The explanation for this apparent anomaly is very simple and can be explained on the basis that the X-ray's scattering power for an atom or ion is governed by the number of extra-planetary electrons, *viz.*, atomic number.

The atomic numbers of potassium (K = 19) and chlorine (Cl = 17) are not very different and the X-rays are unable to detect any difference between the two kinds of atoms. If we turn to figure (19), and imagine all the atoms to be identical, it is evident that the face centered arrangement has become a simple cubic arrangement. This is the reason for the KCl spectrum corresponding apparently to the simple cubic lattice. With KCl, the structure is face centered, but the face centered characteristics are marked by the fact that the two kinds of atoms composing the substance have nearly the same atomic numbers and atomic weights (K = 39, Cl = 35.5). But in the case of sodium chloride, the atomic numbers differ considerably (Na = 11, Cl = 17), and so their scattering powers are different and hence the true structure as two interpenetrating face centered lattices become apparent. It is only the (111) face spectra which allows us to distinguish between the simple cubic lattice and the face centered lattice. The (100) and (110) faces produce similar effects in both the cases.

Another distinction between the structures of the crystals of NaCl and KCl may be observed by applying the expression,

$$d \propto \frac{1}{\sin \theta}$$

to both the crystals. Therefore,

$$\frac{d_{100}\,(\text{NaCl})}{d_{100}\,(\text{KCl})} = \frac{\sin 5.38^\circ}{\sin 5.90^\circ} = \frac{0.0938}{0.103} = \frac{1}{1.09}$$

From this equation, it is clear that the fundamental units are more widely spaced in the crystal of KCl than in the crystal of NaCl.

[III] Structure of Zinc Blende (ZnS)

The crystal is built up on the face centered lattice as shown by the relative positions of the first order spectra from the (100), (110) and (111) faces. The spectra of zinc blende are shown in figure (23), the angle 2θ and intensities being indicated by the positions and heights of the vertical lines. In case of (100) planes, the odd numbers are relatively weak indicating the equidistant alternating (100) planes. Second order reflection from (111) planes is very weak, which suggests that the distance between the successive zinc layers is four times that between a zinc layer and the next sulphur layer. So, structure of zinc blende will have alternate planes of zinc alone and of sulphur alone. The intensities of spectra due to (110) planes are normal in that the intensity of the spectrum decreases regularly as the order increases. It means that the zinc blende structure must contain equal number of zinc and sulphur atoms.

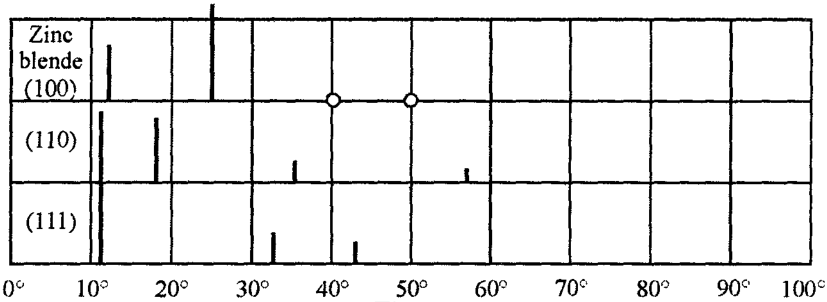


Fig. 23.

Depending upon the above observations the structure is as shown in figure (24). It is clear that both Zn and S atoms possess a face centered cubic lattice each indepenent of each other. The two lattices are embedded in each other in such a way that each S atom occupies the centre of a regular tetrahedron formed by four equidistant Zn atoms and similarly each Zn atom occupies the centre of a regular tetrahedron formed by four equidistant S atoms. From figure (24), it is clear that alternate planes (100) consist of zinc or sulphur points only and also the planes of the latter lie midway between two of the former. Successive planes (110) contain both zinc and sulphur atoms. The planes (111) show alternation and the separation between successive zinc and sulphur atoms is one quarter of the separation between two zinc planes.

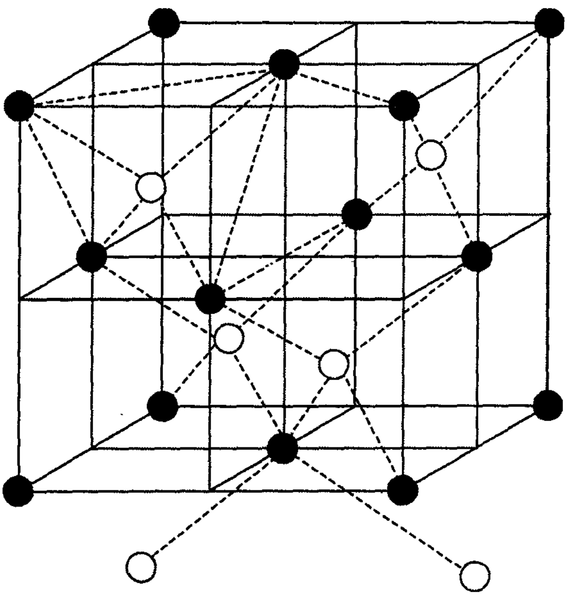


Fig. 24. Structure of ZnS.

[IV] Structure of Diamond

The spectra obtained for diamond are very similar to the spectra of zinc blende as shown in figure (25). Hence, we can consider diamond to be built up on two intersecting or interpenetrating face centered lattices related to one another, in exactly the same way as zinc lattice and sulphur lattice in ZnS.

In diamond, carbon atoms take the place of both zinc and sulphur atoms in ZnS. Interference occurs just in the same places as it occurs in ZnS, but since all the atoms are of one type, the interference is not partial, but complete. Therefore, from (100) face, we not obtain first or third order spectra at all, whereas no second order spectrum is obtained from (111) face.

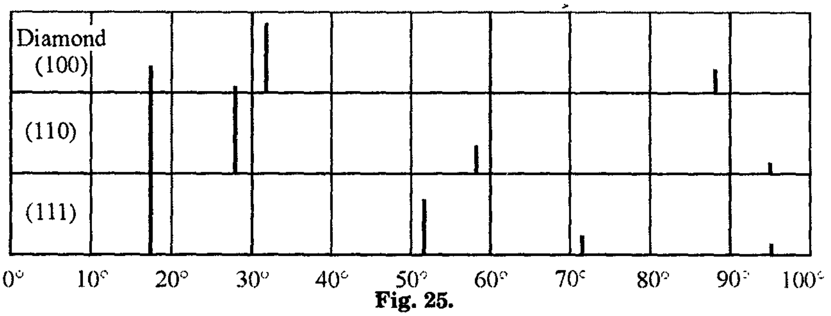


Fig. 25.

An interesting and striking fact is that the structure attributed to diamond involves the further conclusion that each carbon atom is at the centre of a tetrahedron and further that when a sufficient number of carbon atoms are considered, they form an interlocked arrangement of six membered rings analogous to that of benzene as shown in Figure (26a). But in case of (110) planes being vertical and horizontal the interlocked arrangement is as shown in figure (26b).

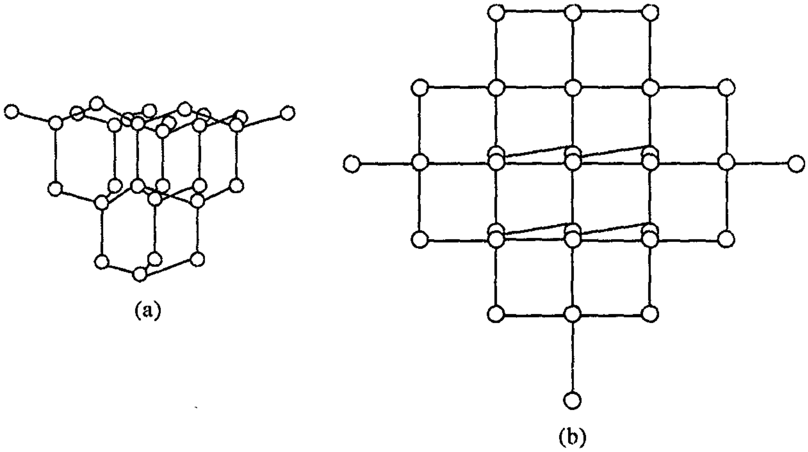


Fig. 26.

Diamond forms crystals belonging to the cubic system. The reflections are shown in figure (25). The first spectra occur at angles whose sines are in the ratio 2 : √2 : √3/2. The spectra reflected from the face (111) are peculiar in that the second order is exceedingly faint, although the first, third, fourth and fifth spectra are quite strong.

The diamond lattice consists of a series of atoms, each of which is placed between four neighbours. The latter occupies the angular points of a regular tetrahedron, while the atom under consideration lies at the centre. The types of structure runs throughout the crystal as shown in figure (27). The C–C bond distance is 0.154 nm. The whole lattice is continuous. The diamond crystal is regarded as a giant molecule. Therefore, it is sometimes known as ***macromolecule***. The crystal is very hard because the covalent links run without a break throughout the whole crystal. The crystal can be cut only by breaking the covalent links. High melting point and boiling point can also be explained by stating that the atoms are very firmly attacked within the crystal. Such phenomenon can also be explained in the cases of compounds of formula AB (where sum of valencies of A and B is 8), *e.g.*, carborundum (SiC), aluminium nitride (AlN).

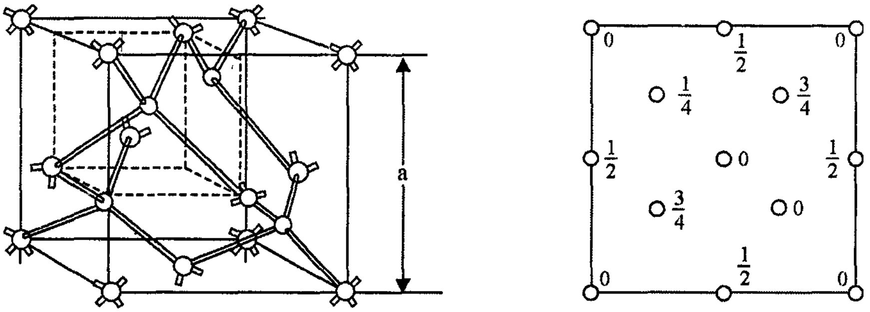


Fig. 27. Two representations of the diamond structure (a) Space model showing tetrahedral bonds. (b) Projection showing fractional coordinates. It is instructive to draw lines showing the bonds in this projection.

[V] Structure of Caesium Chloride

The radius ratio of caesium chloride is $\frac{1.69}{1.81}$ or 0.93. This value indicates that it has a coordination number of 8 and 8 cubic structure. The chloride ions form a simple cubic arrangement, while the caesium ions occupy the cubic interstitial sites, *i.e.*, each caesium ion has eight chloride ions as its nearest neighbours. From figure (28), it can be seen that each chloride ion is also surrounded by eight caesium ions which are directed towards the corners of a cube. Therefore, both types of ions in caesium chloride are in equivalent positions, the stoichiometry is 1 : 1 and the coordination number is 8 : 8.

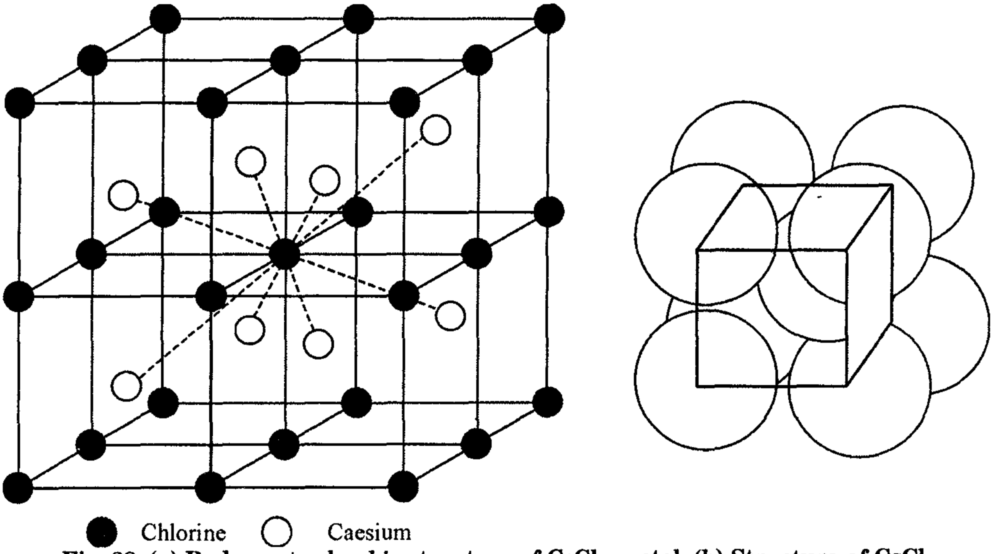


Fig. 28. (a) Body centred cubic structure of CsCl crystal. (b) Structure of CsCl.

As the coordination number of CsCl is higher than that of NaCl, it is expected that the former is more stable than the latter, because each caesium ion has more ions of opposite charge as its neighbours. Actually, caesium chloride is found to be nearly 1% more stable than sodium chloride.

5·19 BINDING FORCES IN CRYSTALS

A number of different types of binding forces are involved in holding crystals together. The physical properties of a crystal are very dependent on the type of bonding.

[I] Ionic Crystals

Ionic crystals are held together by the strong Coulomb attractions of the oppositely charged ions. The lattice energy determined from heat of formation and heat of vaporisation measurements agrees with that calculated on the assumption that the units of the crystal are ions held together by electrostatic forces. NaCl, KCl *etc.*, are ionic crystals. The ionic crystals have the following characteristics :

(1) They are hard and brittle.

(2) The heats of evaporation are very high.

(3) The vapour pressures of such crystals at ordinary temperatures are very low.

(4) The melting points and boiling points are very high.

(5) They are insulators in the solid state as the ions do not move in solid state. However, in molten form or in solution they are good conductors of electricity due to mobility of ions.

(6) They are soluble in water as well as in other polar solvents. They are however, insoluble in non-polar solvents.

[II] Covalent Crystals

Covalent crystals which are held together by covalent bonds in three dimensions are strong and hard and have high melting points. Diamond, graphite, carborundum (SiC) are examples of covalent crystals. The characteristics of covalent crystals are as follows :

(1) They have open structure, *i.e.*, the directional character of the bonding does not lead to maximum filling of space.

(2) These solids are bad conductors of electricity because the bonding orbitals are fully occupied (Graphite is an exception) .

(3) The melting points and boiling points are very high.

(4) Their refractive indices are very high.

(5) They absorb light of different frequency in the solid, liquid or gaseous form.

The great difference between graphite and diamond can be understood in terms of the crystal lattice. Graphite has hexagonal networks in sheets like benzene rings. The distance between atoms in the plane is 142 pm but the distance between these atomic layer planes is 335 pm. In two directions, the carbon atoms are tightly held as in diamond, but in the third direction, the force of attractions appreciably less. As a result, one layer can slip over another. The crystals are flaky and yet the material is not wholly disintegrated by a shearing action. This planar structure is part of the explanation of the lubricating action of graphite, but this action also depends on adsorbed gases and the coefficient of friction is much higher in vacuum.

[III] Molecular Crystals

Molecular crystals are held together by vander Waals forces. Examples are given by crystals of neutral organic compounds and rare gases. Since vander Waals forces are weak, such molecular crystals have low melting points and low cohesive strengths.

The hydrogen bonded crystals are held together by the sharing of protons between electronegative atoms. Hydrogen bonds are involved in many organic and inorganic crystals and in the structure of ice and water. They are comparatively weak bonds but they play an extremely important role in determining the atomic arrangement in hydrogen bonded substances such as proteins and polynucleotides.

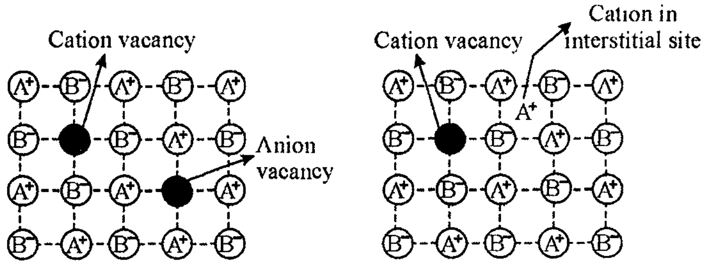
[IV] Metallic Crystals

Metallic bonds exist only between large aggregates of atoms. This type of bonding gives metal their characteristic properties, *e.g.*, opacity, lustre, malleability and conductivity of electricity and heat. Metallic bonding is due to the outer or valence electrons. The overlapping of the wavefunctions for the valence electrons in metals results in orbitals that extend over the entire crystal. The electrons pass throughout the volume of the crystals.

There is a slow transition between metallic and non-metallic properties. Atoms with fewer and more loosely held electrons form metals with the most prominent metallic properties, *e.g.*, sodium, copper and gold. As the number of valence electrons increases and they are held more tightly there is a transition to covalent properties. The close packed structures are often found in metals because the bonding energy per unit volume is maximised.

5·20 DEFECTS IN CRYSTALS

An ***ideal crystal*** is a crystal which has the same unit cell containing the same lattice points throughout the whole of the crystal. At absolute zero, most of the ionic crystals show no defects. With increase of temperature, chances of one or more of the lattice sites remaining unoccupied by the ions increase. This constitutes a ***defect***. The number (n) of such defects per cm^3 is given by the equation :



(a) Schottky defect

(b) Frenkel defect

Fig. 29.

$$n = N \cdot e^{-w/2RT}$$

where N = total number of sites per cm^3, w = work or energy required to produce a defect, T = absolute temperature, R = gas constant and e is base of natural logarithm.

Two types of defects namely *Schottky defect and Frenkel defect* are more common.

[I] Schottky Defect

If some of the lattice points are unoccupied, then Schottky defect arises. The points which are unoccupied are known as ***'holes'*** or ***'lattice vacancies'***. Figure (29-a) shows the existence of two holes, one due to a missing anion and the other due to a missing cation. The crystal as a whole remains neutral because the number of positive and negative ions is the same.

Generally, Schottky defect appears in strongly ionic compounds in which the radius ratio r_+/r_- is not far below unity and have a high coordination number. Thus, NaCl, CsCl having coordination numbers 6 and 8, respectively furnish Schottky defect.

[II] Frenkel Defect

Frenkel defect arises when an ion occupies an interstitial position between the lattice points, as shown in figure (29-b). In it, one of the cations occupies a position in the interstitial space instead of its own fixed site. A hole is thus produced in the lattice. The crystal has a whole is neutral, as the number of positive ions and negative ions is the same. *Positive ions being smaller are more likely to occupy interstitial position than the negative ions.*

Generally, Frenkel defect arises in compounds in which the radius ratio, r_+/r_- is low and the coordination number is also small. For example, in AgBr, ZnS, Ag^+ ions and Zn^{2+} ions, respectively occupy positions in between the other ions in the lattice.

[III] Consequences of Schottky and Frenkel Defects

1. Due to both types of defects, the crystal is able to conduct electricity to a small extent by an ionic mechanism.
2. The closeness of the similar charges brought about by Frenkel defect tends to increase the dielectric constant of the crystals.
3. The presence of holes lowers the lattice energy or the stability of the crystals. Too many holes may cause a partial collapse of the lattice.
4. The presence of holes lowers the density of the crystal.

[IV] Non-stoichiometric Defects

Non-stoichiometric compounds do not obey strictly the law of constant proportions. The number of cations and anions present in such compounds are different from those expected from their ideal chemical formulae. It means that there is an excess of either positive charges or negative charges in the crystal. As a crystal is neutral, then if negative charge is in excess, it is balanced by the presence of extra-positive charges and if positive charge is in excess, it is balanced by the presence of extra electrons. Thus, the crystal structure becomes irregular and defects arise. Such defects are known as ***non-stoichiometric defects,*** which exist in addition to Schottky and Frenkel defects. These are of two types :

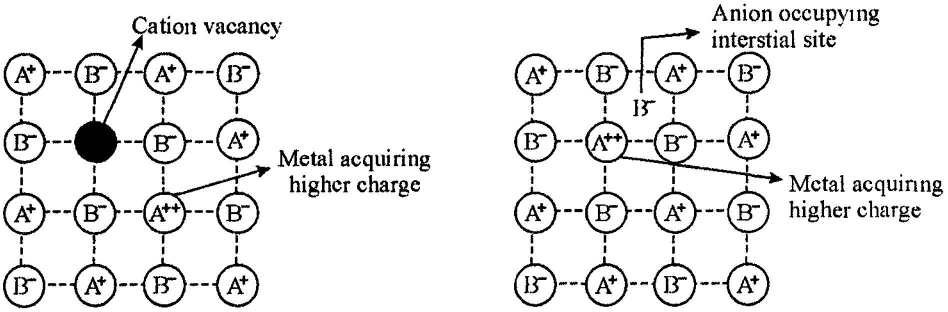
(a) Metal deficiency defects when negative ions are in excess.

(b) Metal excess defects when positive ions are in excess.

(1) Metal deficiency defects : These defects can occur in two possible ways as follows :

(a) Firstly, one of the positive ions may be missing from its lattice point. The extra negative charge may be balanced by some nearby metal ion acquiring two charges instead of one (Fig. 30). The metal must be in a position to acquire variable valency so, this defect is generally found in compounds of transition metals, like FeO, FeS, NiO etc.

(b) Secondly, an extra negative ion may find an interstitial position (Fig. 30-b). The extra negative charge may be balanced by one of the adjacent metal ion acquiring an extra charge. In this case also, the metal ion should also be in a position to acquire variable valency. As negative ions are usually very large, it is expected that they would not be able to fit into the interstitial positions. So, the possibility of finding a crystal showing metal deficiency defect is only theoretical.



(a)
Metal deficiency defect due to a missing positive ion

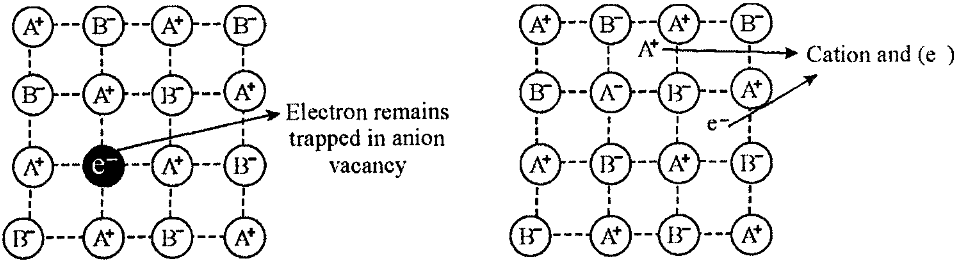
(b)
Metal deficiency defect due to an extra negative ion

Fig. 30.

Consequences of metal deficiency defects : Crystals with such defects may also be semi-conductors. This phenomenon may arise from the movement of an electron from one ion to another. The ion A^+ changes to A^{2+} and the movement of an electron from A^+ ion is an appparent motion of A^{2+} ion.

(2) Metal excess defects : In these defects, the positive ions are in excess and may arise in the following two ways :

(a) Firstly, a negative ion may be missing from its lattice site leaving a hole which may be occupied by an extra free electron to maintain electrical



(a)
Metal excess defect caused by a missing negative ion.

(b)
Metal excess defect due to an extra positive ion.

Fig. 31.

neutrality, as shown in figure (31-a). Thus, there is an excess of metal or positive ions.

This defect though not very common is similar to Schottky defect, but differs in having only one hole and not a pair as in Schottky defect. Those crystals which are likely to form Schottky defects show such an effect. For example, if KCl is exposed to potassium vapour, a lilac coloured non-stoichiometric form of KCl is obtained, which contains an excess of potassium ion.

(b) Secondly, an extra positive ion occupies an interstitial position in the lattice and extra electron also finds a place in the interstitial space to maintain electric neutrality. [Fig. (31-b)].

This type of defect is similar to Frenkel defect but differs from that in not having any holes and in having interstitial electrons. This defect, which is more common, is shown by those crystals which are likely to develop Frenkel defects, *e.g.*, ZnO crystal.

Consequences of metal excess defects : As crystals associated with this type of defect contain free electrons, which can migrate in an electric field and conduct electricity, they can conduct electricity to some extent. As the number of electrons is very small, the crystals can conduct very small current unlike the current conducted by fused salts, metals or salts dissolved in water. These substances are thus called **semi-conductors**.

The crystals showing metal excess defects are generally coloured, which may be due to the presence of free electrons. These electrons get excited easily to higher energy levels by absorption of visible white light and so, the compounds appear coloured. Therefore, non-stoichiometric NaCl, non-stoichiometric KCl, non-stoichiometric ZnO appear yellow, lilac and yellow (when hot), respectively.

5·21 THERMAL DEFECTS AND SEMI-CONDUCTORS

Atoms of Ge and Si have four electrons in the outer shell. Each atom is covalently bonded with four neighbouring atoms and as such there are not free electrons as we have in metals. So, the electrical conductance is very low. If an appreciable amount of energy, say in the form of heat, is given to the crystal, one of the covalent bonds may get broken and electrons are ejected. The released electrons can migrate leaving a positive charge (positive hole) at the site of the missing bond. The crystal can now conduct electricity because on applying the electric field, the electrons and positive holes migrate in opposite directions. This type of conductance is known as ***intrinssic conduction***.

[I] Impurity Defects

Certain defects known as impurity defects in a crystal arise from the presence of chemical impurities. One important application of these defects lie in the use of Ge and Si crystals as *semi-conductors in transistors*. Ge and Si belonging to group IV of the periodic table, in pure states, have very low electrical conductivity. On adding even traces of an element belonging to Group III or V, the electrical conductivity is appreciably enhanced. The reason may be explained as below :

Suppose a group V element like As, is added to a Ge crystal. As a Ge atom is substituted by an As atom, four of the electons in As form covalent bonds with the surrounding Ge atoms, but the fifth electron remains free. Thus, an extra electron gets introduced into the crystal, which can serve to conduct electricity, *i.e.*, it behaves like a conductor – electron as in metals. Thus, Ge containing traces of As (known as arsenic doped germanium) starts to show fairly high electrical conductivity. This type of conduction is known as ***extrinsic conduction***, which is much greater than ***intrinsic conduction***. In this type of conduction, the current is carried by excess electrons in the ***normal way***, it is, therefore, known as ***n-type semi-conduction.***

Suppose indium a group III element having only 3 electrons in the outer shell is added in small traces to Ge. The atoms of indium having one electron short, are unable to complete tetrahedral covalent structures. So, some of the sites normally occupied by electrons will be left empty, giving rise to ***electron-vacancies***. The electron-vacant sites are known as ***positive holes***. When electrical field is applied, adjacent electrons migrate into the positive holes and in this way other electron vacancies or positive holes are formed. The migration of positive holes continues and current is carried out throughout the crystal. Thus, Ge containing traces of In (indium doped germanium) acquires appreciable electrical conductivity. As the current now is carried by positive holes, this type of conduction is called ***p-type semi-conduction.***

From the above explanation, it is clear that both *n*-type and *p*-type of semi-conductors are electrically neutral because each atom of impurity added is neutral in itself, as they contain equal number of protons and electrons. There is thus a shortage or surplus of one valency electron depending on whether an element of group III or group V is added, but the total number of electrons remains equal to the number of positive nuclear charges.

Increase of temperature increases the conductivity of semi-conductors. This is due to the fact that an extra-electron or positive hole, as the case may be, is bound weakly with the crystal and so some energy in the form of heat is required to free it from the crystal lattice for electric conduction.

[II] Applications of Semi-conductors

The combination of *n* and *p*-type of semi-conductors, known as *n-p junctions* is used in the manufacture of transistors. This device shown in figure (32) can conduct electric current more easily in one particular direction than in the reverse direction and so can be used as rectifier for converting A.C. into D.C. The substance on the left side of each junction is *n*-type conductor obtained from arsenic doped germanium. The negative (–) signs represent extra electrons. The material on the right side of the junction is *p*-type conductor obtained from In doped Ge. The positive (+) signs represent positive holes arising from the deficiency of electrons at the indium impurity centres. On applying an external voltage in such a way as to have motion of electrons (*n*-current) from left to right and movement of positive holes (*p*-current) from right to left (figure 32a), current is readily conducted. If direction of voltage is reversed, so that there is a separation of electrons and positive holes (figure 32b)

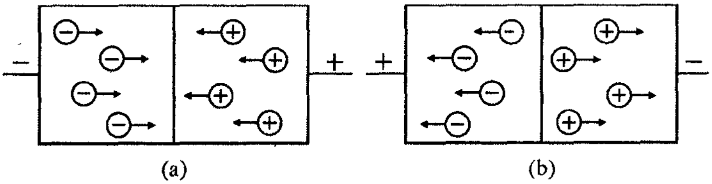


Fig. 32. n-p Junctions.

there is cancellation of *n*- and *p*-currents and so the conduction stops. Therefore, the *n-p* junction allows the current from an outside source to flow only in one direction.

5·22 APPLICATIONS OF X-RAY ANALYSIS

X-rays provide a number of important applications in practically all walks of life. These methods are important, as they involve only small amounts of materials or substances. Some important applications of X-ray analysis are as follows :

(i) X-ray analysis is used to ascertain the constitutional formula of certain organic compounds, in which the weight of a unit cell is determined by means of the number of units present in that particular substance.

(ii) X-ray analysis is used to confirm the crytalline nature of colloidal substances.

(iii) X-ray analysed is used to confirm the microcrystalline structure of rubber, cellulose, plastic etc. which were previously assumed to be amorphous.

(iv) X-ray analysis is used to establishes the existence of atoms in solid substances and also the coefficient of thermal expansion of crystals can be measured by calculating the shift of powder lines on heating or cooling the crystals.

(v) X-ray analysis is used to also helps us to investigate the crystalline structure of alloys and metals. The effects during rolling, heat treatment, annealing etc., can also be studied by X-ray analysis.

(vi) X-ray analysis is used to is used to detect and photograph defects inside the body such as metal plate or other mechanical part.

(vii) X-ray analysis is used to has given valuable assistance in radiography, *i.e.*, in the diagnosis of disease or in showing the effects of accidents affecting the internal parts of the body such as presence of foreign materials, fractures etc.

(viii) By X-ray stereoscopic radiography, it is possible to determine the depth of an object below the surface of the body in which it is embedded. The object examined also stands out in high relief.

(ix) X-rays are also used for their curative properties. They are mostly used for the treatment of cancer. The effect of powerful X-rays on living tissues is destructive, if exposed for a long time, therefore, proper dosage must be fixed both as regards the quantity and quality of radiations used.

5·23 ISOMORPHISM

Isomorphism means the *same form*. Substances are said to be isomorphous when crystals of different chemical substances exhibit the same crystalline form. Mitscherlich deduced that *isomorphous substances have similar chemical formulae, e.g.*, phosphates and arsenates are said to be isomorphous with one another , *viz.*, $Na_2HPO_4.12H_2O$ and $Na_3AsO_4.12H_2O$.

But now-a-days the concept of isomorphism has changed. Just as a liquid may dissolve in another liquid to give a liquid solution, similarly a solid may dissolve in another solid to form a solid solution. The solid crystal thus obtained is perfectly homogeneous and is sometimes called ***mixed crystal*** or ***isomorphous mixture***. (Greek : isomorphous = equal shaped). Such a crystalline body is not a mechanical mixture of two components, but is actually a one phase solid solution.

Solid solutions can be obtained by cooling a liquid solution of two suitable components. The colour and composition of such crystals will depend upon the respective concentrations of the two salts in the original aqueous solution, *e.g.*, by mixing while potash alum crystals and purple chrome alum crystals, we obtain a single type of crystal intermediate in colour and composition between the two alums. A solid solution may be looked upon as an intermediate stage between an ordinary physical mixture and a chemical compound. The X-ray analysis of a solid solution reveals that the various elements replace each other atom for atom in the space lattice of the mixed crystal. There is no indication of two distinct lattices, for the two components go to form the actual lattice of the solid solution.

Goldschmidt established that the factors contributing to isomorphism are the size and the polarisability of ions. *[The polarisation describes the position of outer electrons with reference to the atomic nuclei, while the polarisability describes the lability of these electrons when induced from their normal positions].*

For two substances to be isomorphous, the following conditions must be satisfied.

(i) Their formulae must be analogous, (ii) the size of the ions must not be very different, (iii) the polarisation of the ions must not be very different, (iv) the substances must have similar unit cells containing the same number of positive and negative ions in geometrically similar positions.

In case of non-polar organic compounds, the following conditions must be fulfilled before they can make solid solutions.

(i) Their chemical constitution must be analogous, (ii) their crystal structures must be similar, (iii) their molecular volumes must be very nearly equal.

5·24 MORPHOTROPISM AND POLYMORPHISM

For a given structure, the possibility of substitution is limited to a certain range of ion sizes and polarisabilities and if these limits are exceeded, a new space lattice is produced. *This phenomenon in which there is a change over of the space lattice as a result of substituting one ion for another is known as **morphotropism**, according to Goldschmidt.*

According to Goldschmidt, even polymorphism may be regarded as a case of morphotropism, occasioned not by substitution but by thermodynamic alternation, so that the substance is no longer isomorphous with itself.

So, *the property under which a solid body can exist in two or more than two crystalline states is known as **polymorphism***. But when polymorphism occurs in elements, the phenomenon is generally known as ***allotropy***. As polymorphism is due to differences in the arrangements of fundamental units in the crystal structure of a particular substance, its different polymorphs may exist in different crystal systems or in the same system with different space lattices. Thus, different crystalline allotropic forms of sulphur and carbon exist in different crystal systems. But in the case of NH_4Cl, its polymorphs belong to the cubic system with different space lattices. There are four types of allotropy :

(i) Enantiotropy (ii) Monotropy (iii) Dynamic allotropy

[I] Enantiotropy

When two forms of a solid substance exist together in equilibrium with each other at a particular temperature which depends only on the pressure, the property is known as ***enantiotropy*** and the temperature is known as ***'transition temperature'***. The forms two are known as ***enantiotrophs***.

At all other temperatures except the transition point, only one form is stable, and the other form is in the metastable state. The transition point lies below the melting points of the two modifications, *e.g.*, the transition temperature of transition of rhombic sulphur to monoclinic sulphur is 95.6°C.

[II] Experimental Determination of Transition Temperature

At the transition temperature, there is a sudden change in any physical property, *e.g.*, solubility, refractive index, density, vapour pressure etc. This forms the basis of determining the transition temperature. Some methods used for this purpose are :

(i) Solubility method : This method consists in determining the solubility of a substance at various temperatures. A solubility-temperature curve is plotted. The break in this curve gives the transition temperature.

(ii) Thermometric method : In this method, the solid is taken in a tube which is heated slowly in a water bath with constant stirring. The temperature of the solid is noted after every 30 seconds. A curve is plotted between temperature and time. The point of inflexion gives the transition temperature.

[III] Monotropy

In the case of some solids, only one form in stable at all temperatures. Other forms either change continuously or tend to change into the stable variety, although in some cases, existence of metastable form over geological ages has been met with. This is called ***monotropy***. The two forms are monotropic, if the transition point lies above the melting point. The transition point in this case, cannot be realised under atmospheric pressure as the change takes place in one direction only. In other words, the transformation of monotropic substances is irreversible.

[IV] Dynamic Allotropy

In the case of few elements, the allotropic modifications can exist in dynamic equilibrium with one another over a range of temperature. This phenomenon is known as ***dynamic allotropy***. In such a case, there is no transition point. The reversible transformation of S_λ and S_μ is an example of this type, *i.e.*, $S_\lambda \Rightarrow S_\mu$.

Table–1. Differences between monotropy and enantiotropy.

S. No.	Monotropy	Enantiotropy
1.	Transition point lies above the m.pt.	Transition point lies below the m.pt.
2.	One form is stable and the other metastable.	Both forms are stable.
3.	Transition point cannot be realised under atmospheric pressure.	Transition point can be realised under atmospheric pressure.
4.	Change is irreversible.	Change is reversible.
5.	On heating, the metastable form melts, substance solidifies and remelts at higher temperature.	Slow heating causes the first form to change into the second form and then the latter re-melts at higher temperature.
6.	Examples are : graphite and diamond, violet and white phosphorous etc.	Examples are : rhombic and monoclinic sulphur; grey and white tin etc.

5·25 CLOSED PACKED STRUCTURE

In a crystal lattice, the position of particles present in a unit cell are represented by points connected by lines. It gives an impression as if the crystal particles are far apart. But the fact is different from this. The atoms, ions or molecules in a crystal are in contact with maximum possible number of other fellow particles so that a maximum possible space is occupied. Such an arrangement is known as *closest packing*. This type of packing depends on the nature, shape and size of the constituent particles of the crystal. We shall discuss in brief the close packings of identical spheres and non-identical spheres.

5·26 CLOSED PACKING OF IDENTICAL SPHERES

The arrangement of identical spheres in a plane lends to a packing in which each sphere is in direct contact with six other spheres. The planar array of close packed spheres can be extended into three dimensional arrangement by the addition of layers above and below the first layer. There are two arrangements based on the way the successive layers are placed one above the other.

(a) Haxagonal close packing (hcp) : The spheres are arranged on a flat plane in such a way that each sphere is in contact with six other spheres as shown in figure (33). Here spheres are at the corners of a regular hexagon. Let us designate the first layer as A. Now a second layer B of spheres is placed on layer A in such a way that the spheres of the second layer occupy the alternate holes (XXX) in layer A. This is shown in figure (34) by denoted by dotted circles.

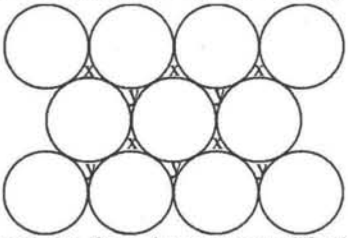


Fig. 33. A sphere in contact with six spheres has two sets of trigonal holes XXX and YYY in a planes.

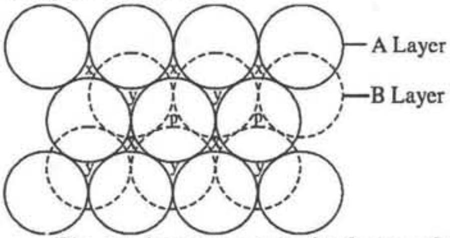


Fig. 34. Arrangement of spheres of the second layer (dotted) on the holes XXX of the first layres.

A third layer of spheres is placed on the second layer so that each sphere in third layer is directly above the spheres in the first layer. Thus the third layer, is identical with the first layer and is designed as layer A. A fourth layer is placed on

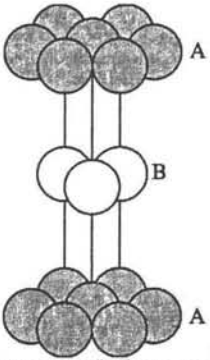


Fig. 35. Haxagonal close packing of identical spheres.

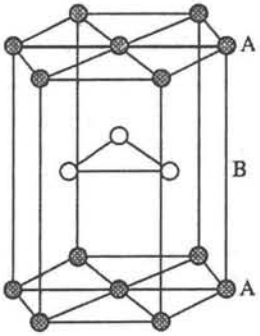
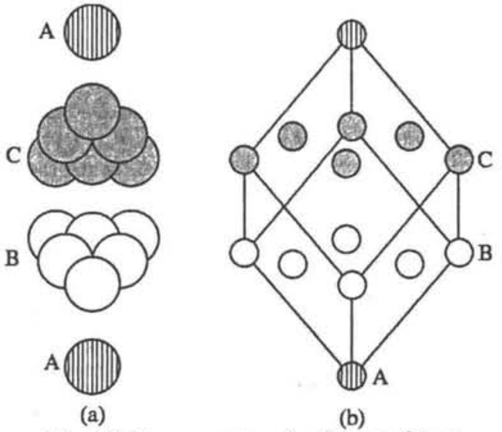


Fig. 36. Haxagonal unit cell.

the third layer so that each sphere in the former is above the spheres of the second layer. Therefore, fourth layer is designated as layer B. This type of packing is referred to a ABABA ...... arrangement. This type of packing is also known as **hexagonal close packing.** It is abbreviated as HCP or hcp. For simplicity, HCP arrangement can be drawn as shown in figure (36).

This is shown in figure (35).

(b) Cubic close packing (ccp) : Another way to pack spheres in the third layer is to place them over hollows marked X (unoccupied hollows of first layer). This gives rise to a new layer labelled as C. However, it can be shown that the spheres in the fourth layer will correspond to those in the first layer. This is shown in figure [37 (a) and (b)]. This gives the ABCABCA ...... type of arrangement. It is also known as **cubic close packing**. It is abbreviated as ccp. For simplicity, ccp arrangement can be drawn as shown in figure (38). It is clear from figure (38) that there is a sphere at the centre of each face of the cube. Therefore, this arrangement is also known as **face centred cubic arrangement**. It is abbreviated as fcc.



(a) (b)

Fig. 37. Face centered cubic packing.

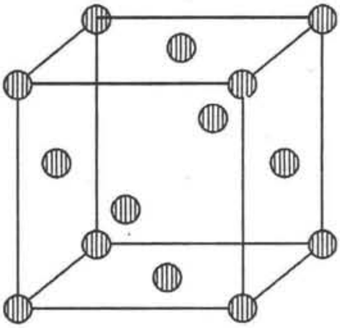

ccp arrangement

Fig. 38.

The hcp and fccp are the best possible packing arrangement of identical spheres. Each sphere has 12 nearest neighbours. The spheres occupy 74 percent of the total volume. Nearly 60 percent of the metals and a few rare gases crystallize either as hexagonal close packing or face centred cubic close packed structures.

(c) Body centred cubic packing (bccp) : Certain metals crystallize in such a manner that each atom is in contact with either other atoms. The central atom occupies a lattice site and has eight nearest neighbours each at the corners of a cube. This is called a *body centred cubic packing (bccp)*. This is shown in figure (39), (40) and (41). The atoms occupy 68 percent of the total volume. Nearly 20 per cent of the metallic elements crystallize in the body centred cubic packing.

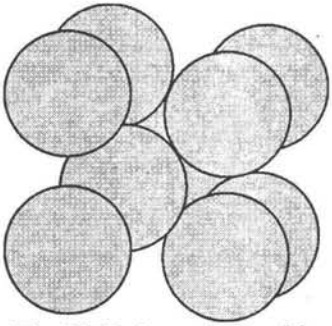


Fig. 39. Body centred cubic packing (bccp).

There is no theoretical method to predict the packing in crystals. For each metal the crystal structure is determined only by experiments. Table–2 includes examples of some elements which show *hcp, fccp* and *bccp* type of arrangement as determined by X-ray experiments.

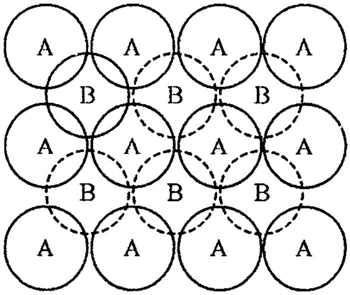


Fig. 40. Body centred cubic packing of spheres.

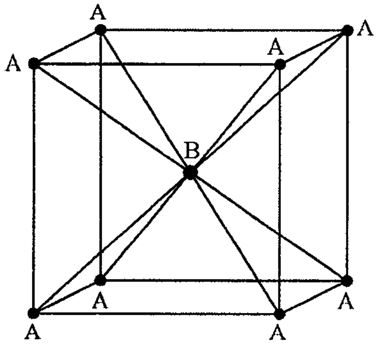


Fig.41. b.c.c Lattice.

Table–2. Type of packing in metals

hccp	Be	Cd	Ca	Li	Mg	Zn			
fccp	Al	Ca	Fe	Cr	Co	Cu	Mg	Pb	Li
bccp	Ba	Ca	Cr	Co	Fe	Li	Mn	Na	Rb

Remarks : It is seen from table–2 that some elements crystallize in various forms. This is an indication that such structures have different stability under different conditions.

[I] Coordination Number

The number of spheres with which a sphere has direct contacts in a close packed structure is called *coordination number* or ligancy. For example : In the simple cube each atom touches six adjacent atoms, hence the coordination number of each particle is 6. In the body centred cube, an atom is in the centre and touches eight corner atoms. The coordination number is, therefore, 8. In the face centred cube, and the hexagonal crystals the coordination number is 12 in each case. In the packing of uniform spheres the highest coordination number is 12. It is not possible to arrange identical spheres into a given space by any other arrangement exceeding ligancy of 12.

Table 3.

Lattice of uniform spheres	Coordination number
Simple cubic	6
Body centred cubic	8
Face centred cubic	12
Hexagonal	12

[II] Volume Occupied in ccp Arrangement

Consider a cubic close packed arrangement as shown in figure (42). Suppose the length of each side be a, so that the volume of the cube is a^3. The volume occupied by spheres can be calculated as follows :

From the figure it is clear that there are eight spheres at the corners and six spheres at the faces. Each sphere at the corner is shared by eight unit cells and its contribution per unit cell is 1/8. Similarly, each sphere in the face is shared by two unit cells and its contribution per unit cell is 1/2.

Total number of spheres per unit cell $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Consider a right angled triangle ABC. We have ΔABC, and as it is a right angled triangle,

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

∴ Face diagonal, $AC = (\sqrt{2}).\, a$

From the figure, it is clear that $AC = 4r$, here r is the radius of the sphere.

$$\therefore \quad 4r = (\sqrt{2}).\, a$$

$$\text{or} \quad r = \frac{\sqrt{2}}{4}.\, a$$

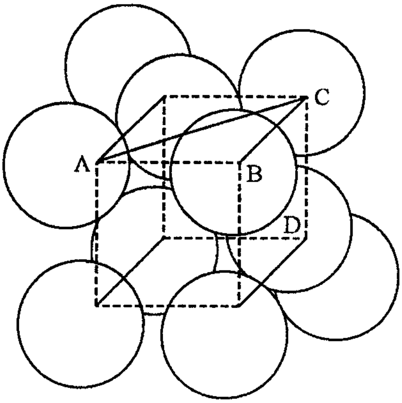


Fig. 42.

As mentioned above, there are 4 spheres per unit cell, so the volume occupied by 4 spheres

$$= 4 \times \frac{4}{3}\pi r^3 = 4 \times \frac{4}{3}\pi\left(\frac{\sqrt{2}}{4}.\, a\right)^3$$

∴ Ratio of volume occupied to total volume

$$= \frac{\text{Volume occupied by spheres}}{\text{Volume of the cube}}$$

$$= \frac{4 \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{\sqrt{2}}{4}a\right)^3}{a^3} = 0.7406$$

∴ Volume occupied in ccp arrangement = 74.06%

[III] Volume Occupied in bcc Arrangement

Consider a body centred cubic arrangement as shown in figure (43). Suppose the length of each side be a and so volume of the cube is a^3.

From the figure, it is clear that there are eight spheres at the corners and one in the body of the unit cell. Each sphere is shared at the corner by eight unit cells and so its contribution per unit cell is 1/8. However, the sphere at the centre of the cube contributes fully to it. So, the number of spheres per unit cell

$$= 8 \times \frac{1}{8} + 1 = 2 \quad \text{...(1)}$$

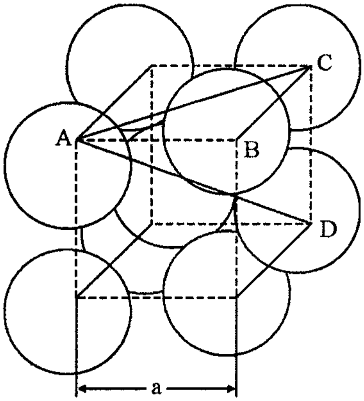


Fig. 43.

From right angled triangle ABC, we have

$$AC^2 = AB + BC^2$$

$$= a^2 + a^2 = 2a^2,$$

$$\text{or} \quad AC = (\sqrt{2}).\, a \quad \text{...(2)}$$

From ΔACD, we have

$$AD^2 = AC^2 + CD^2 = [\sqrt{2}.\, a]^2 + a^2 = 3a^2 \text{ or } AD = (\sqrt{3}).\, a \quad \text{...(3)}$$

The value of body diagonal AD = $4r$, where r is the radius of the sphere. ...(4)

From equations (3) and (4), $4r = (\sqrt{3}) \cdot a$

or
$$r = \frac{(\sqrt{3}) \cdot a}{4}$$

As there are two spheres per unit cell, so volume occupied by two spheres

$$= 2 \times \frac{4}{3} \pi r^3 = 2 \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{\sqrt{3} \cdot a}{4} \right)^3$$

$\therefore$ Ratio of volume occupied to total volume

$$= \frac{2 \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{\sqrt{3} \cdot a}{4} \right)^3}{a^3} = 0.6805$$

$\therefore$ Volume occupied in bcc arrangement = 68.05%.

5·27 INTERSTITIAL SITES IN CLOSE PACKED STRUCTURE

Even in close packing of spheres, there is some empty space left. For example, when spheres are closely packed, the centres of three adjacent spheres lie at the vertices of an equilaterial triangle. In between these three spheres, there is some empty space called a ***hole*** or ***void***. Depending upon the number of spheres surrounding the *hole*, the *voids* have been classified as trigonal, tetrahedral and octahedral.

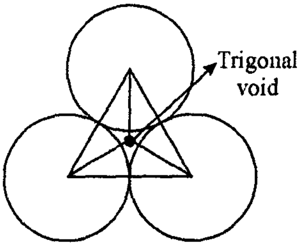


Fig. 44. Trigonal void.

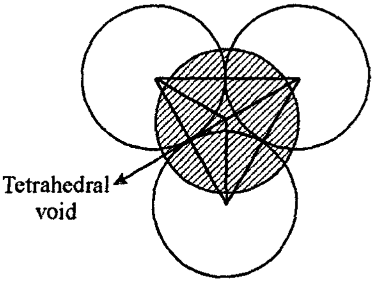


Fig. 45 Tetragonal void fourth sphere is dotted.

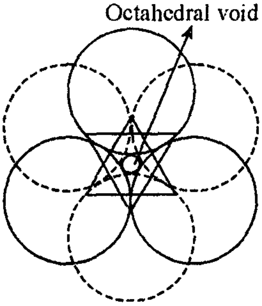


Fig. 46. Octahedral void.

[I] Trigonal Void

The void enclosed by three spheres in contact is called a *trigonal void*. The trigonal void and the spheres surrounding it, are in the same plane. This is shown in figure (44). In a trigonal void only a small sphere of radius 0.155 time of the bigger sphere can fit. Thus, in ionic crystals the cation will occupy the trigonal void enclosed by anions where $r_+ = 0.115\, r_-$.

[II] Tetrahedral Void

This is the void enclosed by three spheres and capped by a fourth sphere as shown in figure (45). Thus, this void exists at the centre of a tetrahedron. This is bigger than the trigonal void. The cation and anion radius ratio should not exceed by 0.2247. Thus, if the anions occupy the corners of a tetrahedron, the void space will be occupied by those cations whose radii fall within the prescribed limit.

[III] Octahedral Void

The void enclosed by six spheres in contact is called an octahedral void as shown in figure (46). This is the largest void in close packed identical spheres. The void exists at the centre of an octahedron whose corners are the centres of six identical touching spheres. The ratio of the radii of cation and anion should not exceed 0.414. All cations with this ratio will occupy the octahedral hole.

We can understand the existence of different types of voids in packed structure if we consider the packed model of identical spheres. In the first layer of close packed structure (Refer fig. 33) there are voids marked as XXX and YYY. These voids are trigonal. (Look carefully on void marked X and enclosed by spheres 3, 4 and P, it is within triangle). Similarly, there are trigonal voids in other layers. When a second layer of close packed structure is placed over the first layer, the alternate voids (XXX) of first layer are enclosed (capped) by the spheres of the second layer (dotted circles). In such a structure, each one of the XXX voids is now surrounded by 4 spheres, 3 of the first layer and one of the second layer as shown in fig. 34(b). This hole is called a *tetrahedral void*. That is, a tetrahedral void is the space formed by a trigonal group of bottom layer and *capped* by a sphere of the top layer.

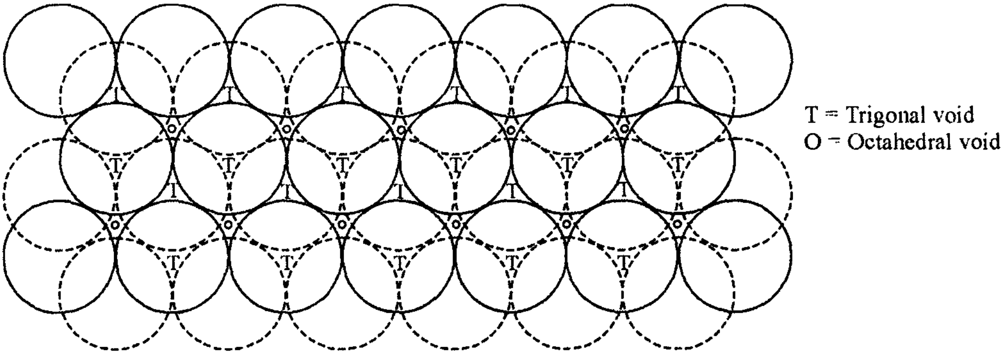


Fig. 47. Tetrahedral (T) and octahedral (O) voids in a close packed structure.

In this structure, there are some trigonal voids of the second layer over the unoccupied trigonal voids (YYY) of the first layer. This gives a new type of void called an *octahedral void*. Thus, an octahedral void is the double trigonal space between the two layers and surrounded by six spheres. This can be understood by referring to figure (47).

[IV] Number of Voids in a Close Packed Structure

In a close packed structure containing x spheres (atoms, molecules or ions) there are $8x$ trigonal voids, $2x$ tetrahedral voids and x octahedral voids. Thus, a sphere in close packed lattice is surrounded by 24 trigonal holes, 8 tetrahedral holes and six octahedral holes.

Comments : This can be visualised if we look at figure (34). The sphere P is surrounded by 6 trigonal voids XXX and YYY when viewed from the top, and by 6 trigonal voids when viewed from the bottom. When a second layer is placed over the first layer, then 6 trigonal voids at the bottom of 2nd layer will surround the sphere P of the first layer. In the same way, if another layer is placed at the bottom of the first layer, then the sphere P will be surrounded by 6 trigonal voids of the another layer. Thus, there are 24 trigonal voids (holes) surrounding a sphere in a close packed structure. In the same way, we can visualise the existence of 8 tetrahedral, and six octahedral voids. It is to be kept in mind that the holes surrounding a sphere are common to other spheres also.

5·28 SIZE OF INTERSTITIAL SITES IN IONIC CRYSTALS

[I] Limiting Radius Ratios

In general, the size of an octahedral site is greater than the size of a tetrahedral site, which in turn is greater than the size of a trigonal site. In case of ionic crystals, the radius of a cation which may occupy a given site created by anions can be calculated by simple geometry. It is done in terms of the ratio of the radius of cation to that of anion (r_+/r_-), also known as ***radius ratio***.

(1) Radius ratio for trigonal site : A trigonal site is formed when the three anions represented by spheres lie at the vertices of an equilateral triangle and a cation shown by a small sphere occupies the trigonal site (Fig. 48). If r_+ and r_- are the radii of cation and anion, respectively, then from equilaterial ΔEBC,

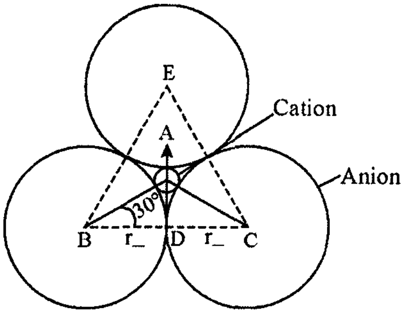


Fig. 48. Section of the structure showing the geometry of a trigonal hole.

$$BC = CE = BE = 2r_-$$

Let A be the centre of the triangle and so of the cation, then

$$BD = r_- \qquad \text{and} \qquad AB = r_+ + r_-$$

In right angled triangle BDA,

$$\cos ABD = \frac{BD}{AB}, \textit{ i.e, } \cos 30^\circ = \frac{r_-}{r_- + r_+} = \frac{\sqrt{3}}{2} \left(\because \cos 30^\circ = \frac{\sqrt{3}}{2} \right)$$

On inverting both sides, $\dfrac{2}{\sqrt{3}} = \dfrac{r_- + r_+}{r_-} = 1 + \dfrac{r_+}{r_-}$

or $$\frac{r_+}{r_-} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

It means that trigonal site is only about 0.155 of the size of the surrounding spheres, *i.e.*, anions.

(2) Radius ratio for octahedral site : An octahedral site is shown in figure (49). It is clear that in it, four anions are at the corners of a square and the cation is at the centre. One anion at the top and one anion at the bottom of the plane formed by the four anions also touch the cation. Let each side of the square be a and r_+ and r_- be the radii of the cation and anion, respectively.

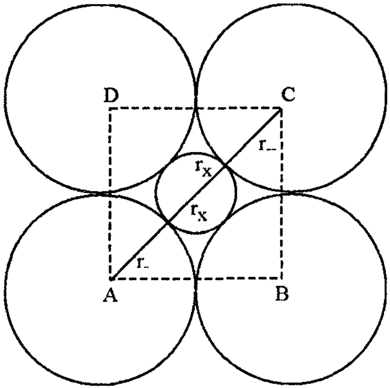


Fig. 49. A section of the structure showing the geometry of an octahedral void.

In a right angled triangle ABC,

$$AC = \sqrt{(AB^2 + BC^2)} = \sqrt{(a^2 + a^2)} = \sqrt{2}\,.\,a$$

$$AC = r_- + 2r_+ + r_- = 2r_- + 2r_+ = \sqrt{2}\,.\,a$$

or
$$r_- + r_+ = \frac{\sqrt{2}\,.\,a}{2} \qquad \text{...(1)}$$

From figure (49), $AB = a = 2r_-$ or $r_- = \frac{a}{2}$ ...(2)

Dividing equation (1) by (2), we get

$$\frac{r_- + r_+}{r_-} = \frac{\sqrt{2}\,.\,a}{2} \times \frac{2}{a} = \sqrt{2}$$

or
$$1 + \frac{r_+}{r_-} = \sqrt{2} \text{ or } \frac{r_+}{r_-} = \sqrt{2} - 1 = 1.414 - 1 = 0.414$$

So, limiting radius ratio for an octahedral site is 0.414.

(3) Radius ratio for tetrahedral site : A tetrahedral site is formed when one sphere is placed over three spheres which touch one another (Fig. 50). In an ionic crystal, such a site can be formed by placing the anions at the alternate corners of a cube. The cation occupies the tetrahedral site. Let the length of the cube be a and. r_+ and r_- are the radii of the cation and anion, respectively.

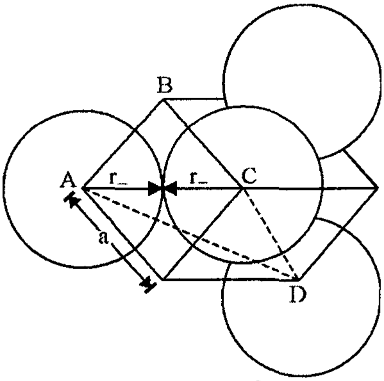


Fig. 50. Geometry of a tetrahedral hole.

In the figure, the face diagonal, $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = (\sqrt{2})\,a$.

As the spheres actually touch each other,

$$AC = r_- + r_- = 2r_-$$

∴
$$2r_- = \sqrt{2}\,.\,a$$

or
$$r_- = \frac{\sqrt{2}\,.\,a}{2} = \frac{a}{\sqrt{2}} \qquad \text{...(1)}$$

The body diagonal, $AD = \sqrt{AC^2 + CD^2} = \sqrt{(\sqrt{2}\,a)^2 + a^2} = \sqrt{3}\,.\,a$ ...(2)

The cation is present at the centre of body diagonal AD, so that half the length of this diagonal is equal to the sum of the cation and anion. So,

$$r_- + r_+ = \frac{AD}{2} = \frac{\sqrt{3}\,.\,a}{2} \qquad \text{...(3)}$$

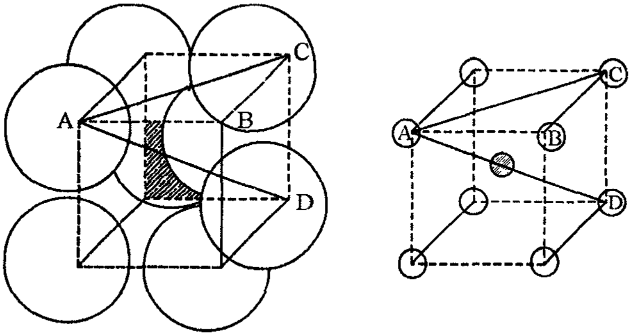
Dividing equation (3) by (1), we get,

$$\frac{r_- + r_+}{r_-} = \frac{\sqrt{3}\,.\,a}{2} \times \frac{\sqrt{2}}{a} = \frac{\sqrt{3}}{\sqrt{2}}$$

or
$$\frac{r_+}{r_-} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414} = 0.225$$

So, the limiting radius ratio is 0.225.

(4) Radius ratio for cubic site : In a cubic site, as shown in figure (51), the spheres are not shown touching one another for the sake of simplicity. Let the length of the cube be a and r_+ and r_- are the radii of the cation and anion, respectively.



(i) (ii)

Fig. 51.

In the figure,

$$AB = 2r_- = a \text{ or } r_- = a/2 \qquad \ldots(1)$$

The face diagonal, $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2} \,.\, a$

The body diagonal, $AD = \sqrt{AC^2 + CD^2}$

$$= \sqrt{(\sqrt{2} \,.\, a)^2 + a^2} = \sqrt{3} \,.\, a$$

But, body diagonal,

$$AD = r_- + 2r_+ + r_- = 2r_- + 2r_+$$

$$\therefore \qquad 2r_- + 2r_+ = \sqrt{3} \,.\, a \text{ or } r_- + r_+ = (\sqrt{3}/2) \,.\, a \qquad \ldots(2)$$

Dividing equation (2) by (1), we get

$$\frac{r_- + r_+}{r_-} = \frac{(\sqrt{3})\, a}{2} \times \frac{2}{a} = \sqrt{3}$$

or

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$

So, the limiting radius ratio for a cubic site is 0.732.

[II] Packing In Ionic Crystals (Packing of Non-Uniform Spheres)

Packing in ionic crystals depends upon the nature and the number of the constituent ions. In a close packed structure, the cations are surrounded by anions, and the anions by cations in such a fashion that the condition of electrostatic neutrality is maintained. The number of anionic nearest neighbours is called the *coordination number of cation*, whereas the coordination number of the anion is the number of nearest cationic neighbours. The common coordination numbers in ionic crystals are 4, 6 and 8.

In ionic crystals, the size of anions and cations are usually different. Therefore, the lattice is viewed as a close packed arrangement of the larger ions with the oppositely charged smaller ions inserted in the holes. Since in ionic crystals the anions are generally large they occupy the main lattice sites and the cations occupy the void space. The size and type of the void space in which the smaller ions are inserted can be determined by knowing the relative size of the anions and cations that is, by knowing the relative size of the anions and cations that is, of the larger ion (usually written as r_+/r_- or r_c/r_a). Conversely, from the nature of the void space we can predict the radius ratio and hence can decide as to which type of packing a particular ionic compound should belong. From geometrical calculations it can be shown in a trigonal void the critical radius ratio r_+/r_- is 0.155, in a tetrahedral void the radius ratio r_+/r_- is 0.225, in octahedral void r_+/r_- is 0.414. Thus :

(i) If the radius ratio is between 0.155 and 0.225, the cation will occupy the trigonal void with its coordination number 3.

(ii) If the radius ratio is between 0.225 and 0.414, the cation may be inserted in a tetrahedral void with coordination number 4.

(iii) When the radius ratio is between 0.414 and 0.732, the cation will occupy the octahedral void with coordination number 6.

(iv) When r_+/r_- is greater than 0.732, that is the anions and cations are approximately of the same size, then the chances of fitting any one of the ions into the voids of the lattice is small. In such cases, the body centred close packing is preferred, when the coordination number is 8. These results are summarized in table 4.

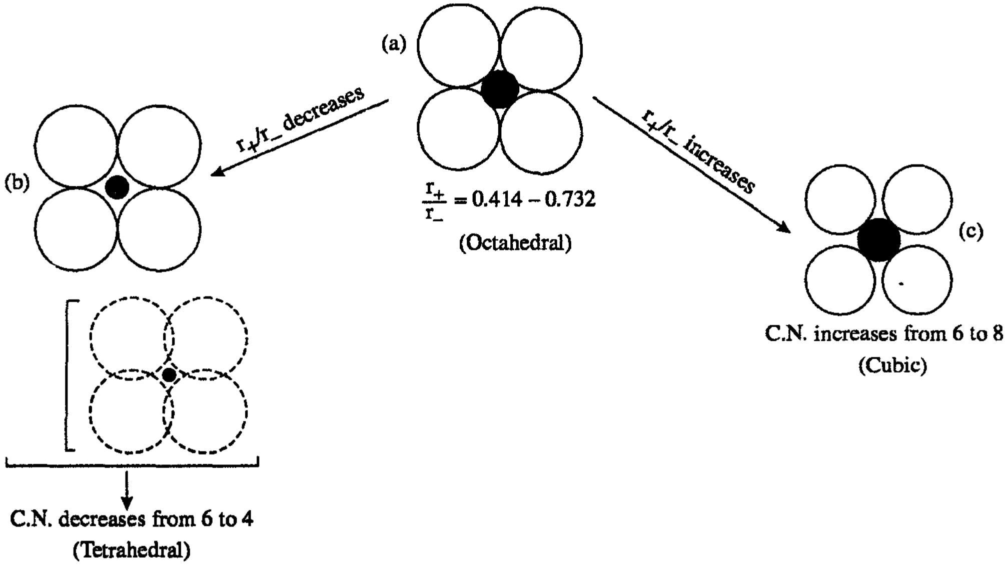


Fig. 52. Effect of radius ratio on coordination number.

Table–4. Summary of the radius ratio for various coordination numbers

Radius ratio	Position of cation	Coordination number
$0.225 > r_+/r_- > 0.155$	Trigonal void	3
$0.414 > r_+/r_- > 0.225$	Tetrahedral void	4
$0.732 > r_+/r_- > 0.414$	Octahedral void	6
$r_+/r_- > 0.732$	Centre of body	8

Problem 1. ***The radius of lithium ion (Li^+) is 60 pm and that of fluoride ion is 136 pm. Calculate the radius ratio r_+/r_-. What would be the coordination number of each ion in the crystal ? To which type of crystal structure LiF should belong ?***

Solution. Given that, $r_+ = 60$ pm, $r_- = 136$ pm

$\therefore$ $r_+/r_- = 60\text{ pm}/136 = 0.441$

Since $r_+/r_- > 0.414$, the coordination number is 6, and LiF should have NaCl-type of structure in which F^- ions form cubic close packing (ccp) structure and Li^+ ions fit into octahedral voids.

Conclusions

(i) Larger the radius ratio, the larger is the coordination number of the cation.

(ii) Trigonal coordination (C.N. = 3) is possible when the radius ratio (r_+/r_-) is in the range 0.155 to 0.225.

(iii) Tetrahedral coordination (C.N. = 4) is possible when the radius ratio (r_+/r_-) is in the range 0.225 to 0.414.

(iv) Octahedral coordination (C.N. = 6) is possible when the radius ratio (r_+/r_-) is in the range 0.4.14 to 0.732.

(v) Body centred coordination (C.N. = 8) is possible when the radius ratio (r_+/r_-) is in the range 0.732 to 1.000.

Problem 1. ***Predict the close packed structure of NaCl given that $r_+ = 95$ pm and $r_- = 181$ pm.***

Solution. The ratio $r_+/r_- = \dfrac{95\text{ pm}}{181\text{ pm}} = 0.525$. This ratio is greater than 0.414 but less than 0.732. Therefore, NaCl should crystallize in cubic close packing (ccp) in which Cl^- ions would form the close packed structure and Na^+ ions would fit into the octahedral voids.

Problem 2. ***In a close packed structure of mixed oxides, the lattice is composed of oxide ions, one eighth of tetrahedral voids are occupied by divalent cations, while one half of octahedral voids are occupied by trivalent cations. What is the formula of the oxide ?***

Solution. Number of oxide ions (O) per unit cell = 1

Number of tetrahedral voids per ion in lattice = 2

$\therefore$ Number of divalent cations (A) = (1/8) × 2 = 1/4

Number of octahedral voids per ion in lattice = 1

$\therefore$ Number of trivalent cations (B) = 1 × 1/2 = 1/2

$\therefore$ Formula = $A_{1/4}\,B_{1/2}\,O \equiv AB_2O_4$

Information From Close Packed Structure

From the knowledge of the close packed structure we can get the following informations :

(i) The coordination number of anion and cation.

(ii) The ratio of the radii of cation and anion (r_+/r_-).

(iii) The type of voids which is occupied by the cations.

(iv) The number of particles (atoms, ions or molecule) per unit cell.

(v) The formula of the compound.

Problem 1. ***In a close packed structure of an ionic compound anions B form the close packed lattice and the cations (A) occupy octahedral voids. Predict the formula of the compound.***

Solution. In a close packed structure the number of octahedral void is 1 per atom of the crystal. Therefore, the number of octahedral void per B ion is 1. One void is occupied by a cation A. Hence, the formula of the compound is AB.

Problem 2. ***A body centred cubic lattice is composed of anions Q and cations P, where ions Q occupy the corners and ions P occupy the centre. (i) What is the formula of the compound ? (ii) What is the coordination number of P and Q ?***

Solution. Since anions (Q) occupy the corners of the cube, the number of ions per unit cell is 8 × 1/8 = 1. Since cation occupies the centre of the cube, the number of P ions per unit cell = 1.

(i) The formula of the compound is PQ.

(ii) The ions P and Q will have same coordination number. Since packing is body centred close packing (bbcp), the coordination number of P is 8 and coordination number of Q is also 8.

Problem 3. ***In a crystal of an ionic compound, the anions (B) form a close packed lattice and the cations (A) occupy one half of the tetrahedral voids. What is the formula of the compound ?***

Solution. In a close packed structure the number of tetrahedral void per atom of the crystal is two. Since, one half of the tetrahedral voids is occupied by the cations, the number of cation is the same as that of the anion in the crystal, **and the formula of the compound is, therefore, AB.**

Problem 4. ***In a crystal of an ionic compound the ions B form the close packed lattice and the ions A occupy all the tetrahedral voids. What is the formula of the compound ?***

Solution. The number of tetrahedral voids is two per atom of the crystal in a close packed structure. Since tetrahedral voids are occupied by A ions, there are two A ions per B ions in the crystal. Therefore, the **formula of the compound is A_2B.**

Problem 5. ***In a face centred cubic structure of a compound the atoms A occupy the corners and atoms B are at the face of the cube. Evaluate the formula of the compound.***

Solution. First we shall compute the contributions of various sites of the unit cell.

Number of corners in cubic unit cell = 1/8

Contribution of each atom (*A*) at the corner to unit cell = 1/8

∴ Number of A atoms per unit cell = 8 × 1/8 = 1

Number of faces in cubic unit cell = 6

Contribution of each B atom at the face to unit cell = 1/2

∴ Number of B atoms = 6 × 1/2 = 3

The formula of the compound is A_3B.

5·29 IONIC RADII

The distance of the outer most energy shell from the centre of the nucleus of an ion is called ionic radius. Since the energy shell represents only probability distribution (hence the orbital), its distance cannot be measured accurately for an isolated ion. Therefore, an estimate of the ionic radius is made by knowing the distance between the nearest ions in a close packed structure of the crystal. The estimation of the ionic radii is based on the relations between the dimensions of the unit cell and the distance between the centres of the ions in close contact. The dimensions of unit cells are measured by X-ray or electron diffraction.

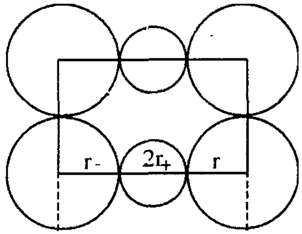


Fig. 53.

In a face centred cubic arrangement of anions and cation (*e.g.*, in NaCl), the edge of the unit cell (a) is related to the radii of cation (r_+) and anion (r_-) as shown in figure (53). So,

$$2r_+ + 2r_- = a \quad \text{or} \quad r_+ + r_- = a/2$$

or (r_+/r_-) = the interionic distance between the sodium and chloride ions.

If the radius of one of the ions is known, then the radius of the other ion can be estimated from a knowledge of the cell dimensions.

Problem 1. ***The edge length of the unit cell of NaCl crystal lattice is found to be 564 pm by X-ray diffraction. Compute the interionic distance between sodium and chloride ions.***

Solution. Sodium chloride crystallizes in fcc lattice. Therefore,

$$r_+ + r_- = a/2$$

Given that $a = 564$ pm

$$\therefore \quad r_+ + r_- = 564 \text{ pm}/2 = \mathbf{282 \text{ pm}}$$

Table–5. Ionic radii in crystals

Cation	r_+ (pm)	Anion	r_- (pm)
Li^+	60	F^-	136
Na^+	95	Cl^-	181
K^+	133	Br^-	195
Rb^+	148	I^-	216
Cs^+	169	O^{2-}	140
Ag^+	126	S^{2-}	184
Mg^{2+}	65		
Ca^{2+}	99		
Zn^{2+}	74		

Importance of Ionic Radii

From a knowledge of the ionic radii of different types of ions, we can estimate the ionic radii ratio. The value of the ratio of ionic radii (r_+/r_-) in turn can be used to predict the coordination numbers of cation and anion in a close packed structure. From such information it is possible to know the type of structure which the cations and anions will attain in the formation of crystals.

Problem 1. ***In a face centred cubic lattice of NaCl, the distance between Na^+ and Cl^- ions is 281 pm, and the density of NaCl is 2.165 g cm^{-3}. Compute Avogadro's number from the given data. Take molar mass of $Na^+ Cl^-$ as 58.3 g mol^{-1}.***

Solution. The desired relation is $\rho = zM/a^3N$

$$\therefore \quad N = \frac{zM}{\rho a^3}$$

In a face centred cubic lattice $z = 4$

and $$a = 2(r_+ + r_-) = 2 \times 281 \text{ pm} = 562 \text{ pm}$$

$$= 562 \times 10^{-12} \text{ m} = 562 \times 10^{-10} \text{ cm}$$

$$\text{Density} = \rho = 2.165 \text{ g cm}^{-3}$$

$$\text{Molar mass} = M = 58.5 \text{ g mol}^{-1}$$

$$\therefore \qquad N = \frac{4 \times 58.5 \text{ g mol}^{-1}}{2.165 \text{ g cm}^{-3} \times (562 \times 10^{-10} \text{ cm})} = \mathbf{5.089 \times 10^{23} \text{ mol}^{-1}}.$$

Problem 2. ***A solid AB crystallizes as NaCl structure. If the radius of the cation is 0.100 nm, what is the radius of the anion ?***

Solution. In NaCl structure the ratio of ionic radii is :

$$0.414 < \frac{r_+}{r_-} < 0.732$$

or

$$\frac{1}{0.414} > \frac{r_-}{r_+} > \frac{1}{0.732}$$

$$\therefore \qquad r_- > \frac{r_+}{0.732} \text{ or } r_- < \frac{r_+}{0.414}$$

Now

$$\frac{r_+}{0.732} = \frac{0.100 \text{ nm}}{0.732} = 0.1366 \text{ nm} \quad \therefore r_- > 0.1366 \text{ nm}$$

Also

$$\frac{r_+}{0.414} = \frac{0.100 \text{ nm}}{0.414} = 0.2415 \text{ nm} \quad \therefore r_- > 0.2415 \text{ nm}.$$

Thus, the radius of the anion is between 0.137 nm and 0.241 nm.

Problem 3. ***KF crystallizes as NaCl structure. Compute the edge length of the unit cell if the density is 2.48 g/cm³. What is the distance between K^+ and F^- ions in KF ? Molar mass of KF is 58 g/mol.***

Solution. The relation between density and edge length is :

$$\rho = zM/a^3 N$$

$$\therefore \qquad a^3 = \frac{zM}{\rho N}$$

For fcc lattice $z = 4$, Molar mass $= 58 \text{ g mol}^{-1}$, $N = 6.023 \times 10^{23} \text{ mol}^{-1}$, $r = 2.48 \text{ g cm}^{-3}$

$$\therefore \qquad a^3 = \frac{4 \times 58 \text{ g mol}^{-1}}{2.48 \text{ g cm}^{-3} \times 6.023 \times 10^{23} \text{ mol}^{-1}} = 155.318 \times 10^{24} \text{ cm}^3.$$

$$a = 5.375 \times 10^{-8} \text{ cm}$$

In a face centred cubic lattice $r_+ + r_-$ = Half of the edge length

$$\therefore \qquad r_+ + r_- = a/2 = 1/2 \times 5.375 \times 10^{-8} \text{ cm} = 2.687 \times 10^{-8} \text{ cm}$$

$$= \mathbf{268.7 \text{ pm}}.$$

5·30 SUPERCONDUCTIVITY

In 1911, Kammerlingh Onnes, a Dutch physicist at the University of Leiden, discovered that the resistivity of mercury suddenly drops to zero as the temperature is lowered below 4.2 K (Fig. 54). The same phenomenon occurs at different characteristic tempeatures for many other metals, alloys and compounds. We mention this by saying that at a critical, temperature T_c, the sample undergoes a phase transition from a normal to a superconducting state. In addition to zero resistivity, superconductors have unusual magnetic properties. When a sample in a weak magnetic field is cooled through T_c, the magnetic flux originally in the sample is ejected. This is known as **Meissner effect**. On the contrary, a superconducting state can be destroyed by a strong enough magnetic field, known as critical field, H_c. The thermodynamic properties of superconductors are also interesting. For example, the entropy of a superconductor decreases appreciably on cooling, showing that the superconducting state is more ordered than the normal state. Studies have shown that the superconducting state consists of two kinds of electrons, *viz.*, *ordered pairs* and *normal electrons*. As the temperature decreases, the number of ordered pairs increases. The temperature dependence of the populations suggest that the normal electrons are in energy states separated from the energy states of the ordered pairs by a gap Δ, which is of the order of $\Omega \sim 3 - 5\ k_B\ T_c$. Some metals, alloys and certain organic solids have been reported to be superconducting at very low temperatures (about 2K to 5K). But to work at low temperatures is difficult and production of low temperatures is a costly affair. Now the scientists are trying to develop such materials which can be superconducting at higher temperatures preferably near the ambient temperature. Till 1986, the highest known temperature was about 23K. In that year, Bednorz and Miiller at the IBM lab in Zurich, discovered that an oxide of La, Ba and Cu became superconducting at about 30K. There is a positive hope in this direction that we shall have a room-temperature superconductor in the near future. Since 1987 some metal oxides have been reported to be superconducting. A compound containing yttrium, barium, copper and oxygen (formula $YBa_2Cu_3O_7$) has been reported to be superconducing at (90K). The most studied of the so called high T_c –superconductors is $YBa_2Cu_3O_{7-x}$ ($x \leq 01$). The non-stoichiometry seems to be necessary for superconductivity. The solid state structure of this compound is in the perovskite family (Fig. 54). The non-stoichiometry means that there are oxygen vacancies in the lattice which play a role in the properties of the material. Speculation has focussed on the sheets and chains of Cu and O atoms in the structure as being necessary for the superconducting state. Some materials and the temperatures at which they show superconductivity are given in the following table.

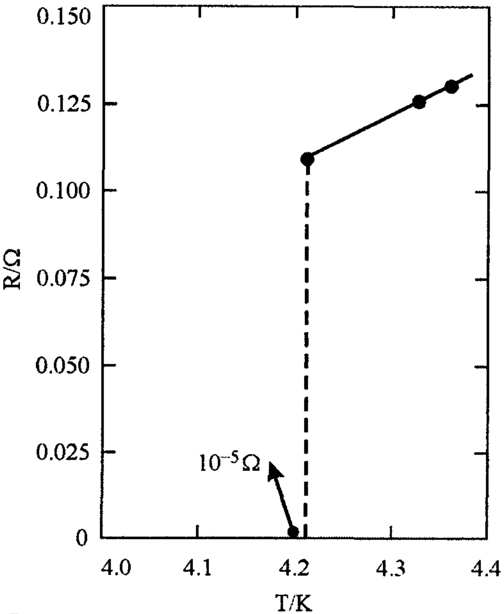


Fig. 54. Resistance in ohms of a specimen of mercury versus temperature. This is the original plot by Kammerlingh Onnes showing his discovery of superconductivity.

Table–6. Materials showing superconductivity

Formula of material	Temperature
1. $Ba_{0.7}K_{0.3}BiO_3$	30K
2. $La_{1.8}Sr_{0.2}CuO$	40K
3. $YBa_2Cu_3O_7$	90K
4. $Bi_2Ca_2Sr_2Cu_3O_{10}$	105K
5. $Tl_2Ca_2Ba_2Cu_3O_{10}$	125K

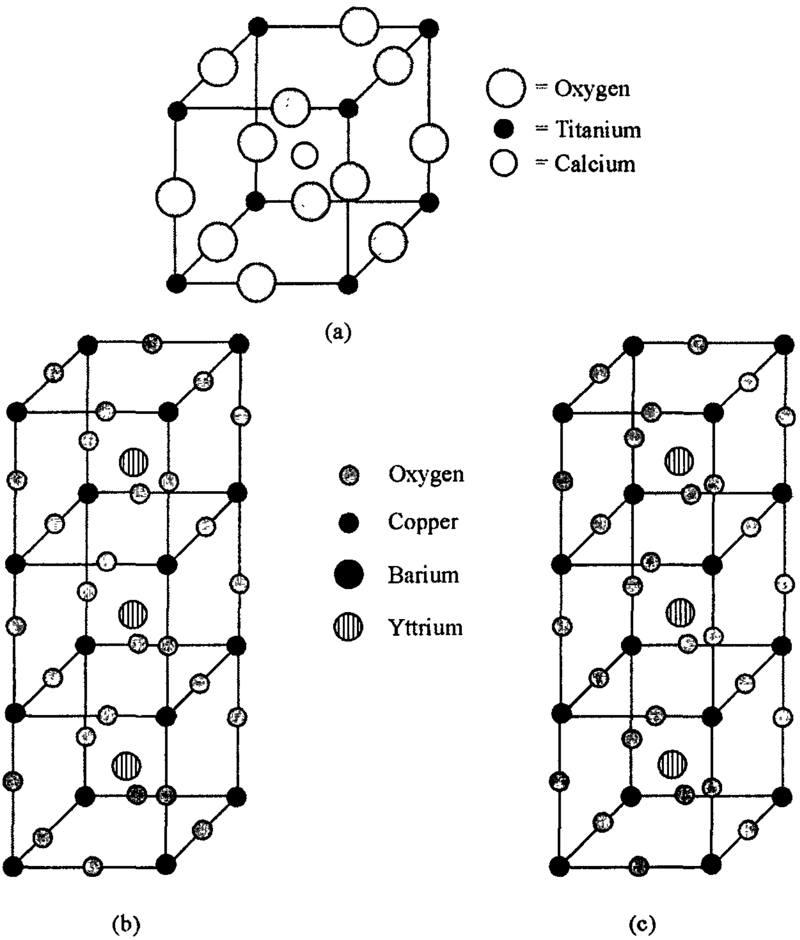


Fig. 55. (a) The perovskite structure of $CaTiO_3$ has a cubic unit cell. (b) Idealized unit cell of the hypothetical $YBa_2Cu_3O_9$ based on a perovaskite substructure. (c) Structure of the 1-2-3 oxide compound $YBa_2Cu_3O_{7-x}$, obtained from X-ray diffraction analysis (ionic sizes are not drawn to scale).

[I] Applications of Superconductors

1. Superconducting materials at liquid helium temperature are used in magnet technology, specially for body scans in medical practice.
2. Superconducting magnets are also used in fusion experiments and high energy physics.
3. Superconducting materials can be used in levitation transportation (for example, the trains which move in air without rails) because these materials are diamagnetic and are thus repelled by a magnetic field.
4. High temperature superconductors would find application in power transmission.
5. Some of the other applications of superconductors would be in the field of electronics, computers, high speed signal processing, millimeter wave detection, high speed samplers and superconducting bolometers.

Chemists have to contribute much in the fascinating field of superconductivity because superconducting materials are real chemical compounds. It is a highly rewarding area of research.

5·31 LATTICE ENERGY OF IONIC CRYSTALS

The *stability* of an ionic crystal is measured in terms of *lattice energy* which is defined as, ***"the energy released during the formation of one mole of the crystal of the solid from the constituent gaseous ions separated from each other by infinite distances."***

The formation of a mole of ionic crystal, $A^+ B^- (s)$ from its constituent gaseous ions, $A^+ (g)$ and $B^- (g)$ is represented by

$$A^+ (g) + B^- (g) \xrightarrow{-U} A^+ B^- (s)$$

With the coming together of positive and negative ions there is a considerable decrease in the potential energy of the system. So, a considerable amount of energy is released during the formation of an ionic solid.

According to first law of thermodynamics, the energy that is released in the formation of one mole of an ionic solid from the constituent gaseous ions is numerically equal to the energy that will be needed to convert 1 mole of the same ionic solid into the gaseous ion.

$$A^+ B^- (s) \xrightarrow{+U} A^+ (g) + B^- (g)$$

Therefore, the higher the lattice energy of the ionic solid, the greater will be its stability. Lattice energy of ionic solids are quite high. This is due to the strong electrostatic attraction between the oppositely charged ions present in the solid. As the coulombic forces of attraction vary directly as the product of the charges, the higher the valency (charge) of the ions the greater will be the lattice energy of the solid. Thus lattice energy increases as we move from uni-univalent ionic solid to uni-bivalent and then to bi-bivalent and then to tri-bivalent solids.

Calculation of Lattice Energy of Ionic Solids

The lattice energy of ionic solid can be calculated theoretically on the basis of coulombic interactions between the ions present in the crystals. There are two types of interactions.

(1) Attractive forces between oppositely charged ions.

(2) Repulsive forces due to interpenetration of electron clouds.

(1) Attractive forces between oppositely charged ions : The potential energy of a pair of ions of opposite charges varies inversely as the distance r between the ions. This may be represented as,

$$\text{P.E. (attraction)} = \frac{(z_+ e)(-z_- e)}{r} = \frac{-z_+ z_- e^2}{r} \qquad ...(1)$$

where e is the electronic charge and z_+ and z_- are the charges on the oppositely charged ions or the valencies of the ions.

(2) Repulsive forces due to interpenetration of electron clouds : As a cation and anion come very close to each other, there is repulsion between them because of interpenetration of similarly charged electron clouds. The P.E. due to this repulsion is seen to be inversely proportional to the nth power of the distance between the ions. So,

$$\text{P.E. (repulsion)} = \frac{be^2}{r^n} \qquad \text{...(2)}$$

where n is called ***Born exponent*** and 'b' is called ***repulsion coefficient***. The net potential energy for a pair of ions of opposite charge is obtained by combining equations (1) and (2), *i.e.*,

$$\boxed{\text{P.E. (net)} = \frac{-z_+ z_- e^2}{r} + \frac{be^2}{r^n}} \qquad \text{...(3)}$$

Equation (3) is known as ***Born equation***. From equation (3), it is clear that the second term be^2/r^n, *i.e.*, the repulsion term increases more rapidly than the first term with the decrease in the value of interionic distance (r).

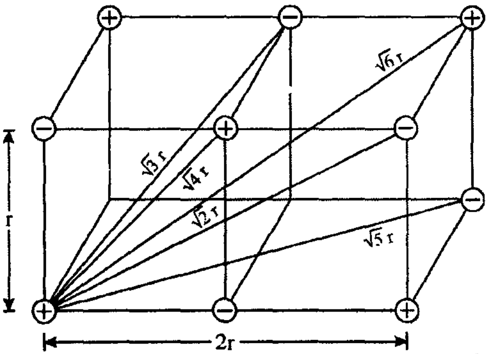


Fig. 56. Inter-ionic distance in NaCl crystal.

Born equation gives the energy released when a cation and an anion separated by infinite distance in the gaseous state are brought together in a crystal at a distance r from each other.

Born equation can be used for considering the attractive and repulsive forces in the crystal. It can be illustrated by taking the crystal of sodium chloride. In the crystal, there is not one cation and one anion, but a large number of anions and cations are arranged together in a specific geometry. So, we have to consider forces of attraction and repulsion between all of them.

So, in a crystal of NaCl (Fig. 56), each sodium ion is surrounded by,

(i) 6 chloride ions at a distance of $\sqrt{1}\, r$.

(ii) 12 other sodium ions at a distance of $\sqrt{2}\, r$.

(iii) 8 more chloride ions at a distance of $\sqrt{3}\, r$.

(iv) 6 more sodium ions at a distance of $\sqrt{4}\, r$.

(v) 24 more chloride ions at a distance of $\sqrt{5}\, r$.

(vi) 24 more sodium ions at a distance of $\sqrt{6}\, r$.

The attractive potential energy between sodium ion and chloride ion at a distance $\sqrt{1}\, r$ is given by,

$$\text{P.E.} = \frac{(z_+ e) \times 6\,(-z_- e)}{(\sqrt{1}\, r)} = -\frac{6z_+ \,.\, z_- e^2}{r}$$

The repulsive potential energy between sodium ion and 12 other sodium ions at a distance $\sqrt{2}\, r$ is given by,

$$\text{P.E.} = \frac{(z_+ e) \times 12\,(z_+ e)}{\sqrt{2}\, r} = \frac{12 z_+^2 e^2}{\sqrt{2}\, r}$$

The attractive potential energy between sodium ion and 8 chloride ions at a distance $\sqrt{3}\, r$ is given by,

$$\text{P.E.} = \frac{(z_+ e) \times 8\,(-z_- e)}{\sqrt{3}\,r} = -\frac{8z_+ z_- e^2}{\sqrt{3}\,r}$$

The repulsive potential energy between sodium ions and 6 other sodium ions at a distance $\sqrt{4}\,r$ is given by,

$$\text{P.E.} = \frac{(z_+ e) \times 6\,(z_+ e)}{\sqrt{4}\,r} = \frac{6z_+^2 e^2}{\sqrt{4}\,r}$$

The attractive potential energy between sodium ion and 24 chloride ions at a distance $\sqrt{5}\,r$ is given by,

$$\text{P.E.} = \frac{(z_+ e) \times 24\,(-z_- e)}{\sqrt{5}\,r} = -\frac{24z_+ z_- e^2}{\sqrt{5}\,r}$$

Thus, the first term in Born equation may be obtained by adding up the effects of all the interactions. So,

$$(\text{P.E.})_1 = -\frac{6z_+ z_- e^2}{\sqrt{1}\,r} + \frac{12z_+^2 e^2}{\sqrt{2}\,r} - \frac{8z_+ z_- e^2}{\sqrt{3}\,r} + \frac{6z_+^2 e^2}{\sqrt{4}\,r} - \frac{24z_+ z_- e^2}{\sqrt{5}\,r} + \ldots$$

$$= -\frac{z_+ z_- e^2}{r}\left[6 - \frac{12z_+}{\sqrt{2}z_-} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}}\frac{z_+}{z_-} + \frac{24}{\sqrt{5}}\ldots\right] \qquad \ldots(4)$$

For NaCl, $\frac{z_+}{z_-} = 1$ and so the term within the bracket of equation (4) is given by

$$\left[\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}}\ldots\right] = 1.7476$$

Thus, sum of all the forms of the infinite series in bracket is constant for an ionic crystal of a given geometry. This constant depends on the geometry of the crystal and is independent of '*r*'. Thus, this constant is known as ***Madelung constant*** and is written as '*A*'. So,

$$\text{P.E.}_{(1)} = -\frac{Az_+ z_- e^2}{r}$$

[Madelung constant of CrCl (coordination number, 8) = 1.7627, ZnS (coordination number, 4), zinc blende = 1.6381, fluorite CaF_2 (coordination number 8, 4) = 5.0388, rutile, TiO_2 (coordination number, 6, 3) = 4.8160].

The second term in Born equation is now considered. As it arises from repulsion between a cation and an anion due to interpenetration of electron clouds, it is enough to consider nearest neighbour only as the term is proportional to $1/r^n$. Others which are farther away will not have any significant effect. For sodium chloride crystal, each sodium ion is surrounded by 6 chloride ions and so the term becomes $6be^2/r^n$. The term $6b$ is replaced by B, where B is the product of b and the number of nearest neighbours. So, the second term becomes Be^2/r^n. Therefore,

$$\text{P.E.} = \frac{-Az^2 e^2}{r} + \frac{Be^2}{r^n} \qquad \ldots(5)$$

The factor z^2 has replaced $z_+ z_-$ as $z_+ = z_- = z$. The value of n for most of the common ions varies from 7 to 12.

It is possible to eliminate B from equation (5) by realising that an ion will be in stable equilibrium position when attraction and repulsion forces acting on it are equally balanced. The P.E. of the ion is then minimum, *i.e.*, $d\,(\text{P.E.})/dr = 0$.

The interionic distance r may be taken as r_0. By differentiating potential energy with respect to r and equating it to zero, we can eliminate B as follows :

$$\text{P.E.} = -Az^2 e^2 r^{-1} + Be^2 r^{-n}$$

$$\frac{d\,(\text{P.E.})}{dt} = -Az^2 e^2 (-1\, r^{-2}) + Be^2 (-n\, r^{-n-1})$$

$$= Az^2 e^2 r^{-2} - Be^2 n\, r^{(-n-1)}$$

Assuming $d\,(\text{P.E.})/dr = 0$, where r is replaced by r_0, we get,

$$Az^2 e^2 r_0^{-2} - Be^2 n\, r_0^{(-n-1)} = 0$$

$$Az^2 e^2 r_0^{-2} = Be^2 n\, r_0^{(-n-1)}$$

$$B = \frac{Az^2 r_0^{-2}}{n\, r_0^{(-n-1)}}$$

$$B = \frac{A}{n} \cdot z^2 r_0^{n-1} = 0 \qquad \text{...(6)}$$

Substituting the value of B in equation (5), we get

$$(\text{P.E.})_0 = \frac{-Az^2 e^2}{r_0} + \frac{A}{n} \frac{z^2 r_0^{n-1} e^2}{r_0^n}$$

or
$$(\text{P.E.})_0 = \frac{-Az^2 e^2}{r_0} + \frac{Az^2 e^2}{nr_0}$$

or
$$(\text{P.E.})_0 = \frac{Az^2 e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad \text{...(7)}$$

The lattice energy, U is defined as the ***amount of energy released in the formation of 1 mole of the crystal from the constituent gaseous ions separated at infinite distance from one another.*** Thus,

$$U = \text{P.E.} \times N$$

where, N is Avogadro number.

$$U = \frac{NAz^2 e^2}{r_0}\left(\frac{1}{n} - 1\right) \qquad \text{...(8)}$$

This equation is known as ***Born-Lande equation***. As n is always greater than unity, U will always be negative. From equation (8), we can calculate lattice energy as all the factors are known except n. Its value can be calculated from the compressibility of the crystals, if the crystal spacing parameters are known. The value of U thus calculated agrees well with the theoretical value.

Problem 1. ***Calculate the lattice energy of NaCl crystal by using Born-Lande equation if*** $z_+ = z_- = 1$, $e = 4.8 \times 10^{-10}$ ***esu,*** $A = 1.7476$, $r_{Na^+} = 0.95Å$, $r_{Cl^-} = 1.81Å$, $n = 8$ $[r_0 = r_{Na^+} + r_{Cl^-}]$.

Solution.
$$U = \frac{NAz^2 e^2}{r_0}\left(\frac{1}{n} - 1\right)$$

$$r_0 = 1.81 + 0.95 = 2.76\ \text{Å}$$

$$\therefore \quad U = \frac{6 \times 10^{23} \times 1.7476 \times 1 \times 4.8 \times 10^{-10}}{2.76}\left(\frac{1}{8} - 1\right)$$

$$= \mathbf{-\,1.5956 \times 10^4\ cals.}$$

5·32 BORN–HABER CYCLE

Born-Haber cycle is used to determine the lattice energy of an ionic solid. We will consider the cycle by taking sodium chloride as an example. The lattice energy of sodium chloride by this cycle is based on the assumption that the formation of 1 mole of crystalline sodium chloride can occur by any of the following two processes.

1. Process involving direct combination of Na(s) and 1/2 $Cl_2(g)$ to form NaCl(s).

In this process, heat is evolved, as it is an *exothermic reaction*. The heat produced is equal to the heat of formation of NaCl(*s*) *i.e.*,

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

$\therefore$ Heat produced = Heat of formation of NaCl(*s*)

or $\Delta H = -Q.$

2. Process for obtaining sodium chloride (solid) in the following steps :

(a) *Conversion of Na atom from solid state to gaseous state, i.e.,*

$$Na(s) \longrightarrow Na(g)$$

This process is called sublimation and is an endothermic reaction, so,

$$Na(s) \longrightarrow Na(g)$$

Heat absorbed = Heat of sublimation of sodium = + S

(b) *Conversion of Na (g) into Na^+ (g)* : This step involves the conversion of gaseous sodium atom into gaseous ion. It occurs by giving one electron and the process is called ionisation. It is an endothermic reaction and for this reaction energy called ionisation energy, *i.e.*, I of Na atom is absorbed. Thus,

$$Na(g) - e^- \longrightarrow Na^+(g)$$

Energy required = Heat of ionisation = $+I$

(c) *Conversion of 1/2 Cl_2 (g) into Cl (g)* : In this step, chlorine molecule in the gaseous state is converted into chlorine atom and the process is called dissociation. For this reaction, the heat is called heat of dissociation (D) of chlorine molecule. It is an endothermic reaction. So,

$$1/2\ Cl_2(g) \longrightarrow Cl(g)$$

Heat required = Heat of dissociation of $\frac{1}{2}$ Cl_2 (*g*) molecule

$$= +\frac{1}{2}D$$

(d) *Conversion of Cl(g) into Cl^- (g)* : The *Cl(g)* formed in step (c) adds up one electron, given up by Na (*g*) in step (b) and is converted into Cl^- (*g*). This energy called the electron affinity of chlorine is represented as E. This change is an exothermic reaction. So,

$$Cl_2(g) + e^- \longrightarrow Cl^-(g)$$

Heat produced = Electron affinity of chlorine = $-E$

(e) *Combination of $Na^+ (g)$ and $Cl^- (g)$ ions to form NaCl(s)* : $Na^+ (g)$ and $Cl^- (g)$ ions formed in steps (b) and (d) combine together to form 1 mole of NaCl (solid). The attractive forces between $Na^+ (g)$ and $Cl^- (g)$ operate and the potential energy of the system is decreased and so energy is released. This energy is called the lattice energy (U) of NaCl (s). Therefore,

$$Na^+ (g) + Cl^- (g) \longrightarrow NaCl (s)$$

$$\text{Energy released} = \text{Lattice energy of NaCl } (s) = -U$$

This formation of NaCl(s) by the above two processes is called Born-Haber cycle. As the two processes are independent of each other, so according to Hess' law, the heat of formation of NaCl (solid) must be the sum of both the processes. Therefore,

$$\boxed{-Q = +S + I + \frac{1}{2}D - E - U}$$

Thus, the lattice energy (U) can be calculated.

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. Write a short essay on various types of solids.
2. What are the various properties of solids ? How are these properties explained ?
3. What are (100), (110) and (111) planes ? Explain with reference to cubic lattice the relationship for the spacings of these planes for (i) simple cubic (ii) face centred and (iii) body centred cubic lattice.
4. Derive Bragg's equation for the diffraction of X-rays by crystal lattice. How is this equation used in elucidating the crystal structure ?
5. Give the principle and method of Debye-Scherrer powder method for determining the structure of crystal.
6. What are the defects found in a crystal ? Explain the uses of semi-conductors. How do they function ?
7. How do you differentiate between gases, liquids and solids in terms of kinetic molecular theory ? What are the forces which bind the units of a solid together ?
8. (a) What are the various properties of solids ? How are these properties explained in terms of the kinetic molecular theory ?
   (b) Explain the terms isotropy and anisotropy.

[II] Short Answer and Very Short Answer Type Questions

1. Explain the terms isotropy and anisotropy.
2. Write a short note on crystalline solid and amorphous solid.
3. Explain the point defects in crystals.
4. State the laws of crystallogrphy.

[**Ans.** That branch of science which deals with geometry, structure and properties of crystals and crystalline bodies is known as crystallography. There are theree fundamental laws of crystallography, *viz.*,

(i) Law of constancy of angle.

(ii) Law of constancy of symmetry, and

(iii) Law of rational intercepts.

(i) **Steno's law of constancy of angle** : According to this law, "under the same physical conditions, the angle between the corresponding faces on various crystals of the same substance is constant."

Steno (1669) gave this law after performing a number of measurements on rock crystal specimens obtained from various places.

For the second and third laws, see the matter described in the text].

5. Explain the symmetry elements with reference to a cubic crystal.
6. Write a short note on law of rational intercepts.
7. Define the following terms :
   (i) Axis of symmetry; (ii) Centre of symmetry; (iii) Interfacial angle; (iv) Unit cell; (v) Space lattice; (vi) Bravais lattice; (vii) Diad axis; (viii) Hexad axis; (ix) Point of symmetry.
8. How many atoms per unit cell are present in :
   (i) Simple cubic (ii) Face centred and
   (iii) Body centred cubic arrangement of atoms.
9. Write short notes on :
   (i) Enantiotropy; (ii) Dynamic allotropy; (iii) Monotropy
10. Write notes on :
    (i) Mitscherlisch's law of isomorphism.
    (ii) Transition temperature (iii) Unit cell
    (iv) Space lattice (v) Isotropy
    (vi) Isomorphous solids (vii) Structure of CsCl crystal.
11. Account for the following facts in terms of kinetic molecular theory :
    (a) Solids are practically incompressible, whereas gases can be easily compressed.
    (b) Solids maintain their definite shape but the liquids flow.
    (c) Solids break into pieces at characteristic angles.
    (d) Diffusion occurs in solids but extremely slowly as compared to liquids and gases which diffuse much more quickly.
12. Why is rotation of crystal not necessary in powder method for the determination of crystal structure ?
13. Explain the terms :
    (i) Space lattice, (ii) Centre of symmetry.
14. Draw diagrams of body centred cubic lattice and face-centred cubic lattice.
15. Why does a purist prefer not to speak of the molecular weight of solid sodium chloride ? Instead of molecular weight he prefers the use of term formula weight.
16. Out of the following in the solid state :
    sodium, germanium, methane, neon, potassium chloride and water, select –
    (a) a non-conducting solid becoming good conductor on melting;
    (b) a substance in which hydrogen bonding is pronounced;
    (c) a high melting solid involving covalent bonded atoms;
    (d) a solid melting far below room temperature and held together by vander Waals forces; and
    (e) a solid having m. pt. of about 473 K and very good conductor of electricity.
17. Account for the following :
    Graphite and diamond are both allotropic forms of carbon yet graphite is soft, while diamond is hard.
18. How will you account for the fact that plane surfaces are produced on fragments on cleavage of sodium chloride crystal ?
19. Explain why carborundum (SiC) is a very high melting, hard substance.
20. State the law of rational indices. What are Miller indices ?
21. Write a note on lattice type determination by powder pattern method.
22. (a) Derive Bragg's equation for the diffraction of X-rays by crystal lattice.

(b) How is Bragg's equation utilized to determine crystal structure ?

23. Give, in outline, the principle of Debye-Scherrer powder method for structure determination of ionic solids.

24. Give the differences between isotropy and anisotropy.

25. Explain the terms : symmetry, plane of symmetry, axis of symmetry and centre of symmetry. Illustrate your answer giving suitable examples.

26. State the law of rational indices. What are Weiss indices ?

27. What do you understand by the terms space lattice and unit cell ? Represent diagrammatically (i) a simple cubic lattice (ii) face-centred cubic lattice and (iii) body-centred cubic lattice.

28. Derive Bragg's equation for diffraction of X-rays by crystals. To what uses can it be put ?

29. Draw a schematic diagram of X-ray spectrometer. Explain how you would proceed to determine the structure of a crystal with its help.

30. Explain what is meant by metallic crystals, ionic crystals, molecular crystals and covalent crystals. Give examples.

31. Describe the structure of diamond and graphite. Why is graphite a good conductor of electricity ? Why is it used as a lubricant ?

32. Write short notes on :

(i) Bravais lattices
(ii) Transition temperature
(iii) Isotropy and anisotropy
(iv) Isomorphism and polymorphism.

33. Discuss in detail the close packing of solid spheres. What is meant by hexagonal close packing and cubic close packing ?

34. On the basis of the structure of metals how would you account for the following : (1) Metallic lustre (2) High electrical conductivity (3) Malleability (4) Ductility (5) Thermal conductivity (6) Tensile strength.

35. What are the two arrangements for the closest packing in a system of uniform spheres ?

36. Aluminium (at. no. 13), silicon (at. no. 14), sulphur (at. no. 16) differ widely in their electrical conductivities inspite of being closely situated in periodic table. Why ?

37. Write short notes on :

(a) Freezing point and melting point.
(b) Sublimation.
(c) Analogy between transition point and melting point.
(d) Atomic and molecular heats.

38. What do you understand by transition temperature ? Describe different methods used for the detemination of transition temperature.

39. What is meant by 'unit cell' in crystallography ?

40. What are the various types of crystals ? Compare their properties giving suitable examples.

41. What do n, d, λ and θ signify in the Bragg's law

$$n\lambda = 2d \sin \theta \text{ ?}$$

42. Giving one example in each case, what type of crystals (covalent, ionic or molecular) should be (i) the hardest, (ii) the softest, (iii) the highest melting, (iv) the lowest melting ?

43. Write a short note on polymorphism.

44. Show that the volume of space occupied for a cubic closed lattice of spheres with radius a is 74%.

45. Calculate the maximum radius ratio r_A/r_B for an atom A to fit in a simple cubic B lattice.

46. Calculate the size of a tetrahedral and octahedral hole in a closed packed structure.

[III] Numerical Problems

1. At what angle would the first order diffraction from (110) plane of KCl be observed using X-rays of wavelength 1.54×10^{-10} m. The dimension of the unit cell is 3.15×10^{-10} m.
2. A metallic element has cubic lattice. Each edge of the unit cell is 3.0 Å. The density of the metal is 8.5 g cm^{-3}. How many unit cells will be present in 50 g of the metal ?
3. The element polonium (atomic mass = 209 g mol^{-1}) crystallises in a primitive cubic system. The first order reflection, using X-rays of wavelength 1.54 Å occurs at sin θ value of 0.225 for the (100) plane. Calculate (i) the side *a* of the unit cell and (ii) the density of polonium.
4. Sodium borohydride, $NaBH_4$, crystallises in a face-centred cubic system. If the formula weight of $NaBH_4$ is 37.8 g mol^{-1}, calculate the density of the crystal given that the unit cell edge length is 6.15 Å.
5. Potassium cyanide, KCN, crystallises in face-centred cubic system. Its molar mass is 65.11 g mol^{-1} and density is 1.52 g cm^{-3}. Calculate the d_{100} distance for the unit cell.
6. The density of CaO is 3.35 gm cm^{-3}. This oxide crystallises in one of the cubic systems with $a = 4.80$ A. Calculate the number of molecules in the unit cell. Which type of cubic system is it ?
7. In the Bragg's experiment using NaCl crystal sin θ was found to be 0.103 for $n = 1$. Calculate the wavelength of X-rays employed in this experiment. Density of NaCl = 2.17×10^3 kg m^{-3}.
8. How many atoms are there per unit cell in (i) simple cubic arrangement of atoms, (ii) body-centred cubic arrangement of atoms and (iii) face-centred cubic arrangement of atoms ?
9. At what principal angle should diffraction occur when copper radiation ($\lambda = 1.54 \times 10^{-10}$ m) interacts with lattice planes that are 1.54×10^{-10} m apart ? ($n = 1$).
10. The smallest interatomic distance in a unit cell of aluminium is 2.86×10^{-10}cm. It crystallises in a fcc lattice. Calculate its density if its atomic weight of aluminium is 27.

[IV] Multiple Choice Questions

1. The number of atoms per unit cell in a simple cubic, fcc and bcc arrangement are, respectively :
   (a) 8, 14, 9 (b) 1, 4, 2 (c) 1, 2, 4 (d) 4, 1, 2
2. CaO and NaCl have the same crystal structure and nearly the same ionic radii. If *U* is the lattice energy of NaCl, the approximate lattice energy of CaO is :
   (a) $4U$ (b) U (c) $2U$ (d) $U/2$
3. In a closed packed array of *N* spheres, the number of tetrahedral holes are :
   (a) N (b) $2N$ (c) $4N$ (d) $N/2$
4. The space occupied by spheres in a bcc arrangement is:
   (a) 46.4% (b) 52.4% (c) 68% (d) 74%
5. The ionic radii of Rb^+ and I^- are 1.47 and 2.16 A, respectively. The most probable type of geometry shown by RbI on the basis of radius ratio rule is :
   (a) CsCl type (b) NaCl type (c) ZnS type (d) Born oxide type
6. Lattice energy of a solid increases if :
   (a) Ions are large (b) Ions are small (c) Ions are of equal size
7. The coordination number of each sphere in hcp arrangement is :

(a) 4 (b) 6 (c) 8 (d) 12

8. If the tetrahedral sites in a ccp array of negative ions (B) were half filled with cations (A), the empirical formula of the compound would be :
(a) AB (b) AB_2 (c) A_2B_3 (d) A_2B

9. An atom containing an odd number of electrons is :
(a) Paramagnetic (b) Diamagnetic
(c) Ferromagnetic (d) Anti-ferromagnetic

10. The presence of F-centres in a crystal makes it :
(a) Conducting (b) Colourless (c) Coloured (d) Non-conducting

11. In a simple cubic structure there is :
(a) 6–6 coordination (b) 8–8 coordination
(c) 4–4 coordination (d) 6–4 coordination

12. The substance shose resistance gets reduced to virtually zero at very low temperatures is known as :
(a) Electrical conductor (b) Superconductor
(c) Inductor (d) Hyperconductor

13. If a is the length of the side of a unit cell, then perpendicular distance (d_{hkl}) between adjacent planes of a set is given by :
(a) $\frac{a}{h^2+k^2+l^2}$ (b) $\frac{h^2+k^2+l^2}{a}$
(c) $\frac{a}{(h^2+k^2+l^2)^{1/2}}$ (d) $\frac{(h^2+k^2+l^2)^{1/2}}{a}$

14. Tetragonal crystal system has the following unit cell dimensions :
(a) $a = b = c$ and $\alpha = \beta = \gamma = 90°$ (b) $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$
(c) $a = b \neq c$ and $\alpha = \beta = 90°; \gamma = 120°$ (d) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$

15. Space lattice of CsCl is :
(a) Simple cubic (b) Face centred cubic
(c) Body centred cubic (d) Hexagonal close packed

16. In the crystal of CsCl, the nearest neighbours of each Cs^+ ion are :
(a) Six Cl^- ions (b) Six Cs^+ ions (c) Eight Cl^- ions (d) Six Cl^- ions

17. X-rays of wavelength 0.134 nm gave a first order diffraction from the crystal surface when the value of θ was found to be 10.5°. If sin 10.5° = 0.1822, the distance between the planes in the crystal parallel to the surface is :
(a) 3.68 nm (b) 0.368 nm (c) 0.0368 nm (d) 3.68×10^{-9} nm

[V] Fill in the Blanks

1. All crystalline materials are .... but not all solids are ....
2. Amorphous solids are generally considered as ....
3. Crystalline solids are ...., while .... materials are isotropic in nature.
4. In cesium chloride crystal, the coordination number of Cs^+ is ....
5. The cohesive forces in molecular crystals are .... forces.
6. The point defect which lowers the density of material is .... defect.
7. Iron is a .... substance.
8. Solids may conduct electricity due to the motion of the ...., ... or ....
9. If a plane makes intercepts a, b and ∞, then Miller indices will be ....
10. The covalent crystals are held together by .... forces.
11. The vapour pressure of ionic solids is generally ....

12. The equation $n\lambda = 2d \sin \theta$ is known as .... equation.

[VI] True or False

State whether the following statements are true (T) or false (F) ?

1. Solids and liquids are considered condensed state of matter.
2. A crystalline solid may crystallise in more than one geometrical shape.
3. Amorphous solids are considered as supercooled solids.
4. Diamond is a covalent crystal.
5. Molecular crystals are generally hard and brittle.
6. In a cubic system, $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$.
7. The smallest geometric portion of the crystal which when repeated in three dimensions to give the entire crystal is known as a space lattice.
8. In a cubic lattice, $d_{100} : d_{110} : d_{111} = 1 : 0.707 : 577$.
9. Bragg's equation is represented by $\lambda = 2nd \sin \theta$.
10. Sodium chloride crystal has a face centred cubic lattice.
11. CsCl belongs to ionic crystal type.
12. When an ion occupies an interstitial position between the lattice points, the defect is called Frenkel defect.
13. In bcc arrangement, the volume occupied is nearly 68%.
14. The radius ratio for a trigonal site is 0.414.
15. Superconductors have nearly zero resistivity.

ANSWERS

[III] Numerical Problems

1.	20°31′	2.	2.178×10^{23}	3.	$a = 3.42$ Å, $\rho = 8.75$ g cm^{-3}
4.	1.08 g cm^{-3}	5.	6.57 Å	6.	4, NaCl type 7. 0.058 nm
8.	1, 2 and 4	9.	30°	10.	2.71×10^2 kg m^2

[IV] Multiple Choice Questions

1.	(b)	2.	(a)	3.	(b)	4.	(c)	5.	(b)	6.	(b)
7.	(d)	8.	(a)	9.	(a)	10.	(c)	11.	(a)	12.	(b)
13.	(c)	14.	(b)	15.	(c)	16.	(c)	17.	(b)		

[V] Fill in the Blanks

1. solid, crystals	2. supercooled liquids	3. anisotropic, amorphous
4. 8	5. vander Waals	6. Schottky
7. ferromagnetic	8. electrons, holes, ions	9. 110
10. strong	11. low	12. Bragg's

[VI] True or False

1.	(T)	2.	(T)	3.	(F)	4.	(T)	5.	(F)	6.	(T)
7.	(F)	8.	(T)	9.	(F)	10.	(T)	11.	(T)	12.	(T)
13.	(T)	14.	(F)	15.	(T)						

❑❑❑

Chapter 6

COLLOIDAL STATE

6·1. INTRODUCTION

Colloid chemistry is usually said to have had its origin in the extensive researches of Graham on diffusion in various kinds of systems. It is true that some earlier investigators had made isolated observations on the properties of some colloidal systems. Thus, Macquer (1774) stated that gold tinctures were nothing but finely divided gold floating in an oily fluid. Berzelius on the basis of obtaining a colloidal solution of Ag_2O_3, suggested that this solution probably may be regarded as a suspension of transparent particles.

Selmi (1845) suggested that substances like silver chloride, sulphur, prussian blue give clear solutions, but are known as *'pseudo-solutions'*. These can be bracketed in the same group as albumin and starch solutions. He considered that in all these systems, there is present a coarser and not a molecular dispersion, as in the case of sodium chloride in water. Bandrimont (1846) said that organic substances like gum arabic, casein, gelatin, etc. are constructed from larger complex particles. Faraday (1857) made a series of optical experiments chiefly with the colloidal gold solutions. Graham (1861), therefore, classified the above mentioned organic and inorganic substances by introducing the term *'colloid'* (Greek : glue like). Colloids are characterised by the following two properties :

(a) their non-crystallinity in the solid state, and

(b) their slow rate of diffusion across a membrane.

These properties clearly distinguish colloids from crystalloids (as NaCl in water), because crystalloids are crystalline in nature and form a homogeneous true solution. But Graham's conception about colloids and crystalloids had undergone a radical change in recent years. Albumin which was previously considered to be a colloid, has now been obtained in the crystalline state. Soap in water acts as a colloid but in alcohol it behaves as a crystalloid. Similarly, NaCl acts as a crystalloid in water, but in benzene it acts as a colloid. So, soap and NaCl can behave both as crystalloid and colloid depending upon the conditions. So, instead of stating that a particular substance is a colloid, it is now stated that a particular substance is in the *colloidal state*, as practically every substance can be obtained in the colloidal state by one method or the other.

6·2. COLLOIDAL SOLUTIONS

Colloidal solutions or sols are those in which the solute particles are larger than the molecules or ions which are found in true solution. Sols give rise to heterogeneous solutions, *i.e.*, colloidal systems are ***biphasic systems.*** The two phases are :

(a) Dispersed phase or inner phase. Substance whose particles are distributed in a medium is known as *dispersed phase.* It is also known as *discontinuous phase.*

(b) Dispersion medium or outer phase. The medium in which the particles are distributed in a medium is known as *dispersion medium.* It is also known as *continuous phase.*

To test which substance is the dispersion medium. When a colloidal solution involves two substances, then either of the substances can be the dispersed phase. For example, if we have a colloidal suspension of oil and water, then it may be considered either as (a) **oil in water type system**, or (b) **water in oil type system**.

The simplest test is to take a drop of the suspension and place it on a glass plate and then add a drop of either phase. Suppose a drop of water is added. If water is the dispersion medium, then the added drop of water will readily unite with the drop of the suspension by the process of dilution. If on the contrary, water is the dispersed phase then the drop of water will not combine, because it must first be dispersed or put into a colloidal state.

6·3. SIZE OF COLLOIDAL PARTICLES

There is no sharp dividing line between solute molecules, colloidal particles and suspended particles, but it is important to have an idea about the order of size of colloidal particles. As a rough approximation, particles having diameter greater than 10^{-4} cm or 1 micron (μ) are considered suspended particles. Particles having diameter between 10^{-5} to 10^{-7} cm or 100 mμ to 1 mμ* (where mμ is known as millimicron) are called colloidal particles. As molecular dimensions are about 10^{-8} cm, it is clear that particles of diameter 10^{-7}cm might contain only a few molecules of a substance of high molecular weight. So, it is evident from microscopic visibility that there is no sharp separation between giant molecules and small colloids, nor between large colloids and fine heterogeneous suspension.

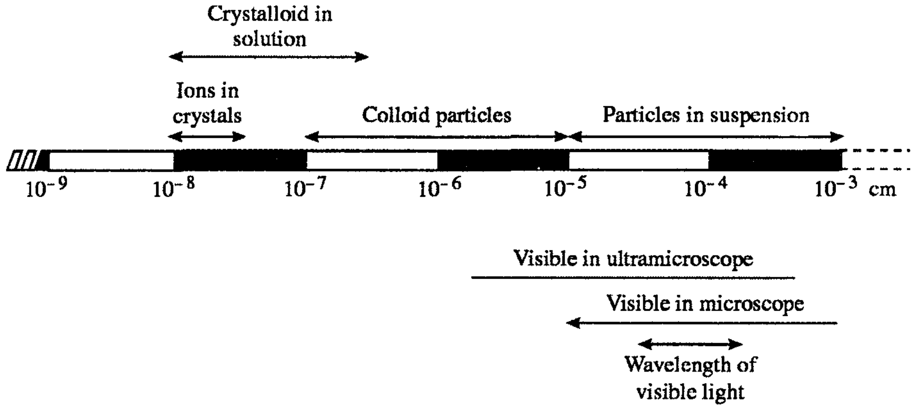


Fig. 1. Comparative sizes of different types of particles.

A terminology given by Siedentopf and Zsigmondy (1907) that finds a limited usage employs the term ***micron*** for particles having diameters exceeding 150 mμ, ***submicrons*** where the diameters range from 6 to 250 mμ, and the term ***amicrons*** where the diameters are less than 7 mμ.

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* 1 millimicron = 1 mμ = 10^{-6} cm. ; 1 micron = 1 μ = 10^{-3} mm. = 10^{-4} cm. ; 1 micromicron = 1 μμ = 10^{-9} cm

6·4. DIFFERENCES BETWEEN SUSPENSION, COLLOIDAL SOLUTION AND TRUE SOLUTION

The characteristics of suspension, colloidal solution and true solution can be summed up in the form of the following table :

Table-1.

S.N.	Characteristic property	Suspension	Colloidal solution	True solution
1.	Nature	Heterogeneous	Heterogeneous	Homogeneous
2.	Size range	Particles are greater than 10^{-5} cm (or 0·1 μ or 100 mμ) in diameter.	Particles are between 10^{-5} and 10^{-5} cms (or 0·1 μ to 1 mμ) in diameter.	Particles are less than 10^{-7} cms. (or 1 mμ) in diameter.
3.	Visibility	Particles are visible under microscope or even with a naked eye.	Particles are generally visible under ultramicroscope.	Particles are not visible even under ultramicroscope.
4.	Diffusibility	Do not diffuse.	Diffuse slowly.	Diffuse rapidly.
5.	Filtrability	Can be filtered even by an ordinary filter paper.	Can be filtered through an animal membrane; through which the particles do not pass.	Cannot be filtered.
6.	Molecular weight	Low	High	Low
7.	Osmotic pressure $\left(\text{O.P.} \propto \frac{1}{\text{M.W.}}\right)$	High	Low	High
8.	Colour	—	Depends upon the shape and size of the particle.	Depends upon the nature of the ion.
9.	Appearance	Opaque	Generally clear	Clear
10.	Setting	Their particles settle under gravity.	Their particles settle only in a centrifuge.	Their particles do not settle.
11.	Tyndall effect	Do not exhibit.	Exhibit	Do not exhibit.
12.	Brownian movement	Do not exhibit.	Exhibit	Do not exhibit.
13.	Electrophoresis	Do not exhibit.	Exhibit	Do not exhibit.
14.	Coagulation	—	Can be coagulated by adding suitable electrolytes.	Can be precipitated by adding suitable electrolytes.
15.	Presence of electric charge	—	Particles carry either positive or negative charge.	Particles do not carry any charge.

6·4. TYPES AND CLASSIFICATION OF COLLOIDAL SYSTEMS

[I] Based on the State of Aggregation of the Two Phases

A colloidal system is a biphasic system consisting of ***(a) dispersed phase*** and ***(b) dispersion phase.*** Therefore, the two phases can either be solid, liquid or gas.

Thus, several different types of colloidal systems depending upon the nature of the dispersed medium and the dispersion phase are possible, which can be summarised in table-2 with examples.

Table–2. Different types of colloidal systems

S.N.	Dispersed phase	Dispersion medium	Name of the colloidal system	Examples
1.	Solid	Solid	Solid sol	Gems, precious stone, etc.
2.	Liquid	Solid	Gel or jelly	Jelly
3.	Gas	Solid	Solid foam	Pumice stone
4.	Solid	Liquid	Colloidal solution	Sols of metals, sulphur, etc.
5.	Liquid	Liquid	Emulsion	Milk
6.	Gas	Liquid	Foam	Soap lather
7.	Solid	Gas	Aerosol	Smoke
8.	Liquid	Gas	Liquid aerosol, cloud, mist, fog	Fog, cloud, mist

A gas dispersed in a gas does not form a colloidal system as we know that all gases are miscible in every proportion forming homogeneous mixtures.

[II] Based on the Nature of the Dispersion Medium Used

When the dispersion medium is a gas, the colloidal system is known as an aerosol. When the dispersion media are water, alcohol, benzene, glycerol, the colloidal systems are known as *hydrosol*, *alcosol*, *benzosol*, *glycerosol*, respectively. When the dispersion medium is a fluid, the colloidal system is known as a sol.

[III] Based on the Method of Formation of Colloidal Systems

A substance which passes into the colloidal state, simply by bringing it in contact with water is known as a ***hydrophilic colloid*** (*hydro* = water; *philic* = loving). However, if any solvent like organic liquid is used instead of water, then the more general term *lyophilic colloid* (*lyo* = solvent; *philic* = loving) is used. Gum, starch, soap are lyophilic colloids. These colloids when once precipitated can again be brought back directly into the colloidal state, hence they are also known as ***reversible colloids*** (colloidal state $\rightleftharpoons$ precipitate). Reversible colloids are also termed as ***resoluble or non-electrocratic colloids.***

Substances like metals, metal sulphides cannot be brought into the colloidal state simply by bringing them in contact with water and, therefore, special methods are devised for the purpose. Hence, they are known as ***hydrophobic colloids*** (*hydro* = water; *phobic* = hating). In case of any solvent, the general term ***lyophobic*** is used. Further, if these colloids are precipitated, then it is not very

Suspensoids and Emulsoids. Sols in which the dispersed phase has only little affinity for the dispersion medium are called *suspensoids*. Among the hydrosols, colloidal gold, silver are examples of suspensoids, because gold or silver have negligible affinity for water.

Sols in which the dispersed phase has a considerable affinity for the dispersion medium are called *emulsoids*. Gelatin, starch etc. have a great affinity for water, hence they produce an emulsoid with water.

easy to reconvert the precipitate directly into the colloidal state. Hence, they are termed as ***irreversible colloids*** (colloidal state → precipitate), ***irresoluble*** or ***electrocratic colloids***.

Table–3. Distinction between lyophilic and lyophobic sols

S.N.	Property	Lyophilic sol (Intrinsic sol)	Lyophobic sol (Extrinsic sol)
1.	Preparation	Formed very easily by shaking or warming the substance with solvent.	Formed by special methods, *e.g.*, electro-dispersion, peptization, oxidation etc.
2.	Nature	Particles are true molecules.	Particles consist of aggregates of molecules.
3.	Molecular weight	Have in general a lower molecular weight.	Have a comparatively higher molecular weight.
4.	Osmotic pressure, depression in freezing point, lowering of vapour pressure, etc.	Have a higher O.P., greater depression in freezing point, more lowering of V.P. etc.	Have a comparatively less O.P., smaller depression in freezing point, less lowering of V.P. etc.
5.	Surface tension	Substances like silicic acid, stannic acid, starch have nearly the same surface tension as that of the dispersion medium, but substances like proteins, gum, soap etc., *i.e.*, which are strongly surface active, lower the S.T. of water quite appreciably, *i.e.*, in these cases the S.T. is generally lower than that of the dispersion medium.	Surface tension is not sensibly different from that of the medium.
6.	Viscosity	Viscosity is much higher than that of the medium. Even dilute solutions are often more viscous than water, whereas more concentrated solutions are quite viscid.	Viscosity is about the same as that of the dispersion medium. The viscosity of a lyophobic sol is given by Einstein's formula : $\eta_C = \eta_M (1 + 2\cdot5\ \phi)$ where, η_C = viscosity of lyophobic sol. η_M = viscosity of pure liquid. ϕ = volume of particles per unit volume of sol.
7.	Visibility	Particles cannot be easily detected even under an ultramicroscope.	Particles can be readily detected under an ultramicroscope.

S.N.	Property	Lyophilic sol (Intrinsic sol)	Lyophobic sol (Extrinsic sol)
8.	Quantity of dispersed phase used.	The amount of the dispersed phase contained in lyophilic sol is generally high.	These sols are usually clear, amount of dispersed phase contained in lyophobic sol is comparatively small, *e.g.*, the more concentrated Fe_2O_3 sol prepared by Geffcken contained 35 g per litre.
9.	Tyndall effect	Less distinct	More distinct.
10.	Density	The density of lyophilic sols cannot be calculated from the composition of the sol.	The density of lyophobic colloids follows the straight line mixture law. The density of colloids, d_{coll} can be calculated from the composition of the sol by the formula : $d_{\text{coll}} = xd_1 + (1-x)\,d_2$ where, $d_1 =$ density of the dispersed phase, $d_2 =$ density of the dispersion medium, $x =$ mole fraction of the dispersed phase.
11.	Adsorption	The adsorption of the particles of lyophilic sols by adsorbents such as charcoal, kaolin etc. resembles appreciably with the adsorption of truly dissolved substances.	The adsorption of the particles of lyophobic sols by adsorbents differs from the adsorption of truly dissolved substances.
12.	Conductivity	With lyophilic sols, high conductivities can generally be measured.	Owing to their sensitivity to electrolytes, the conductivity of lyophobic sols can rarely be measured over a considerable range of concentration.
13.	Cataphoresis	The measurement of cataphoresis is more difficult than for lyophobic sols.	It is usually marked and readily measurable.
14.	Action of electrolytes	The addition of small quantities of electrolytes has little effect. Large quantity of electrolyte is needed for coagulation.	The addition of a small quantity of electrolyte is sufficient to cause coagulation.
15.	Reversibility	Reversible.	Irreversible.

S.N.	Property	Lyophilic sol (Intrinsic sol)	Lyophobic sol (Extrinsic sol)
16.	Migration in an electric field	The particles may migrate in either direction or not at all in an electric field.	The particles migrate only in one direction in an electric field.
17.	Solvation	Colloid particles are strongly solvated.	Colloid particles are weakly solvated.

[IV] Based on Chemical Composition

We can classify colloids as inorganic and organic colloids based on the chemical composition. The former can be either metals (Pt, Cu, etc.), non-metals (S, etc.), oxides and hydroxides (ferric hydroxide, stannic oxide, etc.), while the latter can be homo-polar sols (rubber in benzene), hydroxy sols (starch) and hetero-polar sols (proteins, soaps, etc.).

[V] Based on the Shape of Colloid Particles

On this basis, colloids can be sphero as well as linear colloids. The former consists of compact globular particles, while the latter consists of long fibrous units. Organic colloids may be sphero, while silicic acid sol has long chain particles.

[VI] Based on the Structure of Colloids

Staudinger classified the substances into three types :

(a) Multimolecular colloids. When a large number of atoms or small molecules (having diameters of less than 1 nm) of a substance combine together in a dispersion medium to form aggregates of the size in the colloidal range, the substances are called *multimolecular colloids*. In multimolecular colloids, the species (atoms or molecules) forming the dispersed particles are held together by vander Waals forces.

Examples of multimolecular colloids are gold sol, sulphur sol etc. A gold sol may contain particles of different sizes made up of several atoms of gold. Similarly, a sulphur sol may contain particles containing about a thousand of S_8 molecules.

(b) Macromolecular colloids. Certain substances form large molecules whose dimensions are comparable to those of colloidal particles. Such molecules have very high molecular masses and are called *macromolecules*. When such substances are dispersed in a dispersion medium, the resulting colloidal solution are called macromolecular colloidal solution and the sbstances are called *macromolecular colloids*.

Lyophilic colloidal substances are generally macromolecular colloids, *e.g.*, starch, proteins, gelatin, nucleic acids, cellulose, etc are macro mlecular colloids. Synthetic polymers like polyethylene, synthetic rubber, etc. also form macromolecular colloids when dispersed in suitable solvents.

(c) Associated colloids (or micelles). Those colloids which behave as normal strong electrolytes at low concentrations but show colloidal properties at higher concentrations due to the formation of aggregated molecules are called *associated colloids*. The aggregated particles that are formed are called *micelles*.

The associated colloids are usually formed by surface active agents, *e.g.*, soaps and synthetic detergents. These substances form micelles when present in solution at a concentration greater than critical micelle concentration. The formation of a micelle can be understood by taking the example of soap solution.

Soaps are generally sodium or potassium salts of higher fatty acids like palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$) *etc.*, The most commonly used washing soap is sodium stearate ($C_{17}H_{35}COONa$). The general formula of a soap may be represented by RCOONa, whose R is a long chain alkyl group. When dissolved in water, soap ionises to give Na^+ and $RCOO^-$ ions. The $RCOO^-$ ion consists of two parts, *viz.*, long hydrocarbon chain R and the polar group COO^- shown in figure (2a). The hydrocarbon chain R is hydrophobic, while $-COO^-$ group is hydrophilic in nature. Thus, $RCOO^-$ ions tend to orient themselves in such a way that $-COO^-$ end dips in water and the group R—stays away from water. The COO^- groups of different $RCOO^-$ ions tend to stay away from one another due to similar charges, whereas the R – groups try to approach each other to form a bunch. This leads to the formation of a micelle as shown in figure (2b). Therefore, a soap micelle is a negatively charged colloidal particle in which the COO^- groups are arranged in a spherical way at the surface, while the hydrocarbon chains point towards the centre. The COO^- groups present at the surface of the micelle get surrounded by Na^+ ions which tend to drag the micelle in the bulk of the solution. So, a micelle may contain as many as 100 molecules or more.

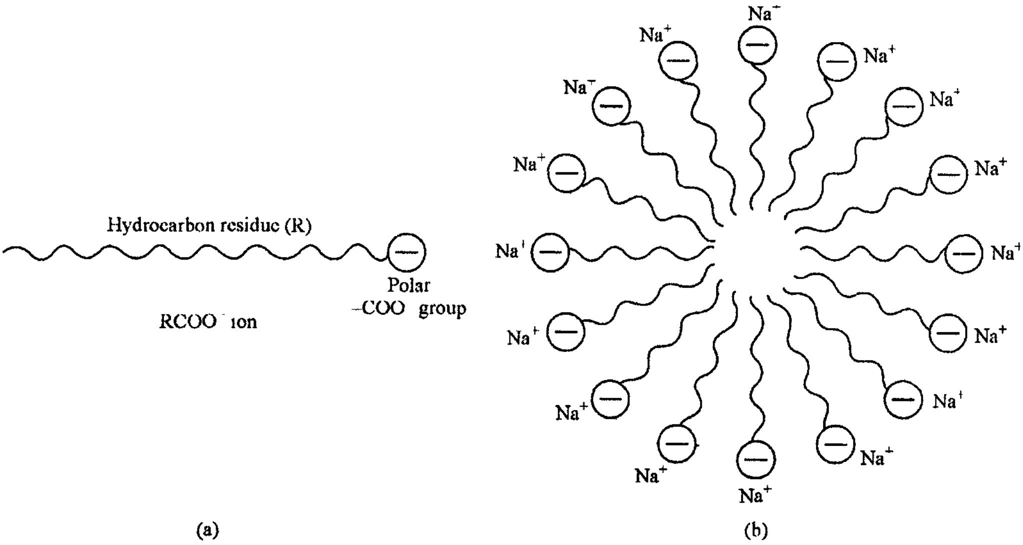


Fig. 2 (a) Diagrammatic representation of soap anion.
(b) Aggregation of $RCOO^-$ ions to form a micelle.

[VII] Based on the Charge on Dispersed Phase

Colloids can either have positive or negative charge, therefore, they can be classified as positively charged colloids (hydroxides, TiO_2 etc.) and negatively charged colloids (metal sulphides etc.).

6·6. PREPARATION OF COLLOIDAL SOLUTIONS

[I] Preparation of Lyophilic Sols

Substances having high molecular weight such as gelatin, gum, starch etc. form lyophilic sols very easily, when they are warmed with a suitable liquid. The sols of this type are of reversible nature and are thermodynamically stable.

[II] Preparation of Lyophobic Sols

Lyophobic sols cannot be prepared by simple contact or slight shaking of the substance with the solvent. Svedberg (1908–12) suggested that there are two ways for obtaining lyophobic sols.

(i) Dispersion methods. In these methods, larger lumps of the insoluble substance are pulverised by mechanical or by other means till particles of colloidal dimensions are obtained.

(ii) Condensation methods. In these methods, a molecular or ionic distribution is first prepared which then by suitable coarsening gives rise to particles of colloidal dimensions.

(1) Dispersion Methods

(a) Mechanical dispersion. In this method, the solid is first finely sub-divided by grinding. Solid particles of the dispersed phase along with the dispersion medium are introduced into a 'colloid mill' which usually consists of two metal discs rotating in opposite directions at a very high speed (7,000 revolutions/min). The distance between the two discs is so adjusted that particles of colloidal dimensions are obtained. Actually, the distance between the two discs controls the size of the colloidal particles to be finally obtained. The simplest 'colloids mill' is due to Plauson.

(b) Electro-dispersion method. Bredig (1898) used this method for preparing the sols of metals in water. This method consists in striking an arc between two electrodes of the metal immersed in water [Fig. (3)]. A current of 1 ampere and voltage of 100 volts is used. The vessel in which water is kept, is surrounded by ice. On striking an arc, the vapours of metal are formed which then immediately condense to form particles of colloidal size. Sometimes, it is necessary to add traces of electrolytes, *e.g.*, alkali hydroxide is added in water, to obtain best results.

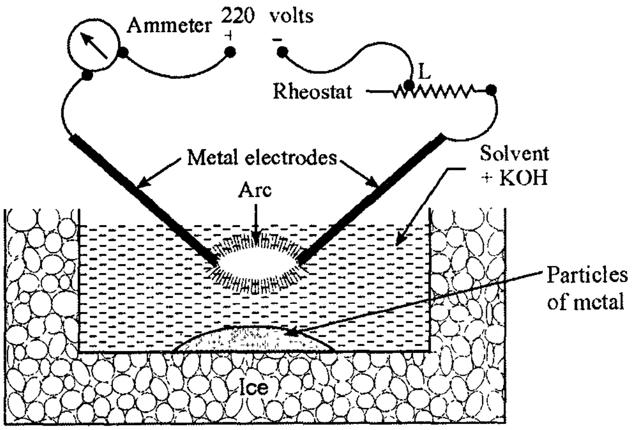


Fig. 3. Bredig's arc method.

Svedberg modified the Bredig's arc method and prepared sols in non-aqueous media like pentane, diethyl ether by striking an arc with high frequency alternating current, which greatly diminishes the decomposition of the liquid. Practically, any metal can be obtained in the colloidal state in a liquid with which it does not react chemically.

(c) Peptization. Peptization is a process by means of which a stable colloidal solution can be produced from substances originally present in massive form, when the particles of colloidal size pre-exist in the substance to be dispersed. It is converse of coagulation. In other words, *peptization is the process of transforming back a freshly prepared precipitate into colloidal form.*

Freshly prepared precipitate of $Fe(OH)_3$ can be changed into colloidal state when the precipitate is treated with a small amount of $FeCl_3$ solution. The substance which brings about peptization is known as peptizer. In this case, $FeCl_3$ acts as a peptizer. The sol thus obtained is positively charged due to the perferential adsorption of Fe^{3+} ions (from $FeCl_3$) on the sol particles of $Fe(OH)_3$. The particle exists as $[Fe(OH)_3]Fe^{3+}$. The excess of $FeCl_3$, if any, can be removed by dialysis. It should be noted that only freshly prepared precipitates can be peptized. A precipitate of prussian blue passes into a colloidal state on adding oxalic acid solution.

Sometimes, peptization is brought about by repeated washing of a precipitate, *e.g.*, a colloidal solution of $BaSO_4$ can be obtained by washing the precipitate of $BaSO_4$ several times. Pure water is not used for washing, but water containing some electrolyte is used. The precipitate of hydroxides of III group can be peptized by the addition of small amount of acid to water. Thus, we can say that *peptization is due to the existence of electrical charge on particles.* If the precipitate contains too much or too little of electrolyte, then peptization will not occur. It has been observed that under these conditions, the particles which are joined by vander Waals forces attraction, discharge the particles. Thus we conclude that *optimum peptization will occur only at a definite medium concentration of electrolyte.*

(d) Dispersion by ultrasonic waves. The application of ultrasonic waves (sound waves of very high frequency such as 20,000 cycles sec^{-1} and above) for the preparation of colloidal solutions was introduced by Wood and Loomis and later on used by Sollner.

A high frequency current is passed through a circular quartz crystal by connecting it to two electrodes. When an alternating current is passed through the crystal, the latter begins to oscillate, the frequency of oscillation depends upon the size and nature of the crystal. Liquids can easily be dispersed in water by the application of this method. By this method, emulsions of oils and sols of mercury and of low melting alloys have been obtained. This method has been proved to be of great importance, because the colloidal solutions can be prepared without adding foreign substances into the system.

(e) Removal of agglomerating agent. It is clear that if a mass results from the precipitating action of certain substances, there is the possibility of regaining the colloidal state by removing these substances. In many analytical examples, a precipitate is formed instead of a colloidal suspension by the adsorption of ions or molecules. When such a precipitate is washed with water, it happens that the adsorbed material is not removed. If, however, certain acids are added to the wash water, the agglomerating agent may be displaced or dissolved and a colloidal solution will again be formed.

(f) Electrolytic distintegration method. The metal to be dispersed is generally made the cathode, while sodium hydroxide is taken as the electrolytic solution. On passing a current of high voltage through the cell, the electrolysis of the solution takes place. Sodium is discharged at the cathode and forms an alloy with the metal. The alloy in turn reacts with water, thus liberating sodium which goes into water and the metal is then dispersed into a colloidal form.

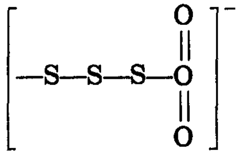
(2) Condensation Methods

(a) Oxidation. Sols of some non-metals are obtained by oxidation. For example, sol of iodine is obtained by oxidising hydroiodic acid by iodic acid as, $HIO_3 + 5HI = 3H_2O + 3I_2$. It can be made stable by adding a small amount of gelatin.

Selmi (1847) and Raffo (1878) prepared sulphur sols. Selmi's sol is formed as :

$$2H_2S + SO_2 = 3S\downarrow + H_2O$$

but other reactions also occur. Colloidal sulphur can be prepared by decomposing thiosulphates and polysulphides with acids. The stable sols formed by the decomposition of thiosulphates are probably also stabilized by attached sulphonate ions.



$$\left[-S-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{O}}\right]^-$$

An unstable colloidal solution of sulphur is prepared by pouring an alcoholic solution of sulphur into a large volume of water. The sulphur is molecularly dispersed in the alcoholic solution but is insoluble in a dilute solution of alcohol in water. This sol is unprotected and coagulate in a few hours, depositing a white precipitate of sulphur. This sol could be stabilised by adding the solution of sulphur into a solution of a water-solution stabilising colloid.

(b) Reduction. Sols of some metals are obtained by the reduction of their salts. Colloidal silver can be prepared by the same methods as used to prepare colloidal gold. Many colloidal silver preparations are used in medicine. These are all stabilised by protective colloids. Argyrol, for example, is a colloidal silver sol which is protected by the protein vitellin, obtained from egg yolk.

Faraday (1857) prepared colloidal gold by the reduction of gold chloride ($HAuCl_4.3H_2O$) by means of phosphorous. When 2·5 ml. of 0·6% $HAuCl_4 . 3H_2O$ and 3·8 ml. of 0·18 N K_2CO_3 in 120 ml. of distilled water are treated with 0·5 ml. of a solution of phosphorous in ether, a red gold sol is obtained which is known as Zsigmondy's nuclear gold sol. Zsigmondy showed that when a solution of gold chloride is neutralised by K_2CO_3 and treated with HCHO, a red sol of colloidal gold is obtained. Assuming that K_2CO_3 converts the auric ion to the aurate ion, we can write the reduction in the following two half reactions:

$$2Au(OH)_4^- + 6e^- = 2Au\downarrow + 8OH^-$$

$$3HCHO + 9OH^- = 3HCOO^- + 6H_2O + 6e^-$$

The gold is formed as a highly supersaturated solution which condenses to a colloidal solution. This is an unstable sol and very small traces of polyvalent cations coagulate it to a blue sol. Larger concentrations will produce a black precipitate. The stabilising charge on the gold particles may be due to $AuOH^-$ ions or $AuCl^-$ ions.

A red sol of gold is obtained by reducing a neutralised solution of gold chloride with a solution of ascorbic acid, containing some stable colloid as a stablising agent. At least 65 different reducing agents have been used to prepare sols of colloidal gold. Many reducing agents have been used, when different coloured gold sols varying from brown to blue are obtained. Reduction with hydrazine, hydroquinone, pyrogallol and gallic acid (reducing agents) give a clear dark blue, brown or pink sol. Nordenson used hydrogen peroxide as the reducing agent when he also obtained a red gold sol.

$$2HAuCl_4 + 3H_2O_2 = 2Au + 8HCl + 3O_2$$

Giles and Salmon prepared sols of silver in pure stearic acid by dissolving silver stearate in molten stearic acid at 0°C and passing a current of hydrogen when a dark red sol of silver is obtained. However, if reduction were carried to completion, no sol could be formed.

(c) Hydrolysis. This method is generally employed for the preparation of sols of a number of hydroxides and hydrous oxides. A beautiful red sol of ferric hydroxide is obtained by boiling ferric chloride in a beaker containing distilled water (500 ml).

$$FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$$

The excess of ferric chloride may be removed by electro-dialysis, as its presence renders the sol unstable. Boiling promotes the reaction because HCl formed is removed along with water vapours from the system. In this reaction iron oxychloride, FeOCl formed due to incomplete hydrolysis of $FeCl_3$ is believede to act as a stabiliser.

$$FeCl_3 + H_2O \longrightarrow FeOCl + 2HCl$$

The stabilizer action can be due to $FeCl_3$ or HCl. The stabilizing action of $FeCl_3$ is due to Fe^{3+} ions which it gives in solution. Evidence in favour of HCl comes from the fact that the surface of ferric hydroxide sol has a number of hydroxyl groups which are capable of adsorbing the hydrogen ions given by HCl. So, the structure of $Fe(OH)_3$ sol can be represented by any of the following formulae, depending on which substance acts as a stabilizer.

(i) $(m\ [Fe(OH)_3]\ n\ FeO^+.(n-x)\ Cl^-)\ x\ Cl^-$

(ii) $(m\ [Fe(OH)_3]\ n\ Fe^{3+}\ .\ 3(n-x)\ Cl^-)\ 3x\ Cl^-$

(iii) $(m\ [Fe(OH)_3]\ nH^+.\ (n-x)\ Cl^-)\ x\ Cl^-$

(d) Double decomposition. This is the usual way of forming sols of insoluble salts. If the solutions containing the component ions of an insoluble substance are mixed, a precipitate will be formed. If the substance has a low enough solubility, the precipitate will be colloidal. For example, silver halides give colloidal solutions by mixing silver nitrate and alkali halide solutions.

$$AgNO_3 + NaX = AgX + NaNO_3 \quad \text{(where X = Cl, Br or I)}$$

The colloidal precipitate of AgX will be left in the solution with the counter ions (Na^+, NO_3^-) of the salts and the precipitating ions which happen to be in excess.

Sols of arsenious sulphide and mercuric sulphide are obtained by passing hydrogen sulphide into the saturated solution of corresponding soluble salts of their oxides or cyanides.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

$$Hg(CN)_2 + H_2S = HgS + 2HCN$$

(e) Exchange of solvent. Colloidal solutions of a number of substances can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is soluble, *e.g.*, preparing a sulphur sol by pouring its alcoholic solution in water.

(f) Controlled condensation. When a precipitation reaction is carried out in the presence of a protective colloid, *e.g.*, gum, starch, gelatin etc., a colloidal solution of the insoluble substance is obtained. A little amount of starch is added in a beaker containing distilled water. Now a few ml. of potassium ferrocyanide solution and a few drops of ferric chloride are added. A blue sol of prussian blue is obtained which can be purified by dialysis.

(g) Condensation of heated vapours. Sols of certain elements can be obtained by passing their vapours in a cooled dispersion medium. A mercury or sulphur sol is obtained by boiling mercury or sulphur and passing the vapours into cold water containing a suitable stabilizing agent.

(h) Cathodic reduction. Many metals can be obtained in a colloidal state by rapid electrolysis of solutions of their simple ions. Electrolysis may be regarded as direct reduction by electrons. The colloidal metal frequently sticks to the cathode as a porous deposit, but may come off as an unstable sol. Platinum black (used for electrodes) is prepared by the electrolysis of platinum chloride on a gold or platinum electrode. When lead salts are electrolysed, a sol of lead is obtained at the cathode.

(i) Excessive cooling. A sol of ice in any organic solvent like pentane, chloroform etc. may be obtained by cooling excessively a solution of water in the organic solvent. The preparation of ice-cream is based on this principle.

6·7. PURIFICATION OF SOLS

Most of the sols contain a large or smaller quantity of impurities after the preparation. These impurities must be removed in order to make the sol stable. This is done by either of the following methods.

[I] Dialysis

The purification of colloidal solution by dialysis is based on the inability of the sol particles to pass through an animal membrane or a parchment paper which allows only the molecules or the ions to pass through. The vessel in which dialysis is carried out is known as a *dialyser*. A dialyser

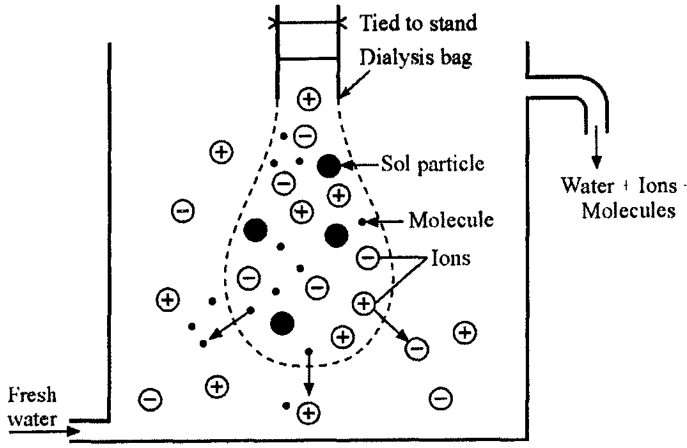


Fig. 4. Ordinary dialysis

consists of a special type of vessel open at both the ends. To the lower end a membrane is stretched. This membrane allows only the solvent and other molecules to pass thorough it, but is impermeable to the colloidal particles. The dialyser is then suspended in a larger vessel containing pure distilled water [Fig. (4)]. The distilled water is periodically renewed on allowing water to flow into the outer larger vessel and removing it by means of a syphon. Dialysis is continued till no further contamination of the washing liquid occurs.

Choice of membrane is the most important factor for carrying out dialysis. For most aquosols, collodion membranes are very suitable, as they can be prepared of any permeability very easily. For non-aqueous solvents, denitrated collodion cellophane may be used. Ordinarily, dialysis is a slow process and it takes several hours and sometimes even days for complete purificaton. So, electrodialysis is generally performed.

[II] Electrodialysis

Electrodialysis was first adopted by Morse and Pierce (1902—03) and later applied on a larger scale by Dhere (1908), Pauli (1923—25) etc. The removal of ionic impurities from a sol can be greatly facilitated under the influence of an electric field. In this case, the outer vessel is fitted with two electrodes [Fig. (5)]. The application of the electric field allows the passage of ions towards the oppositely charged electrodes. *Electrodialysis is not meant for the removal of non- electrolytes, e.g., carbohydrates, organic substances etc.* Electrodialysis is really very effective at the end of ordinary dialysis, when concentration gradient and thus the rate of diffusion is small.

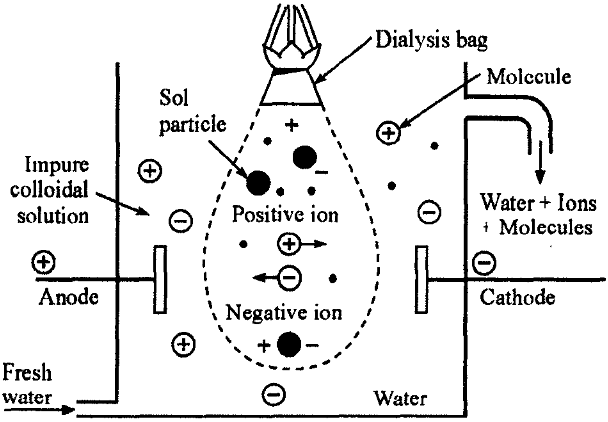


Fig. 5. Electrodialysis.

[III] Hot dialysis

In hot dialysis, a temperature of 65—90°C increases the rate of dialysis by about three times. Heating is done by placing an electric heating unit in the dialyser. All hydrophobic sols cannot withstand the high temperature and the membranes may give off undesired colloidal impurities.

[IV] Ultrafiltration

Ordinary filter papers have pores larger than 1000 mμ, so that the colloidal particles having a smaller size can easily pass through them. But if the pores are made smaller, then the colloidal particles may be retained on the filter paper. Ultrafiltration is a method not only for purification of the sol but also for concentrating the sol. In ultrafiltration due to Bechold, special type of filter paper known as ***ultrafilter*** used, which is effective throughout the range of colloidal and even molecular sizes. Thus, ***ultrafiltration is a process of separating colloidal particles from the solvent and the solutes present by specially prepared***

filters which allow all other particles except the colloidal particles to pass through it. In ultrafiltration, the colloidal particles are removed both from the liquid dispersion medium as well as the substances in true solution. Pressure is applied to the solution, so that the passage of the liquid through the very small pores of ultrafilters may be accelerated.

Preparation of ultrafilter. The preparation involves the impregnation of special filter paper with collodion (4% solution of nitrocellulose in a mixture of alcohol and ether) and subsequently hardening by dipping it in a solution of HCHO and finally drying. The size pores of ultrafilter may be altered by varying the concentration of collodion solution. The pore size of ultrafilters can be determined by the rate of penetration of water or by forcing air through the wetted membrane. During ultrafiltration, the sol particles remain behind on the ultrafilter, which can be redispersed in the pure dispersion medium.

Uses of ultrafilters. Ultrafilters have many uses. Bechold not only used them for separating sol particles of different sizes, but also to separate a coarser colloid from a finer one, *e.g.*, prussian blue from haemoglobin. Ultrafilters are extensively used in bacteriology for removing the bacteria from solutions. They are also used in the determination of hydration of the colloid particles that are held back.

[V] Electro-decantation

If electrodialysis is carried out without agitating the sol in the middle compartment of the dialyser, the sol particles accummulate in a relatively thin layer on the bottom of the cell with a colloid free supernatant liquid. This process is known as *'electro-decantation'* and was introduced by Pauli (1932) and is explained by a circulation in the cell caused by density differences.

Figure (6) shows a simple arrangement for electro-decantation. A starch solution containing a soluble β-amylose, and a suspended α-amylose constituent, as well as salt, was placed in the larger vessel closed at the bottom by the collodion a; the positive electrode was placed in an outer jar. The negative electrode is placed in a narrow tube with another membrane, dipping in the starch solution. After applying 110 volts for sometime, the α-amylose travells to the bottom, separated by a visible boundary from the solution above, which was siphoned off.

Suppose a negatively charged sol is electrodialysed. The sol particles are drawn towards the anodic membrane, leaving a particle free layer adjacent to

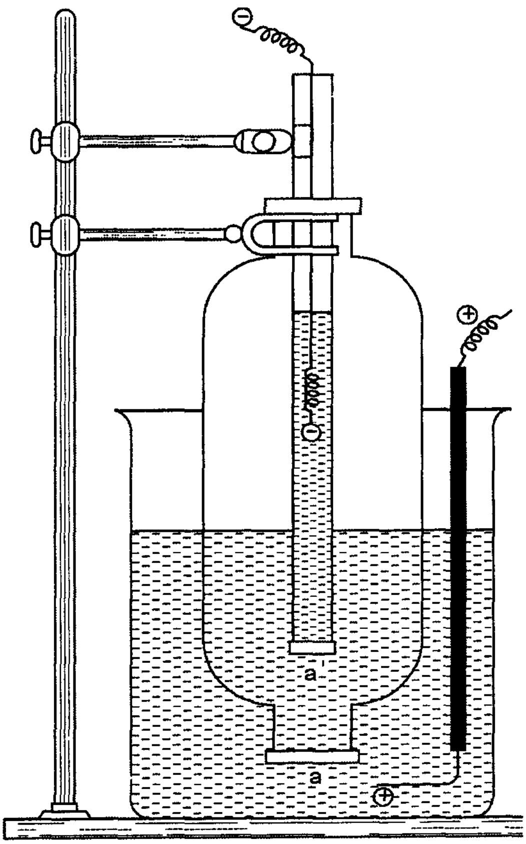


Fig. 6. Electrodecantation method.

the cathodic membrane. This less dense layer then moves to the top of the cell and dense anodic layer sediments at the bottom. This process continues till all the sol particles are removed from the field between the electrodes. With this process, a sol of 10% concentration can be obtained.

Electro-decantation is slow in the initial stages of elecrodialysis and in the later stages, electro-decantation is not helpful for removing because electrolytes are also decantated. It is to be mentioned that the continuous electro-decantation is a very mild treatment since the particles are under the influence of current only for a short time. The process is applicable in the concentration and purification of unstable sols.

6·8. GENERAL PROPERTIES OF COLLOIDAL SYSTEMS

(a) Heterogeneity. As already explained, every colloidal system is a heterogeneous system and consists of two phases, *viz,* dispersed phase and dispersion phase. X-ray investigation of a gold sol reveals that the particles are crystalline in nature.

(b) Filtrability. Colloidal particles can pass through ordinary filter paper, but can be stopped by means of an ultrafilter paper.

(c) Visibility. Most of the sols appear to be true solutions with naked eye, but the colloidal particles can be seen through an ultramicroscope.

(d) Diffusibility. The colloidal particles do not readily diffuse through a parchment paper or any other animal membrane.

(e) Colligative properties. As colligative properties depend upon the number of particles and we know that colloidal particles are aggregate of molecules, therefore, all the colligative properties would be reduced. Hence, colloidal systems have very low osmotic pressure, and freeze and boil at about the same temperature as the pure dispersion medium.

(f) Size of colloidal particles. As described before, the colloidal particle vary from 100 μ to 1 mμ in diameter.

(g) Shape of colloidal particles. Different sol particles have different shapes. For example, red gold sol, silver sol, platinum sol, As_2S_3 sol etc. have spherical particles, whereas $Fe(OH)_3$ sol, blue gold sol have disc or platelet-like particles. Rod-like particles appear in V_2O_5 sol, tungstic acid sol etc.

(h) Colour. All sols do not possess colour. But the colour of a sol is characterised by a peculiar softness, richness and tendency to opalesce.

The colour of a sol depends upon : *(i) Size of sol particles, (ii) Wavelength of the source of light used, (iii) Mode of receiving the light by the observer, (iv) The specific selective absorptive power of the substance, (v) Method of preparing the sol.*

Ordinary Zsigmondy's gold sol is red in colour, but as the size of the particles increases, it becomes purple. Similarly, a silver sol passes from brown to black and finally to silvery spangles. Diluted milk gives a bluish tinge in reflected light, while it gives a reddish tinge in transmitted light.

(i) Concentration and density of sols. It has been shown that the concentration of most of the colloids is small. Metal sols usually contain 0.1 to 0.5% metal, sols of metallic hydroxides contain 1 to 5% of the solid. The concentration of fibrous molecular colloids is also small, *i.e.*, 0.2 to 1%. Similarly, quite concentrated sols of metallic hydroxides, metallic sulphides have been recently obtained.

Cholodny (1923) observed that the density of sols increases with the increase of concentration according to the equation :

$$d_s = d + c \,.\, \frac{d - d_0}{d}$$

where d is the density of the dispersed substance, d_0 is the density of the solvent, d_s is the density of the sol and c is the concentration of the dispersed substance in one ml. The density of particles can be determined by means of this equation. The density of particles in the case of sols of silver, selenium etc. is found to be the same as that of the substance in bulk. In lyophilic sols, the density of dispersed phase and dispersion medium is nearly the same.

(j) Surface tension. It is a characteristic property of most of the organic and inorganic colloids. In the case of inorganic lyophobic colloids, their water/air surface tension does not differ very appreciably from that of pure water. Thus, sols of Al_2O_3, etc. and even the inorganic lyophilic sols, *e.g.*, silica, stannic oxide show no significant difference in surface tension as compared to water.

Most of the organic colloids are lyophilic in nature so they have a low surface tension. If protein is dissolved in water, it will lower the surface tension to some extent. In presence of surface active substances like soap, fluorochemicals and other synthetic natural substances having the properties of detergents, the effect on surface tension is more appreciable.

It has been observed by du Nouy that the surface tension of many colloidal solutions changes with time after the addition of surface active agents, *e.g.*, the surface tension of a soap sol at first decreases and then rises rapidly to its original value.

(k) Viscosity. It is an important property of sols as it is directly related to the shape of particles. So, some important conclusions can be made from the effect of concentration, temperature, shear stress and of different additives on the viscosity of colloids.

The effect of viscosity on concentration has been studied for a number of sphero colloids. Einstein (1906) correlated these experimental facts and gave the following equation based on laws of hydromechanics.

$$\eta_{rel} = 1 + 2{\cdot}5\phi \qquad \ldots(1)$$

where η_{rel} is the relative viscosity and ϕ is the relative volume—concentration of the colloid particles. From the above equation, it is clear that the viscosity of sphero colloids is proportional to its concentration. Staudinger modified the above equation as

$$\eta_{sp} \frac{\rho}{c} = k = 0{\cdot}0025 \qquad \ldots(2)$$

where, c is the amount of dispersed phase in gL^{-1}. Later experiments show that two kinds of deviations are observed in equation (2).

(i) The constant k in equation (2) may also be greater than 0·0025. In case $k > 0{\cdot}0025$, it means that the particles are solvated or hydrated. If $k = 0{\cdot}0025$, hydration is negligible.

(ii) The equation (2) holds good at low and moderate concentration of the sphero colloids.

Viscosity and particle size. Equations (1) and (2) do not involve any term for particle size, so it follows that the viscosity of sphero-colloid is independent of particle size. According to Buzagh and Erenyl (1940) the above statement is correct for systems having comparatively coarse particles like finely quartz but not for smaller particles for which viscosity decreases with increase of particle size.

Fikantscher gave an empirical relation between relative viscosity and concentration of linear colloids.

$$\log \eta_{rel}/c = \frac{0{\cdot}75\,k^2}{1 + 1{\cdot}5kc} + k \qquad \ldots(3)$$

where k is a constant and is characteristic of linear colloids. Equation (3) holds good for different concentrations of several linear colloids.

6·9. OPTICAL PROPERTIES OF COLLOIDAL SOLUTIONS

[I] Tyndall Effect

The dimensions of colloidal particles are too small of a microscopic observation. It is only through their scattering power for light, that their presence can be observed. In ultra-microscopic observation, one makes use of light scattering of separate particles. In such a case, the particles are illuminated from the side and one observes a spot of light in ultramicroscope.

Faraday (1867) observed that when a beam of light is passed through a solution it cannot be seen unless the eye is kept directly in the path of light [Fig. (7)]. But when the same beam of light passes through a colloidal solution, one sees that a part of light is scattered sideways and there is a blue shine of the scattered light.

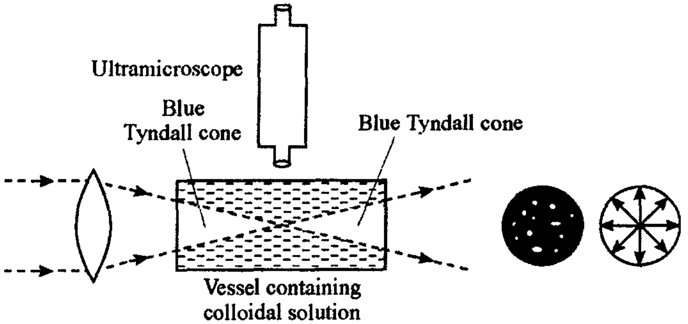


Fig. 7. Tyndall effect.

Tyndall (1868–70) observed that the zone of scattered light is much larger than the particle itself. This is why the colloidal particles appear like bright specks when seen under a microscope at right angles to the beam of light as shown in figure (7). So, Tyndall effect may be defined as **the scattering of light by colloidal particles in a colloidal solution**. The illuminated path is known as **Tyndall cone**.

The cone is not an essential part of the effect in as much as the path of light can be diverging or with parallel boundaries, as well as converging. Tyndall was the first to recognise that the diffracted light is polarised. (*Diffraction is the* *deviation of rays of light by objects in their path. But here diffraction refers to the lateral scattering of certain elements of rays).*

Tyndall effect looks to resemble flourescence. But the difference between the two can be seen by the fact that (i) The wavelength of the scattered light is always equal to that of the incident light, and (ii) the scattered light is partially polarised in most directions, even when the incident light is unpolarised.

The reason for the blue colour of the Tyndall cone can be sought in the fact that *'the intensity of the scattered light increases as the wavelength of the light decreases'.* If, therefore, incident light is white, then shorter wavelengths predominate in the scattered light. As a result of this, the scattered light acquires a blue colour. The transmitted light shows the complementary yellowish colour.

The intensity of the scattered light depends upon the difference between the refractive indices of the dispersed phase and the dispersion medium. In the case of lyophilic sols, this difference is small and Tyndall effect is, therefore, weak. But in the case of lyophobic sols, the difference is appreciable, hence an intense blue colour of the scattered light is observed. In the case of freshly prepared silicic acid, albumin sols, the difference is very nearly equal to zero, hence there is little or no Tyndall effect.

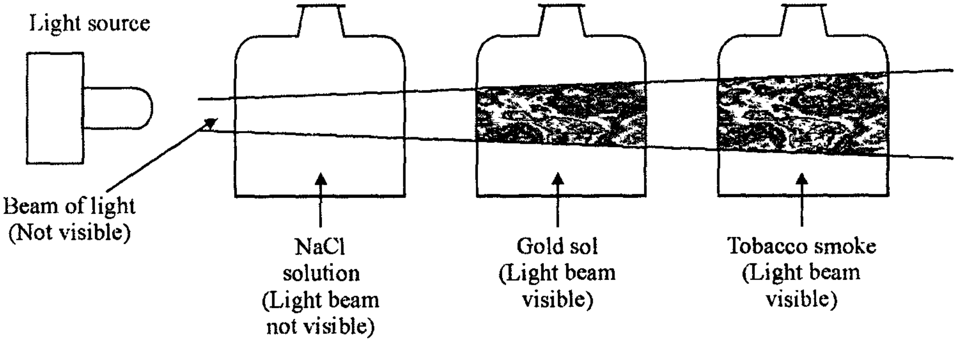


Fig. 8. Sodium chloride solution being a true solution does not scatter light, whereas gold sol and tobacco smoke being colloidal in nature scatter light.

Tyndall effect is not observed in the case of true solutions. The reason is that the particles (ions or molecules) present in a true solution are too small to scatter light. So, Tyndall effect can be used to distinguish a colloidal solution from a true solution [Figure (8)]. The phenomenon has been used to devise an instrument called an **ultramicroscope**. This instrument is used for the detection of particles of colloidal size. Tyndall effect also confirms the belief that colloidal systems are heterogeneous on nature.

[II] Ultramicroscope

The ultramicroscope is a microscope arranged so that light illuminates the object from the sides instead of from below. No light from the source reaches the eye and particles which reflect light are seen as bright specks against a dark field. For this reason, the ultramicroscope is frequently called a ***dark field microscope***. Ultramicroscope is intended to ensure that the incident light does not strike the eye of the observer and thus observes the scattering produced by the sol particles, against a dark background. An actual image formation is not obtained but the presence of a particle can be seen. So, it means that ultramicroscope is not concerned with reflected light, but with diffracted light.

The ultramicroscope was devised by Siedentopf and Zsigmondy and although it does enable the images of particles smaller than 0.13 μ to be seen, it does, however, enable their presence to be shown by means of light from a powerful source being reflected by the particles and the flashes observed when viewed at the proper angle with the incident rays. In the earlier experiments of Siedentopf (1900), a beam of light from the sun or arc light was passed into a sol and the illuminated path was then examined by a microscope whose axis made an angle of 90° with that of the incident light rays. The points of light which were thus produced by reflections from the dispersed particles were termed ultramicroscopic particles.

There are two types of ultramicroscopes, *viz.*, those with (i) ***orthogonal*** : and (ii) ***co-axial,*** illumination. The difference between orthogonal and co-axial illumination consists is that in the former type, illumination from one side is obtained, whereas in the latter, illumination from all sides is obtained. In other words, when the axis of the illuminating system forms a right angle with the axis of the viewing microscope, the system is orthogonal and when the two axes coincide the illumination is co-axial.

1. Orthogonal Ultramicroscope

The slit-ultramicroscope due to Zsigmondy and Siedentopf follows the orthogonal principle. It can be seen that it is comprised essentially of an illuminating system and a compound microscope is used for purposes of observation. An illumination from a powerful source of light (S) is used which may be self regulating arc. Its light falls upon a horizontal slit P after passing through a lens L_1. The light then passes through another lens L_2 and the illumination objective lens A throws a greatly diminished image in the interior of the vessel V containing the sol. The microscope M is so adjusted that this image of the slit falls into the middle of the field of vision and is kept at right angles to the incident beam.

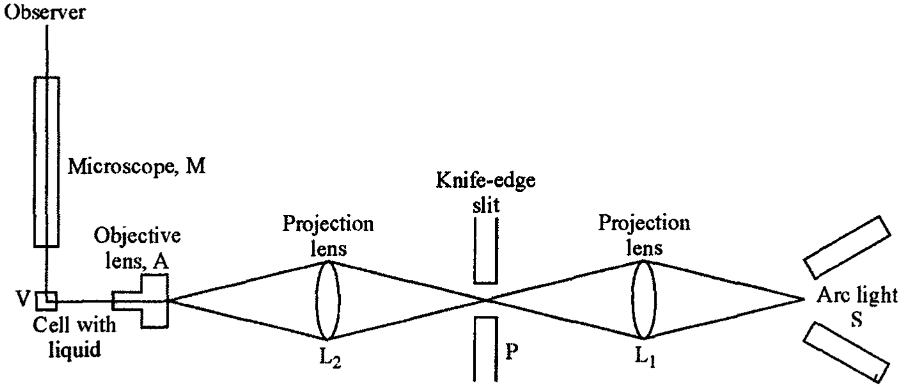


Fig. 9. Orthogonal ultramicroscope.

As each particle can be detected as '*spot*'of light, the slit-ultramicroscope helps to determine the number of particles in a definite volume. The great value of the slit consists in the ability by its use to suction off a portion of the fluid which is being examined. Zsigmondy (1912) revised an immersion ultramicroscope, which was used with strongly coloured liquids. In it, illumination objective and microscope objective are brought as close as possible, and the liquid to be investigated can be used as a drop between the two lenses.

2. Cardioid Ultramicroscope

Cardioid ultramicroscope is based on the principle of coaxial illumination and was supplied by C. Zeiss. The light from an arc lamp is rendered parallel by means of a lens. It is then thrown by means of a mirror through the cardioid condenser into the microscope. The condenser is opaque in the middle, so that no light enters the microscope. It passes through a narrow ringshaped space and is so reflected from the condenser surfaces, that upon exit and crossing itself at one point, it passes through the space below the microscope objective. It then leaves at an angle of 135°, so that none of it enters the latter directly. It then passes through a vessel containing the sol. This specially designed vessel consists of an object glass and a cover glass both of quartz. A very thin layer of sol is contained between the two glasses. Both the glasses should be thoroughly cleaned, otherwise reflected light from dust particles enters the microscope.

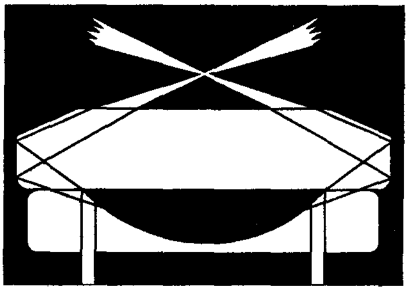


Fig. 10. Cardioid ultramicroscope.

Intensity of illumination in cardioid ultramicroscope is so great, that the systems may rapidly undergo photochemical alteration or coagulation as suggested by Haines (1935).

Limits of the ultramicroscope

In Tyndall phenomenon, we had observed that the reflection of light is not determined entirely by the size of the particles but depends upon the character of the surface, relative refractive indices of the two phases. It follows, then, that the presence of all particles that are present in colloidal solution cannot be shown by means of an ultramicroscope and furthermore, it must not be inferred that heterogeneity can only be determined by the ultramicroscope. Zsigmondy states that King using direct sunlight was able to note the smallest dispersed particles in a gold sol and the calculated size was 4 mμ. With the arc light illumination, gold particles of radius 4 mμ can be determined. Under most exacting conditions and using sun as the source of illumination, Zsigmondy determined the gold particles down to a limit of 7 mμ.

6·10. KINETIC PROPERTIES OF COLLOIDAL SOLUTIONS

Brownian Movement

Brownian movement is a phenomenon of fundamental importance for all colloidally dispersed systems. R. Brown (1827) observed that pollen grains of *clarkiapulehella* when placed in water moved about hither and thither continuously. Zsigmondy also found the same type of motion, when he examined a colloidal solution ultramicroscopically. It was seen that the particles in these solutions were in constant motion having no definite set path, but travelling in zig-zag directions all over the field of view. So, ***the continuous and irregular movement of the colloidal particles is known as Brownian movement.***

It has been shown that this motion was independent of the nature of the colloidal particles, but was more rapid the smaller the particles and less viscous the solution. It was also proved, that Brownian movement is not due to any external influence such as vibration of the apparatus, some external force or the effect of light, etc. Wiener and Gouy proved that the motion of the particles is due to the unequal bombardment of the suspended particles by the molecules of the dispersion medium in which they are dispersed. On this basis, Einstein suggested that colloidal particles must behave like dissolved molecules and gas laws should apply to these systems, just as they were applied to true solutions. As the particles increase in size, the probability of unequal bombardment diminishes and eventually the collision on different sides equalise each other. As the size is reduced, the probability of unequal bombardment rapidly increases, whereby making the Brownian movement more and more violent.

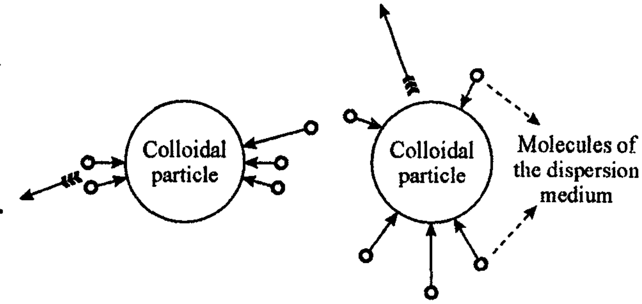


Fig. 11. Brownian movement (unequal bombardment of the suspended particles by the molecules of the dispersion medium).

Brownian motion is a clear indication of the kinetic theory. The two characteristics of Brownian motion are (a) *amplitude*, the distance between extreme and mean positions of particles and (b) *period of oscillation,* the time taken by the particle in order to make a complete oscillation. The former property for a colloidal particle of a fixed size was found to be proportional to the viscosity of the dispersion medium.

6·11. COAGULATION

It has been known for some time that on the addition of a very small amount of suitable electrolytes to emulsions or colloids, the corresponding substances are thrown out of the solution and form a precipitate. In the case of emulsions, the oil collects as a separate layer on the surface. If a suitable quantity of sodium chloride is added to a ferric hydroxide sol, then the sol becomes opalescent, turbid and ultimately precipitates. The electrolyte thus causes the colloid particles to coalesce. The gradual precipitation in this manner can be studied microscopically, the Brownian movement slowly decreasing and finally ceasing. So, the process *by means of which the particles of the dispersed phase in a sol are precipitated is known as* ***coagulation or flocculation.***

It was found that suspended particles which showed a marked cataphoretic effect could be precipitated by proper electrolyte and this electrolyte was determined by the process of experimentation. The coagulating effect of electrolytes on hydrophobic sols was studied and shown by Schulze (1884), Hardy (1900), Linder and Picton (1903—1906), which led to very important conclusions which are as follows :

(i) An ion having an opposite charge to that of the sol is responsible for coagulation. This ion is thus known as active ion, e.g., in the coagulation

of negatively charged sol, the cations will be the active ions and anions in the coagulation of negatively charged sol.

(ii) The coagulating or flocculating power of the active ion increases with the valency of the active ion.

Schulze and Hardy gave a law, after observing the regularities concerning the sign and valence of the active ion, and is known as **'Schulze—Hardy law'**, which can be defined as, ***'greater the valency of the active ion, greater is its power to cause coagulation.*** Thus, in the case of a positively charged sol, the coagulating power of anions is in the order of $PO_4^{3-} > SO_4^{2-} > Cl^-$, whereas the coagulating power is in order of $Al^{3+} > Ba^{2+} > Na^+$ in the case of negatively charged sols. The precipitate after being coagulated is known as ***'coagulum'***.

The amount of electrolyte required to produce coagulation depends upon the total surface exposed by the colloidal particles. Hence, more concentrated sols require more electrolyte for coagulation. *The minimum concentration of an electrolyte required to bring about coagulation or flocculation of a sol is known as* ***coagulation*** or ***flocculation value.*** It is evident, therefore, that polyvalent ions are the most effective active ions in causing coagulation.

Attempts were made to find general numerical values for the ratio of concentrations required for mono, bi and trivalent active ions. It is seen that if an effective concentration of trivalent ions is arbitrarily taken as unity, then the numerical values of bivalent ions range between 10 to 100 times greater and those of monovalent ions between 500 and 10,000 times greater.

The reciprocal of coagulation value is known as ***coagulating power.*** Whetham showed that the coagulating powers of a series of ions of the same sign is proportional to a constant, raised to the power representing the valency of each ion. If P_1, P_2 and P_3 represent the coagulating powers of mono-, bi-and trivalent ions, then

$$P_1 : P_2 : P_3 = x : x : x^3$$

where x is a constant greater than unity.

To compare the coagulating values of changes from ions of different values, we can take the precipitation of a standard amount of As_2S_3 in suspension by NaCl, $BaCl_2$, $AlCl_3$. The ratio of the weights required for precipitation in millimoles is 0.58 : 0.69 : 0.093 or in terms of milli-equivalents 58 : 1.38 : 0.279. Since the precipitating efficiency is inversely proportional to the amount used, the ratio of efficiency is

$$\frac{1}{58} : \frac{1}{1.38} : \frac{1}{0.279}$$

or
$$0.017 : 0.72 : 3.58 = 1 : 42 : 211$$

Since one of the positive charges from Ba^{2+} in this particular precipitation is 42 times as efficient as one positive charge from Na^+, the entire Ba^{2+} can precipitate 84 times as much As_2S_3 sol as the entire Na^+ ion. Similarly, the entire Al^{3+} can precipitate 633 times as such.

[I] Effect of Salt Mixture in Coagulation

The effect of mixture of salts like NaCl and KCl; $BaCl_2$ and $CaCl_2$ was also studied in the case of colloidal solution and the effect was found to be additive. For example, 0.1 M $BaCl_2$ will have the same coagulating power as 0.1 M $CaCl_2$. A mixture of both, *i.e.*, $BaCl_2$ and $CaCl_2$ of molarity 0.2 M will have the same coagulating power as 0.2 M $BaCl_2$ and 0.2 M $CaCl_2$.

[II] Measurement of Coagulation Value

The easiest and the simplest way to determine the coagulation value of a series of electrolyes for a given sol is to place 10 ml of a sol in a number of test tubes. The sol is then mixed with electrolytic solutions of increasing concentrations in the test tubes. After a specified time, we see the tubes which correspond to coagulation. Then a second series is started with concentrations of electrolyte ranging from that of the last test tube showing no coagulation to that of the first test tube showing coagulation. If necessary, a third series with smaller concentration differences between the tubes is employed. Coagulation value is expressed as number of millimoles of electrolyte per litre.

[III] Methods for Coagulating a Sol

In addition to coagulation by means of suitable electrolytes, it is also possible to coagulate a sol by the following methods :

(a) By changes in degree of solvation. In certain sols, especially lyophilic sols, the protecting layer of solvent which is closely held or bound to the surface of the suspended particles becomes an important factor in precipitation, because it is evident that this layer must be removed before coalescence occurs.

The salting out of such sols by the addition of strong solution of neutral salts as $(NH_4)_2SO_4$, $MgSO_4$ etc. is a dehydration process which follows the primary neutralisation of the suspended particles by the first addition of electrolyte. The two steps in the process are : (i) reduction of charge to a critical value by selective adsorption of a small amount of salt, and (ii) change in the degree of solvation of the suspension by the withdrawal of a certain amount of water by molecules of salt.

(b) By hydrated ions. Till recently, the study of coagulating action of ion has been limited to the nature of the ions and the number of charges carried. Since ions can also differ in the degree of hydration or solvation, this factor also plays an important role in the precipitation of sols.

(c) Bacterial agglutination. Mudd, Nugent and Bullock (1932) said that since a liquid containing bacteria can come within the colloidal range, the removal of bacteria becomes, in a part, a problem in coagulating a sol.

(d) By physical agencies. Coagulation of suspension also often results from stirring or shaking. Another physical method is to boil or freeze a sol. In the case of lyophilic sols, coagulation cannot be carried out by electrolytes in low concentration. Heating, as well as the addition of strong solutions of salts or certain acids, will cause coagulation.

Bridgmann (1914) showed that high pressure will also coagulate suspensions. Ultraviolet light will also coagulate certain metallic suspensions, probably due to the discharge of electrons from the surface of the particles, whereby the stabilizing charge is decreased.

(d) By addition of other colloids or mutual coagulation of sols. When two hydrophobic sols having the same charges are mixed, no chemical change in either takes place, and the resulting sol is a stable sol containing two different kinds of dispersed particles. The behaviour of the resultant sol is the average between the two original sols.

If the two sols are oppositely charged, some characteristic changes take place, as shown by Biltz (1901–05) and which depends upon the relative amounts of the two sols. If one of the two sols is in excess, no coagulation occurs, but the mixed sol is turbid and possesses the properties and colour of the sol which is in excess, *e.g.*, if a small amount of As_2S_3 sol (negative) is added to an excess of $Fe(OH)_3$ sol (positive), the resultant sol is stable and still positively charged. When the two sols are, however, in equivalent proportions, then both the sols coagulate each other and form conglomerates having little or no charge at all. This coagulation is due to the mutual discharge of the particles following mutual adsorption.

[IV] Effect of Concentration of Sols

Mukherjee (1919), Burton (1919), Kruyt (1929) showed that the coagulation value depends upon the dilution of sols. If a univalent ion is used for coagulating a hydrophobic sol, the coagulating power increases with increasing dilution of the sol. But if a polyvalent ion is used, the coagulating power decreases with increasing dilution of the sol. This rule is, however, known as ***Burton's rule***. This rule is widely obeyed, but there are few exceptions. For example, very dilute prussian blue sol is less stable for all kinds of electrolytes. Figure (12) shows the dependence of coagulation value on the concentration of the sol. From table-4, it is clear that in case of As_2S_3 and Sb_2S_3 sols, the coagulation power in case of a univalent electrolyte increases with decreasing concentration of the sol, but for bivalent and trivalent electrolytes, the coagulating power decreases with decreasing concentration of the sol.

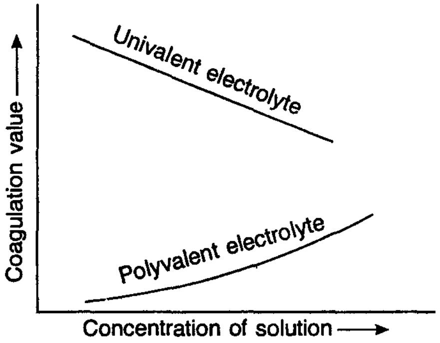


Fig. 12.

Table–4. Coagulating powers of different electrolytes

Name of sol	Concentration of sol (g /litre)	NaCl (millimole per litre)	$BaCl_2$ (millimole per litre)	$AlCl_3$ (millimole per litre)
As_2S_3	10.25	19.6	0.58	0.25
	1.02	58.8	0.23	0.083
Sb_2S_3	5.50	15.0	0.29	0.083
	0.55	50.0	0.19	0.041

[V] Theories of Coagulation

Several theories have been proposed to account for coagulation. These are '***adsorption theory***' and '***condensation theory***.'

(i) Adsorption theory. Freundlich (1910) developed a theory and showed experimentally that there is a close relationship between adsorption, reduction of charge on the particles and coagulation.

In the coagulation of a negatively charged As_2S_3 sol by barium chloride., it is assumed that some of the electrolyte is taken up or adsorbed by the colloidal particles, whereby the negative charge on the particles is neutralised by Ba^{2+} ions, thus reducing the charge on the particles. The particles then become unstable, aggregate and finally settle down in the form of a precipitate. The Cl^- ions are left in the solution.

The above fact was confirmed experimentally. Before coagulation, the solution contained 0.1523 gram of barium but after coagulation only 0.1253 gram of barium was present in the solution, in the case of a negatively charged sol, say As_2S_3. The amount of chlorine remained practically the same.

(ii) Hardy's theory. According to this theory, it is assumed that an electric charge, *i.e.*, a potential difference between the colloid and the medium, is necessary for the stability of the colloid. When by the addition of ions of opposite sign, such ions are selectively adsorbed, the colloid particle loses its potential difference with respect to the medium and the isoelectric point is reached and coagulation occurs.

(iii) Electrical double layer theory. Gouy (1910) and Burton (1926) explained the coagulation of a sol on the basis of the formation of an electrical double layer. Out of the two layers, the active ions are adsorbed on the fixed part of the double layer. For example, the sol of As_2S_3 is represented as follows (peptized by H_2S) :

$$[As_2S_3]\ S^{2-} : 2H^+$$

On adding barium chloride solution, the composition becomes :

$$[As_2S_3]\ Cl^- : Ba^{2+}$$

Ba^{2+} ions replace H^+, ions, as the former is more effective in bringing about coagulation. These H^+ ions pass into the bulk of the solution and thus becomes acidic. By adding sufficient amount of $BaCl_2$, the thickness of the double layer decreases and the zeta potential falls.

(iv) Ostwald theory. Ostwald (1949) suggested that coagulation does not depend upon the discharge of particles, but on some physical properties of the dispersion medium. The coagulation occurs when a certain value of activity coefficient is attained, when the particles are put out of the dispersion medium.

(v) Verwey theory. Verwey and Overbeek gave a clear picture of the process of coagulation. They said that coagulation occurs when the particles of the sol approach each other. They also calculated the forces and energies of repulsion between two particles surrounded by their ionic atmospheres. The attractive forces acting at the surface are the vander Waals forces. London suggested that these attractions depend upon the distance of the approaching particles and not on the dispersion medium.

Verwey calculated the relative concentration of uni-univalent, uni-bivalent and uni-trivalent electrolytes like NaCl, $BaCl_2$, $AlCl_3$ on a negatively charged arsenious sulphide sol. The concentration ratios is :

$$1 : (1/2)^6 : (1/3)^6 \quad \text{or} \quad 100 : 1.6 : 0.13$$

This theory, however, proved successful in explaining Schulze-Hardy law.

6·12. PROTECTION

[I] Protection and Protective Colloids

Protection is a process which is the reverse of precipitation and it consists in an attempt to neutralise or render ineffective the forces and conditions by which precipitation can be brought about. If ions or suspensions of opposite sign can bring about precipitation, it follows that, where adsorption increases the charge by the addition of like charged bodies, a protective action should result.

When hydrophilic and hydrophobic sols are mixed, and hydrophilic sol is in excess, then the resultant sol is avoided from being coagulated. In other words, the protection of hydrophobic sol has taken place. The sol now is more stable to temperature changes and is not readily precipitated by electrolytes. Faraday and Bechhold (1904) showed that the protected sols possess some important features, *e.g.*, they may be evaporated to dryness, leaving a residue which may again be redispersed in water, to give a sol. Hydrophilic colloids thus used for protecting the hydrophobic colloids are known as ***protective colloids***. Different protective colloids have different protective powers. Protective action may be shown by observing how a soluble soap can carry charcoal and finely divided ferric oxide through filter paper, when in the absence of the soap none will pass through, as shown by Spring (1909). Zsigmondy investigated the protective action quantitatively and gave the concept of gold number.

[II] Gold Number

Gold number may be defined as, ***'the weight in milligrams of a protective colloid which will just stop the coagulation of 10 ml of a given gold sol on adding 1 ml of 10% sodium chloride solution'***. If no protective colloid is present in the gold sol, it will turn from red to blue. The smaller the gold number of a protective colloid, the greater is its protective power.

Table–5. Gold numbers of protective colloids

Colloid	Gold number	Reciprocal gold number
Gelatin	0.005-0.01	200-100
Casein	0.1	10
Gum arabic	0.15-0.25	6.7-4
Dextrin	6-20	0.17-0.05
Starch (potato)	25.0	~ 0.04
Colloidal SiO_2	∞	0

The reciprocal gold numbers are also given as they give a more realistic impression of the relative values. Ostwald (1919) introduced ***rubin number*** which may be defined as *'the amount of protective colloid in gram per 100 ml of solution which prevents the change of colour of a Congo rubin sol.'*

Problem 1. ***Gold number of starch is 25. Calculate its amount to be added into 100 ml of gold sol so that it is not coagulated in presence of 10 ml of 10% NaCl solution.***

Solution. Gold number of starch is 25. It means that 25 mg of starch is added to prevent coagulation of 10 ml of gold sol by 1 ml of 10% NaCl solution. For 100 ml of gold sol, 250 mg of starch is needed to prevent coagulation by 1 ml of 10% NaCl solution. But for 10 ml of 10% NaCl solution, only $\frac{250 \times 1}{10}$ mg or 25 mg of starch is required.

[III] Theories of Protection

(i) Bechhold (1905) suggested that the protective effect may be due to homogeneous encircling of the dispersed particles by the particles of the protective colloid, thereby forming protective layer of sheath to each particle of the hydrophobic sol. Zsigmondy showed that this explanation of the protective action can be accepted in the case of coarse suspensions, but not in respect of ultramicrons of size not far removed from molecular dimensions.

(ii) Billitzer (1905) concluded that the protective colloid adsorbs any precipitating electrolyte. Zsigmondy demonstrated that gold particles in the form of foil adsorb a layer of gelatin, which cannot be removed by boiling water and which prevents the amalgamation of gold with mercury. He suggested the mutual adsorption of the particles of the two sols. This is confirmed by the fact, that protection is not complete immediately after mixing two sols, showing that a definite time is required for the union of the particles. Zsigmondy's view of mutual adsorption, therefore, suggests a union of the particles of the two colloids, to form a complex which has the stability of the particles of the protective colloid. The course of protection in the case of gelatin and gold sols can be observed by an ultramicroscopical examination.

(iii) Williams and Change suggested that an envelope is formed by hydrophilic substances over the particles of hydrophobic sol particles. Therefore, hydrophilic particles must be present in larger numbers as compared to that of hydrophobic particles and also the size of the latter is greater than the former. It has been observed that the same amount of the hydrophobic colloid is sufficient to cover the same amount of the hydrophobic colloid. In most cases, hydrophobic colloid particles are covered by a unimolecular layer of the protecting molecules. It was shown that in fact the protective action is due to the fact that the negatively charged hydrophilic colloid particles form a layer around the negatively charged particles. Similarly, positively charged hydrophilic colloid particles will form a layer around the positively charged hydrophobic colloid particles.

6·13. STABILITY OF SOLS

[I] Definition

Preventing coagulation of a colloidal solution by any manner or means is known as stabilising the colloid. Bancroft (1915) gave the position with regard to stability. He said that '*any substance may be brought into a colloidal state, provided the particles of the dispersed phase are so small that the Brownian movement keeps the particles suspended and the coagulation of the particles is prevented by a suitable surface film*'.

It was observed that lyophobic sols are stable due to their electric charge. As most of the lyophobic sols are prepared by preferential adsorption of ions, the mutual repulsion of particles is responsible for their stability. The sols become unstable, as soon as they are robbed of their charge. However, in case of lyophilic sols, the stability is due to electric charges as well as solvation—a phenomenon in which the colloid particle is surrounded by a thin film of the solvent. This layer of the solvent forms an envelope around each colloidal particle and thus prevents the particles from coming together. Groups like —COOH and —NH_2 in proteins and —OH in hydroxides and polysaccharides can bind water molecules. Lyophilic sols are coagulated when first the solvent layer and then the charge of the ion are removed.

[II] Factors Affecting Stability of Sols

There are numerous factors which confer stability on the colloidal system.

(i) Brownian movement. As a result of this movement, the particles are in constant rapid motion whereby aggregation of particles is prevented, so that the sol remains stable. But as soon as Brownian motion ceases, the sol becomes unstable. It is, therefore, expected that a sol will be more stable, the higher the dispersity and greater the charge on the particles.

(ii) Addition of electrolytes. As described before, a sol becomes unstable by the addition of suitable quantity of electrolytes. It is now established that the presence of electrolytes has a powerful effect on the potential difference between the particles of the dispersed phase and the dispersion medium and that this potential difference is closely connected with the stability of sols.

(iii) Effect of concentration of the sol. Ghosh and Dhar (1927) showed that a number of positively charged sols follow the rule that, greater the concentration of the sol the greater the amount of electrolyte required to coagulate the sol. In other words, the greater the concentration of the sol greater is its stability.

(iv) Effect of dilution. Choudhury (1928) showed that the dilution of a sol also affects the stability, which is decreased. The reason is the diminution of the charge and the total surface of sol particles with dilution decrease the stability of the sol. Mukherjee (1930) attempted to find out a relation between dilution and stability of a sol by measuring the migration velocity of the particles, but found the relation to be complicated.

(v) Rate of addition of the electrolyte. Dhar (1925) showed that the amount of electrolyte required to confer stability on a sol depends upon the rate at which it is added—this phenomenon is known as '***acclimatization of sols***'. There are two types of acclimatizations : in some cases, less electrolyte is required, when it is added slowly or in small quantities at a time, and in other cases the amount required is more. The former and latter are known as ***positive*** and ***negative acclimatization***, respectively. This phenomenon is probably due to changes occurring in the stabilisation by electrolytes.

(vi) Effect of temperature. It is seen that decrease of temperature confers more stability on the sols. Reid and Burton (1928) showed that heat alone is sufficient to cause coagulation.

(vii) Mechanical agitation. It has been seen that mechanical agitation decreases the stability of sols. Freundlich and Loehmann (1922) showed that the sol of CuO was found to be coagulated by mechanical agitation. The rate of coagulation is proportional to the square of the rate of stirring.

(viii) Ultra-violet light and X-ray radiations. Many lyophobic sols are coagulated by U-V light and X-rays of even from radiations of radium. It is seen that the coagulating effect of the rays is independent of the sign of the colloid. Lal and Ganguly (1930) studied the coagulating influence of U-V light on sols of AgI, Au, Ag, V_2O_5, $Th(OH)_2$, As_2S_3 etc.

(ix) Charge on the particle. The presence of charge on the colloid particles also confers stability on sols. If the charge is removed (as shown in cataphoresis) by any manner, the sol becomes unstable.

(x) Stabilization by protecting films. A typical example of protection by a film is shown by preparing two sols of hydrous ferrous oxide, the first by adding dropwise a few drops of conc. $FeCl_3$ to boiling water and the second by adding a small amount of 1% gelatin to the $FeCl_3$ before using. The relative stability of the two sols will be shown by the greater amount of electrolyte required to coagulate the second sol. The reason for this is that gelatin forms a protective layer around each sol particle and thus prevents it to some extent from being precipitated. Generally, lyophilic colloids are used for this purpose.

Isoelectric point. It is that point at which the concentration of the positive ions in solution becomes equal to that of the negative ions. Similarly, in case of colloidal solutions, a sol may be positively charged in presence of an acid, due to the preferential adsorption of H^+ ions. On the contrary, a sol may be negatively charged in presence of an alkali, due to the preferential adsorption of OH^- ions. However, there must be an intermediate H^+ ion concentration at which the colloidal particles are neither positively nor negatively charged. Hence, the isoelectric point in case of colloidal solutions, *is that point at which the colloidal solutions have no charge at all.*

Isoelectric point plays an important part in the stabilization of a sol. The stability of a sol is due to the presence of zeta potential (see subsequent pages) which is zero at the isoelectric point. At this point, the colloidal particles will not move towards any electrode under the influence of electric field. Hardy said that at isoelectric point, the colloidal particles are electrophoretically inert. Isoelectric point also occurs in protein sols. A protein solution is amphoteric. In acidic medium, a protein sol is positively charged while in an alkaline medium, it is negatively charged. At a certain point or at a certain pH, the particles will have equal positive and negative charges. Different protein sols have different isoelectric points, *e.g.*, isoelectric point for a gelatin sol occurs at pH = 4.7. Below pH 4.7, the colloidal particles of gelatin move towards the cathode, while at pH greater than 4.7, particles move towards the anode.

[III] Theories of Stability of Sols

The stability of colloidal solutions of the lyophobic type is due to repulsion between like charges on the particles which prevents coagulation. The charges usually arise due to adsorption of ions from the solution, but in some cases they may be due to defect structures in the solid particle itself. For example some, clay minerals carry a charge due to substitution of Al^{3+} by Mg^{2+} or Li^+, etc. The surface charges on a particle are compensated by an array of ions of opposite sign, thus forming an electrical double layer.

(1) Solvation theory. Kruyt (1892-28) showed that *'hydration or solvation'* of colloids is a fundamental factor in the stability of the sols. Every lyophilic colloid possesses and forms a very thin layer of solvent around each particle, thereby preventing the colloid from being coagulated easily. The sol can now be coagulated by the previous addition of some dehydrating agents which remove the solvent layer, and so helps the electrolyte to coagulate the sol. So, the stability of a lyophillic colloid in water is determined, both by the electric charge on a colloidal particle and by hydration also.

(2) Perrin-Rice theory. Perrin (1905) and Rice (1926) put forward an explanation connecting the stability of a sol with negative free surface energy of the double layer. They calculated a certain degree of dispersion for which there is an equilibrium between normal positive free energy of the interface and negative free energy of the double layer. This means that a colloidal suspension could be stable in thermodynamic sense and would not be subject to coarsening. As far as is known, no lyophobic system is ever stable in this strict sense. Hence, this theory is not applicable in practical cases.

(3) Powis theory. Powis (1915) pointed out that in order to bring about coagulation it is not necessary that the charge on the particles should be removed completely. A lowering of potential at the interface to a *certain value*—called the critical potential—will bring about coagulation, *i.e.*, decrease the stability. The work by Picton, Powis and other showed that stability of colloids is governed by charge on the particles. The condition of such a sol and the manner in which its stability is destroyed can be understood as follows :

(i) Each particle of the colloid is protected by an electric charge of the double layer and although the particles are in constant rapid motion, they do not collide with each other and do not form bigger particles, as all the particles carry the same charge.

(ii) If no charge were present, each collision will result in the union of the particles, rendering the sol unstable.

(4) Gyemant-Lewis theory. Gyemant (1926) and Lewis (1932) considered the possibility of colloids as a consequence of the interplay of surface tension and charge.

(5) Verwey and Overbeek theory. The theory of the stability of lyophobic colloids was worked out by Verwey and Overbeek (1942) and independently by Derjaguin and Landau. It is often called the D.L.V.O. theory. They calculated the free energy of interaction between particles and surfaces of various shapes. They took the sum of the electrical interaction between the double layers and the vander Waals interaction between the surfaces. Although vander Waals forces between individual molecules have a very short range, the situation is different for bigger colloidal particles which have an attractive interaction over a much longer range.

As in the Debye-Huckel theory of interionic forces, the presence of ions in colloidal solutions tends to shield the charged particles from electrostatic interactions. The higher the ionic strength of the medium, the shorter the radius of the ionic atomosphere. So, as the ionic strength of the medium increases, ultimately a condition is reached in which vander Waals attraction between the particles overcomes the electrical repulsion and then the coagulation of the sol occurs.

6·14. ELECTRICAL PROPERTIES OF COLLOIDAL SOLUTIONS

It is now well confirmed that colloid particles carry an electric charge, whether positive or negative. The polarity of a sol not only depends on the dispersed phase, but also on the dispersion medium. The charges carried by sols are shown in table-6.

Table–6. Charge on different sols

Positive sols	Negative sols
Metal hydroxides	Metals, *e.g.*, Ag, Au, Pt
Metals, *e.g.*, Bi, Pb, Fe	Metal sulphides
Methyl violet, methylene blue	Silicic acid, stannic acid Mastic, congo red, eosin, prussian blue.

[I] Electrophoresis

Electrophoresis was first observed by Linder and Picton (1892) and is used to indicate the migration of colloidal particles in an electric field. When the particles move towards the cathode, the phenomenon of migration of particles is known as *cataphoresis* and migration towards the anode is known as *anaphoresis*. But in practice, a more general term *electrophoresis* is used.

Electrophoresis can be studied by a simple apparatus which consists of a U-tube fitted with a funnel shaped reservoir and a stop cock. A small amount of water is placed in the U-tube and then some quantity of the sol is taken, so as to form a layer under the pure dispersion medium. An electric current is then applied by connecting the two electrodes dipped in the solution. It will be seen that the particles begin to migrate towards the oppositely charged electrode. If the sol is coloured, then the movement of the particles can be observed directly by naked eyes. But if the sol is not coloured, then the cataphoretic migration can be observed by microscope or ultramicroscope. When the colloidal particles reach the electrode, they lose their charge and are generally coagulated into coarse particles. The velocity of electrophoretic migration was measured by Burton, Cotton and others. They measured the rate of movement of the boundary over a certain period of time. Svedberg and Tiselius (1925) measured the velocity of migration of protein particles by fluorescence photography.

Applications of Electrophoresis

(i) In the determination of the charge. The nature of the charge on a colloidal particle can be ascertained by its migration in an electric field.

(ii) In electro-deposition of rubber. The latex obtained from the sap of certain trees is an emulsion of negatively charged rubber particles dispersed in water. This can be deposited on any substance which is made the anode.

(iii) In the removal of colloidal smoke from outgoing gases The removal of negatively charged carbon particles from smoke can be made by passing the smoke between positively charged metal electrodes. This principle has been utilised in the construction of ***Cottrell precipitator.***

(iv) Electrophoresis has proved to be of great importance in medicine, industry etc., *e.g.*, in characterising proteins causing disease as well as in the isolation of enzymes. Flavine enzyme was similarly isolated from yeast by Theorell (1932).

[II] Electro-osmosis

Electro-osmosis also known as electro-endosmosis was discovered by Reuss (1808), but was investigated by Wiedemann (1852-56) and Quincke (1861). It is defined as ***'the movement of a liquid (dispersion medium) with respect to solid (dispersed phase) as a result of an electric field'.*** It can be observed as shown in figure (13).

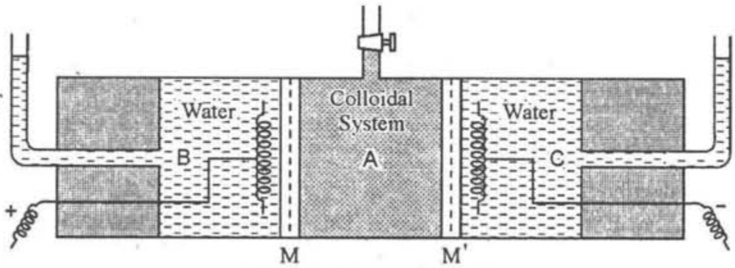


Fig. 13. Electro-osmosis.

The colloidal system is put in a central chamber A, which is separated from the side chambers B and C filled with water, by the dialysing membranes M and M′. The water in the chambers B and C extends to the side tubes T and T′, respectively. The membrane does not allow the colloidal particles to pass through it. So, when a potential difference is applied across the electrodes held close to the membranes in chambers B and C, the water starts to move. If the particles carry negative charge, the water will carry positive charge. So, it would start moving towards the cathode and so the level of water in side tube T′ would be observed to rise. If on the contrary, the particles carry positive charge the water will carry a negative charge. The level of water will now start moving towards the anode and its level in the side tube T would start rising. The theoretical interpretation of electro-osmosis has been given by Helmholtz, Lamb, Perrin, and von Smoluchowski.

Applications of Electro-osmosis

(i) In the preparation of pure colloids. The case in point is the preparation of colloidal silicic acid of low molecular weight, *i.e.*, in a state of fine sub-division.

(ii) In the tanning of hides and impregnation of similar materials.

(iii) In the manufacture of gelatin for photographic emulsions. The object is to get a gelatin free from fat, mineral and reducing constituents. The phenomenon is also applied in the manufacture of high grade glue.

(iv) In the dying of peat, a process due to von Schwerin (1903).

6·15. ORIGIN OF CHARGE

Colloid particles are electrically charged, as established by Linder and Picton (1802). Although for most systems, we can give a reasonable explanation for the existence of the electrical double layer, it is generally not possible to form a rule which can be applicable to all types of systems, including hydrosol and organosol, because there are several mechanisms by which the charge can come into being, and any one of them may be applicable depending upon the particular circumstances.

Following are the views which have been given to explain the origin of charge on a colloidal particle:

(i) Charge being ionic in nature. It has been shown that colloids, *e.g.*, sodium palmitate and soap dissociate producing ions and thus the charge is produced as a result of the formation of ions. But this view does not hold good for non-electrolytic colloids such as clay, smoke etc. as they also carry a charge.

(ii) Charge being frictional in nature. In earlier days, it was regarded that the source of the charge on colloid particles is essentially physical and it was suggested that the charge resembled the frictional electricity produced by the contact of such substances as glass and silk and in this case, substance with a higher dielectric constant takes up the positive charge. This explains why most of the hydrosols are negatively charged. This is because water has a very high dielectric constant. But some colloids, *e.g.*, hydroxides which are positively charged, show that dielectric constant is not the only factor which determines the charge. The second difficulty in assuming the charge to be frictional is that if the charge were frictional, the whole liquid should bear a charge, whereas the liquid as a whole is electrically neutral.

(iii) Dissociation of dispersion medium. It was suggested that the dispersion medium dissociates into ions and these ions are adsorbed by the colloid particles. This view was put forward by Hardy, who showed that it was possible to change the sign of the charge on a colloid by placing it in an environment of ions, of an opposite charge to that which it possesses. Thus, when mastic is suspended in water it is found to have very little charge indeed, but when placed in an acid solution it becomes positively charged, presumably because of the adsorption of H^+ ions. In alkaline solution, it becomes negatively charged due to the adsorption of OH^- ions. But this theory fails when the dispersion medium is an organic substance, *i.e.*, non-ionisable medium.

(iv) Association of electrolytes. It has been observed that small quantities of electrolytes are associated with colloidal systems and that if they are removed by persistent dialysis or by other methods, the sols become unstable and the particles grow in size and are finally precipitated. It is probable that in many cases, traces of ions present in the sol are responsible for the charge and the stability of colloidal particles. It is seen that stable sols of gold, silver etc. can be obtained by Bredig's arc method by passing an electric current between electrodes of the metals in water. Water contains a little KOH or any other alkali. One ion is retained by the colloidal particles, giving the same charge to the colloid and the other ions is retained by the dispersion medium.

(v) Formation of electrical double layer. von Helmholtz postulated the existence of an electrical double layer of opposite charge at the surface of separation between a solid and a liquid, *i.e.*, at a solid-liquid interface.

According to modern views, when a solid is in contact with a liquid, a double layer of ions appears at the surface of separation [Fig. 14]. One part of the double layer is fixed on the surface of the solid. It is known as ***fixed part*** of the double layer and it consists of either negative or positive ions. The second part of the double layer consists of a ***mobile*** or ***diffuse layer of ions*** which extends into the liquid phase. This layer consists of ions of both the charges but the net

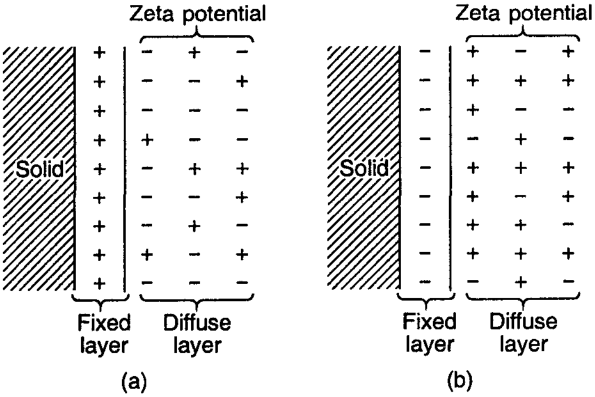


Fig. 14.

charge on the diffuse layer is equal and opposite to that on the fixed part of the double layer. This arrangement is shown in figure (14). In figure 14 (a), the fixed part of the double layer comprises of positive charges while in figure 14 (b), the fixed part of the double layer consists of negative charges. The ions which are preferentially adsorbed by the sol particles, are held in the fixed part of the double layer. It is these ions which give the characteristic charge to the sol particles.

It is supposed that the charge on a colloidal particle is due to the preferential adsorption of either positive or negative ions on the particle surface. If the particles have a preference to adsorb negative ions they acquire negative charge or vice versa. The negative charge on As_2S_3 sol is due to the preferential adsorption of sulphide ions on the particle surface. These ions are given by the ionisation of hydrogen sulphide, which is present in traces. Similarly, the negative charge on metal sol particles obtained by Bredig's method is due to the preferential adsorption of hydroxyl ions given by the traces of alkali present. The positive charge on a sol of $Fe(OH)_3$ prepared by the hydrolysis of ferric chloride is due to the preferential adsorption of ferric ions on the surface of the particles. These ferric ions are obtained by the dissociation of ferric chloride present in traces in the sol.

From the above, it is clear that the *ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed by it.* So, in As_2S_3 sol, sulphide and not hydrogen ion is preferred and in $Fe(OH)_3$, ferric and not chloride ion is preferred.

Now consider stannic oxide sol. If a freshly prepared precipitate of stannic oxide is peptised by a small amount of HCl, the colloidal solution carries a positive charge. If the precipitate is peptised by a small amount NaOH, the colloidal solution carries a negative charge. In the first type of sol, a small amount of stannic chloride $SnCl_4$ is formed and Sn^{4+} ion is preferred over Cl^- ion. The sol gets ***positively charged***. In the second type of sol, a small amount of sodium stannate Na_2SnO_3 is formed and now the SnO_3^{2-} ion is preferred over Na^+ ions. The sol gets ***negatively charged***. The structure of the sol particles in the two cases can be represented [Fig. (15)] as:

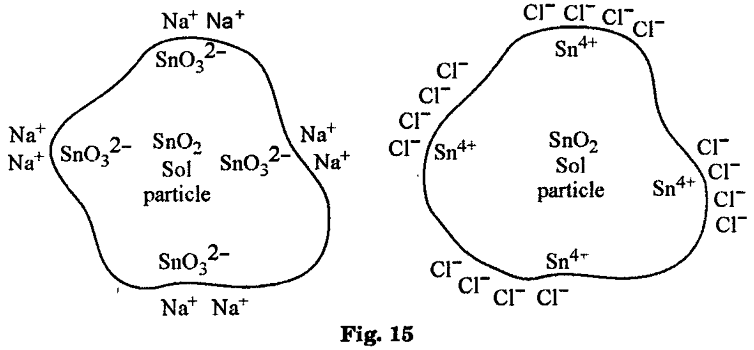


Fig. 15

Positive sol : $[SnO_2]\ Sn^{4+} \mid 4Cl^-$

Negative sol : $[SnO_2]\ SnO_3^{2-} \mid 2Na^+$

The chloride and sodium ions form the diffuse part of the electrical double layer.

Another case is the formation of positively and negatively charged sols of silver iodide. If a dilute solution of $AgNO_3$ is added to a slight excess of NaI solution, a negative sol of AgI is obtained, due to the adsorption of iodide ions. The structure

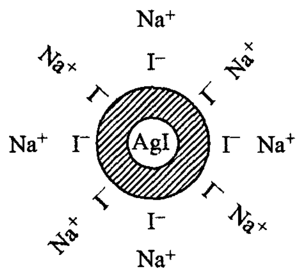


Fig. 16. (a) Negatively charged sol of AgI

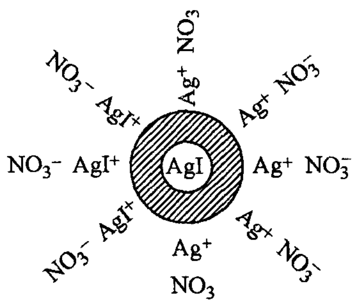
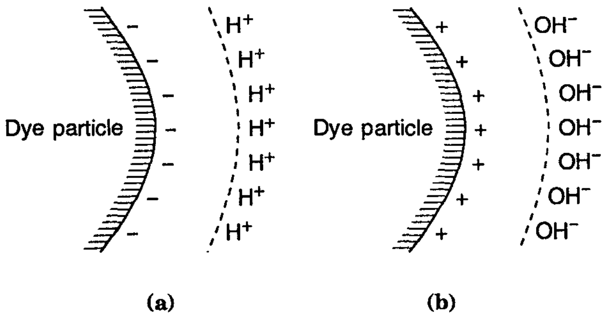


Fig. 16. (b) Positively charged sol of AgI

of the particles is represented as [AgI] | I^- | Na^+ [Fig. 16 (a)]. If a dilute solution of NaI is added to a slight excess of $AgNO_3$ solution, a positive sol of AgI is obtained, due to the adsorption of silver ions. The structure of the particle is shown as [AgI] | Ag^+ | NO_3^- [Fig. 16 (b)]. If on the contrary, equivalent amounts of $AgNO_3$ and NaI are mixed, there is complete precipitation of silver iodide and ***no sol is formed.***

(vi) Ionisation theory. Colloidal particles may aquire an electrical charge due to the direct ionisation of the substance constituting the particles. This phenomenon is commonly seen in the case of acidic and basic dyestuffs. An acid dyestuff ionises to give hydrogen ion in solution and thus leaving an equivalent amount of negative charge on the sol particles. The structure of the colloidal particles of dye is shown in figure (17-a). A basic dyestuff, ionises to give hydroxyl ions in solution and thus leaving an equivalent amount of positive charge on the sol particles. The structure of the colloidal particles of dye is shown in figure (17-b).



(a) (b)

Fig. 17

(vii) Orientation theory. The theory of orientation of molecules at surface has received much prominence of late and experimental data from several sources would seem to show that molecules with polar groups are oriented when adsorbed at the solid-liquid interface. By this means, if the positive ends of adsorbed molecules are turned outward, the suspension will have the characteristics of a positively charged body. When the charge is reversed in another fluid, it can be accounted for by a 180° reversal of the oriented molecules at the interface.

6·16. ELECTRICAL DOUBLE LAYER

Helmholtz (1879) explained qualitatively the electrical properties of colloids on the concept of electrical double layer at solid-liquid interface. The concept of this double layer has been explained in the preceding article. According to Stern, an electrical double layer consists of two parts;

(a) One part of the double layer, known as ***fixed part*** remains almost fixed to the solid surface. It has positive or negative ions. There is a sharp fall of potential.

(b) The second part of the double layer, known as ***diffuse part*** extends some distance into the liquid phase. This layer contains ions of both signs. Its net charge is equal and opposite to that on the fixed part. There is a gradual fall of potential into the bulk of the liquid where the charge distribution is not uniform.

Consider once again the formation of silver iodide sol from the double decomposition reaction

$$AgNO_3\,(aq) + NaI\,(aq) \longrightarrow AgI\,(s)\downarrow + NaNO_3\,(aq)$$

Suppose that the electrolyte used in excess is sodium iodide. This would result in the preferential adsorption of I^- ions giving a negatively charged sol of silver iodide as shown in figure (18). The ions preferentially adsorbed on the surface of a particle of a colloidal system are called ***potential determining ions*** and these ions form the fixed layer.

The negatively charged surface of silver iodide particle attracts the positive ions (Na^+) and repels the negative ions (NO_3^-). Due to this, the positive Na^+ ions tend to form a compact layer in the vicinity of the potential determining I^- ion layer. This is known as ***Stern layer*** (Fig. 18). The ions present in Stern layer are known as ***counter ions.***

The effect of the surface charge decreases with distance and so does the number of ions and, therefore, at a certain distance from the surface of the particle, the concentration of Na^+ ions equals the concentration of NO_3^- ions and a condition of electroneutrality occurs (Fig. 18). It must be noted that the system as a whole is neutral even though there exists regions of unequal distribution of anions and cations. The diffuse layer between the Stern layer and the electrically neutral part of the system is known as ***Gouy-Chapman layer.***

The presence of charge gives rise to potential at the surface of the particle. This potential drops to zero at some distance away from the surface depending on the concentration of the counter ions in the bulk phase. The area in which the effect of the charge is

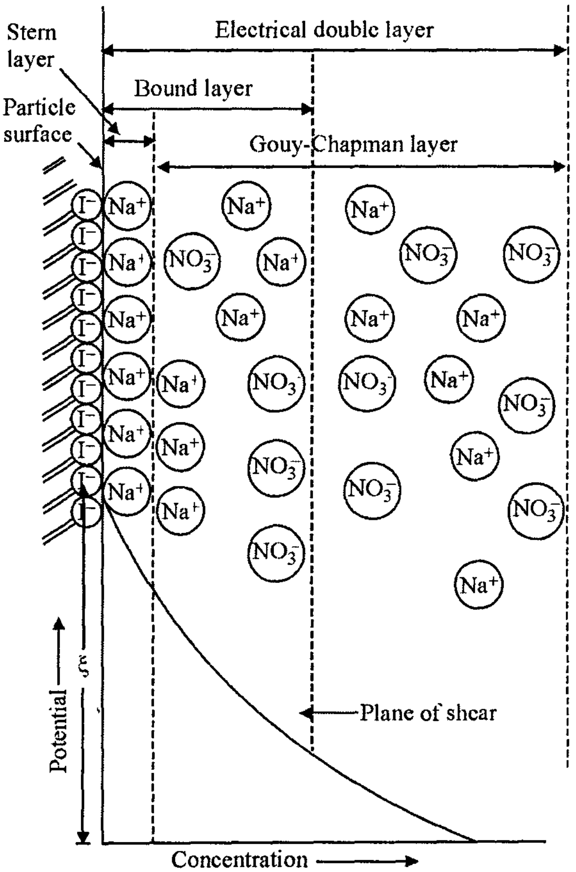


Fig. 18. The electrical double layer in colloidal systems.

appreciable is called the ***electrical double layer.*** The double layer consists of two parts, *viz.*, the Stern layer, the thickness of which is of the order of ionic dimensions and the Gouy-Chapman diffuse layer the thickness of which is given by,

$$r_d = \left(\frac{DRT}{2\rho F^2 \mu}\right)^{1/2}$$

where ρ, F, D and μ are, density, faraday constant, dielectric constant and ionic strength of the solution, respectively. The value of r_d is of the order of 1–100 nm. It decreases with increase in ionic strength of the solution, more rapidly for counter ions of high valency.

For the diffuse part of the double layer, thermal agitation allows the free movement of the particles, but the positive and negative ions are not uniformly distributed. The electrostatic field at the surface will result in preferential attraction of ions of opposite sign.

The presence of charges of opposite signs on the fixed and diffuse parts of the double layer produces a potential between the two layers. This potential is known as ***electrokinetic potential*** or ***zeta potential.*** It is represented by ζ. It is, therefore, the electromotive force which is developed between the fixed layer and the dispersion medium.

6·17. DETERMINATION OF SIZE OF COLLOIDAL PARTICLES

We know that under an ultramicroscope, the true image of the particle does not appear, but only a '*halo*' of light surrounding the particle, only indicating its position appears. Lobry de Bruyn considered that colloidal particles would not have a diameter less than 5-10 mμ (1 mμ = 10^{-7} cm), since smaller particles do not polarise light.

There are several methods by which the size of the colloidal particles may be determined indirectly. Some of them have already been discussed, while the other important ones are discussed below.

[I] From Electromagnetic Theory

According to electromagnetic theory of light, the wavelength (λ) which suffers maximum absorption on passing through a colloidal solution is connected with the radius of the colloid particle by the expression :

$$r = \frac{\sqrt{3}\,.\,\lambda}{4\pi n}$$

where n = refractive index of the dispersion medium.

For gold sols, the maximum absorption occurs at λ = 4900—5200 Å. Hence, r for gold particle = 4·9 to 4·2 × 10^{-6} cm, n being 1.33. Similarly, value of r for Ag and Pt sols are given as 4·0 × 10^{-6} cm, 4·8 × 10^{-6} cm, respectively.

[II] Ultra-filtration Method

The size of the pores of the ultrafilters can be calculated from the measurement of the pressure required to force air through the membrane saturated with water, or by measuring the volume of water forced through unit area of the membrane in unit time by a known pressure. It may be repeated that in addition to the size of the particle, adsorption and electric charge will hold the particles and may simulate a lower porosity than should be present according to the size of the pores of the ultrafilters.

By finding which of a series of ultrafilters will just permit the particles of a sol to pass into the filtrate, while the next ultrafilter just stops the passage, the diameter of the colloidal particles can be determined, provided the particles are assumed to be spherical. The results agree satisfactorily with those obtained by other methods.

[III] From Tyndall Effect

The volume of a particle in a sol may be approximately determined by means of Tyndall light, the intensity of which may be measured by *'Tyndall meter'* or photographically. Rayleigh (1871) showed that the intensity of the scattered light (I_s) by a suspension from a beam of known intensity (I) is given by the relation

$$I_s = I \cdot \frac{V^2}{d^2 \lambda^4}$$

where V is the volume of the colloid particles, d is the distance between the particle and the observer and λ is the wavelength of the scattered light. The formula holds for insulating materials and not for metallic particles.

As the expression involves the volume term, the radius of the particle (r) can be calculated by the relation, $V = \frac{4}{3}\pi r^3$ (particles assumed to be spherical). One difficulty with this method is that the amount of light scattered depends not only on the size but also on the shape of the particles. If we have two sols of equal concentrations, consisting of particles of different sizes, we have

$$\frac{V_1^2}{V_2^2} = \frac{I_{s_1}}{I_{s_2}} \cdot \frac{\lambda_1^4}{\lambda_2^4} = \frac{r_1^6}{r_2^6}$$

This is a good method for finding the ratio of the size of the colloid particles.

[IV] From Brownian Motion

Colloidal particles suspended in a liquid medium exhibit Brownian motion. They tend to settle down due to gravity. Due to the influence of both these effects, the colloidal particles distribute themselves in a vertical column according to the equation

$$\frac{2{\cdot}303\,RT}{N} \log_{10} \frac{n_1}{n_2} = \frac{4}{3}\pi r^3 g\,(h_2 - h_1)\,(\rho - \rho')$$

where N is Avogadro's number, n_1 and n_2 are the number of particles at heights h_1 and h_2 of the vertical column (they can be counted by an ultramicroscope), ρ and ρ' are the densities of the dispersed phase and dispersion medium (they can be determined by usual methods) and r is the radius of the particles. Thus, the value of r can be calculated.

[V] From Scattering of Light

Zsigmondy used ultramicroscope for determining the size of colloidal particles. Each spot of light seen in an ultramicroscope, corresponds to a particle. So, the number of particles in a given volume of a solution can be counted. The observation is made a number of times and an average is taken. The length and breadth of the field of vision are measured by an eye piece micrometer. The depth is measured by rotating the slit through 90°. From this data the exact volume of the solution containing the observed number of particles can be measured. Thus, the number of particles per unit volume of the solution can be calculated. Let the number be n.

Next, a known volume of a colloidal solution is evaporated to dryness. From the weight of the residue, the mass of colloidal particles per unit volume is calculated. Let it be m gm. Now, assuming the colloidal particles to be spherical and density (d) of the colloidal particles to be the same as that in the bulk state, the volume of colloidal phase is m/d.

$$\therefore \qquad \frac{m}{d} = \frac{4}{3}\pi r^3 . n$$

$$\text{or} \qquad r = \left(\frac{3m}{4\pi dn}\right)^{1/3}$$

[VI] Sedimentation Method By Ultracentrifuge

The most modern and widely used method to determine the molecular weight is due to Svedberg (1927-31). The determination of molecular weight of proteins has been a difficult problem, because proteins have resisted colloidal chemical investigation due to unfavourable optical properties. Secondly, sedimentation methods are difficult on account of high dispersity and low density of the material.

The method described by Svedberg and his co-workers is to rotate the solution in a specially designed high speed instrument known as *ultracentrifuge*. The rate of sedimentation of suspended particles under the influence of gravity is very small. It can, however, be increased considerably by subjecting it to ultracentrifuge technique. The force exerted on the particles in this manner can be as great as million times the gravity. If ω is the angular velocity of rotation, *i.e.*, rotational speed in radians per second, then the force exerted on a particle at a point distant x from the axis of rotation is $\omega^2 x/g$ times the gravity, where $\omega = 2\pi$ times the number of revolutions per second. The rate of sedimentation can thus be increased by increasing the number of revolutions per second. Two different methods based on the use of ultracentrifuge are discussed as follows :

(a) Sedimentation equilibrium method. Perrin observed that when an equilibrium is established under the influence of gravity in a sedimenting column, *i.e.*, when the rate at which the particles settle down becomes equal to the rate at which they diffuse back due to Brownian and thermal motions. We, thus get the following equation

$$\log \frac{n_1}{n_2} = \frac{Nmg\,(x_2 - x_1)}{2.303\,RT} \cdot \left(1 - \frac{d'}{d}\right) \qquad \text{... (1)}$$

where N is Avogadro's number, n_1 and n_2 are the number of particles per unit volume at depths x_1 and x_2, d is the density of the particles suspended in a liquid of density d', m is the mass of the particle and g is acceleration due to gravity. From equation (1), we now have,

$$\log \frac{n_1}{n_2} = \frac{Mg\,(x_2 - x_1)}{2.303\,RT}\left(1 - \frac{d'}{d}\right) \qquad \text{... (2)}$$

where $M = mN =$ molecular weight of the polymer.

It takes several months for the sedimenting column containing macromolecules to attain equilibrium, if it is subjected to normal gravity. However, if the same column is subjected to a centrifugal field, the equilibrium can be attained in a few days. From theoretical calculations, we can show that the gravitational factor $g\,(x_2 - x_1)$ can be replaced by centrifugal factor $\frac{1}{2}\,\omega^2\,(x_2^2 - x_1^2)$. The equation (2) for sedimentation equilibrium is then given by

$$\log \frac{n_1}{n_2} = \frac{M\omega^2(x_2^2 - x_1^2)}{2.303 \times 2RT}\left(1 - \frac{d'}{d}\right) \qquad \dots (3)$$

The apparatus is shown in figure (19). It consists of a rotor A revolving at a very high speed about the axis BB. The solution under examination is taken in a cell C, made of quartz windows. A beam of light is allowed to pass through the solution which is then allowed to fall on a photographic plate, P. The amount of light absorbed at two depths x_1 and x_2 can be measured by blackening the plate P. Assuming the amount of light absorbed at any level as proportional to the number of molecules present at that level, the ratio n_1/n_2 can be obtained. The angular velocity ω can be calculated by knowing the speed of rotation of the ultracentrifuge. Knowing the values of d and d', we can calculate M, the molecular weight of the polymer from equation (3).

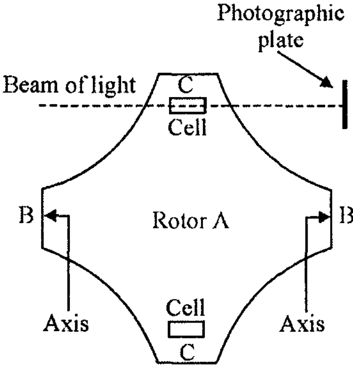


Fig. 19. Ultracentrifuge

(b) Sedimentation velocity method. The sedimentation equilibrium method takes several days for completion. This is because in this method, low centrifugal forces, *i.e.*, of the order of 10,000 to 100,000 times the gravity have to be used to obtain accurate results. A quicker method, based on sedimentation velocity is perferred. As much higher centrifugal forces of the order of 5,00,000 times the gravity can be used without introducing any error. Moreover, the process can be completed within a few hours.

The apparatus used is the same as in figure (19). As the colloidal particles undergo sedimentation on rapid rotation of the solution, a moving boundary is formed, behind which there is only solvent. The beam of light which passes through the system and then falls on a photographic plate, P records the position of the boundary at various intervals of time.

A particle undergoing sedimentation in a liquid column is subjected to a gravitational force, F, given by

$$F = (\text{Mass of particle} - \text{Buoyancy})\,g \qquad \dots (4)$$

The buoyancy factor is equal to the product of the volume of the particle and the density of the liquid medium.

Assuming the particle to be spherical of radius r, we have

$$F = \left(\frac{4}{3}\pi r^3 d - \frac{4}{3}\pi r^3 d'\right)g$$

$$= \frac{4}{3}\pi r^3 (d - d')\,g \qquad \dots (5)$$

where d and d' are the density of the particle and liquid medium, respectively.

The particle undergoing sedimentation meets a frictional resistance, R which is proportional to its velocity, dx/dt, at the given moment and is given by

$$R = f \,.\, \frac{dx}{dt} \qquad \ldots (6)$$

where f is the frictional coefficient. For spherical particles,

$$f = 6\pi\eta r$$

where η is the coefficient of viscosity of the liquid medium. Therefore,

$$R = 6\pi\eta\, r \,.\, \frac{dx}{dt} \qquad \ldots (7)$$

Due to the influence of the above two opposing forces, the particles attain a state of equilibrium, *i.e.*, zero acceleration and attain a uniform velocity. The two forces R and F balance each other, therefore,

$$\frac{4}{3}\pi r^3 (d - d')\, g = 6\pi\eta r \,.\, \frac{dx}{dt}$$

or

$$\frac{dx}{dt} = \frac{2r^2(d - d')\, g}{9\eta} \qquad \ldots (8)$$

Substituting g by $\omega^2 x$ in equation (8), we get

$$\frac{dx}{dt} = \frac{2r^2(d - d')\,\omega^2 x}{9\eta}$$

or

$$\frac{dx}{x} = \frac{2r^2(d - d')\omega^2}{9\eta} \,.\, dt \qquad \ldots (9)$$

dx/dt is the velocity of the particle when it is at a distance of x cm from the axis of rotation. As the particle undergoes sedimentation, the values of x and dx/dt go on changing continuously.

Consider that the particles are at a distance x_1 after time t_1 and at a distance x_2 after time t_2, then on integration of equation (9) within proper limits, we get

$$\log \frac{x_2}{x_1} = \frac{2\omega^2 r^2 (d - d')}{9\eta}\, (t_2 - t_1)$$

or

$$\frac{\log x_2/x_1}{\omega^2 (t_2 - t_1)} = \frac{2r^2(d - d')}{9\eta} \qquad \ldots (10)$$

The quantity $\frac{\log x_2/x_1}{\omega^2 (t_2 - t_1)}$ is known as sedimentation coefficient, S.

So,

$$\frac{\log x_2/x_1}{\omega^2 (t_2 - t_1)} = S = \frac{2r^2 (d - d')}{9\eta}$$

Knowing S*, we can easily calculate r, radius of the particle.

Assuming the particles to be spherical, the molecular weight, M is given by the relation

---

* If the value of S for successive time intervals is constant, then the system is **monodisperse**, *i.e.*, it contains particles of uniform size. If the boundaries are distinct, the system will be **polydisperse**, *i.e.*, it contains particls of different sizes.

$$m = \frac{4}{3}\pi r^3 Nd.$$

The sedimentation method gives us the weight average molecular weight, $\overline{M}_\omega$. The value of M can be calculated by either of the following two methods.

(i) Optical method. A beam of light is passed through the cell containing the colloidal system and allowed to fall on a photographic plate. This is done after various intervals of time (t) without stopping the centrifuge and the position (x) of the upper boundary of the particles is noted. If the absorption of light is assumed to be proportional to the concentration of the particles, then the ratio c_2/c_1 can be very easily determined at two depths x_1 and x_2 photometrically from the blackening of the photographic plate. Then substituting the value of c_2/c_1 at two depths x_1 and x_2, the value of M can be evaluated as given above.

(ii) Graphical method. A quantity proportional to log c derived from the intensity of the photographic plate at various points, is plotted against x^2, then the slope of the straight line so obtained will give the value of $M\,\omega^2\,(d - d')/2RTD_1$. Thus, M can be easily evaluated. But if two or more lines are obtained, then the molecular weight of substance can be calculated from the various slopes, each straight line corresponding to one set of particles.

By the second method, it is seen that most of the protein solutions are monodisperse and value of M varies from 18,000 to 60,00,000. Experiments with purified egg albumin point to a molecular weight 34,400. Gelatin is a polydisperse protein system, the molecular weight varying from 10,000 to 70,000. The monodisperse proteins are egg albumin, haemoglobin etc.

It may be pointed out that the sedimentation method gives weight average molecular weight, $\overline{M}_\omega$.

6·18. SURFACTANTS

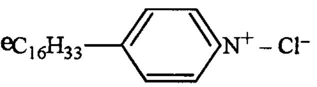
Surfactants are those substances which get preferentially adsorbed at the air-water, oil-water and solid-water interfaces forming an oriented monolayer, wherein the hydrophilic groups point towards the aqueous phase while the hydrocarbon chains point towards the air or towards the oil phase. In other words, substances that drastically lower the surface tension of water even at low concentrations are called **surface active compounds** or **surfactants.** Surfactants can be of the following types :

[I] Anionic Surfactants

Sodium salts of higher fatty acids such as sodium palmitate $C_{15}H_{31}COONa$, sodium oleate, $C_{17}H_{33}COONa$, sodium stearate, $C_{17}H_{35}COONa$ are anionic surfactants. The salts of sulphonic acids of high molar mass and general formula $C_nH_{2n+1}SO_3$ M (alkyl sulphonates) or $C_nH_{2n+1}C_6H_4SO_3M$ (alkyl aryl sulphonates) where M is univalent cation of sodium, potassium or ammonium are also anionic surfactants. Sodium dodecyl sulphate (SDS), $CH_3(CH_2)_{11}OSO_3^- Na^+$ is an example of anionic surfactant.

[II] Cationic Surfactants

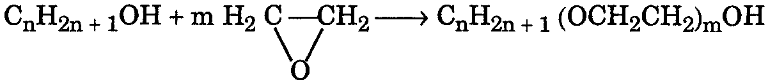
Cationic surfactants are those which dissociate in water to give positively charged ions, *e.g.*, octadecyl ammonium chloride, $C_{18}H_{37}\ NH_3^+\ Cl^-$, cetyl pyridinium

chloride  , cetyl trimethyl ammonium chloride

$C_{16}H_{33}\ (CH_3)_3\ N^+\ Cl^-$ etc.

[III] Non-ionogenic Surfactants

Non-ionogenic surfactants are those whose molecules cannot undergo dissociation. When an alcohol having a high molar mass reacts with several molecules of ethylene oxide, a non-ionogenic surfactant is formed.



$$C_nH_{2n+1}OH + m\ H_2\underset{\diagdown\ O\ \diagup}{C - CH_2} \longrightarrow C_nH_{2n+1}\ (OCH_2CH_2)_mOH$$

Schematically, such a surfactant can be represented as,

At concentrations c below about 10^{-3} mol dm^{-3} most ionic surfactants in aqueous solutions, display conductance properties similar to other strong electrolytes, a slow decrease in molar conductance Λ with $\sqrt{c}$. The surface tension γ declines steeply with c in this range. Between 10^{-3} and 10^{-1} mol dm^{-3}, however, sharp breaks occur in the Λ and γ curves vs. c. An example of this behaviour is shown in fig. (20). The concentration at which the break occurs is called ***critical micelle concentration*** (cmc). At this concentration, individual surfactant molecules aggregate to form **micelles** containing well defined number of molecules. Usually, 50 to 100 molecules take part in a micelle.

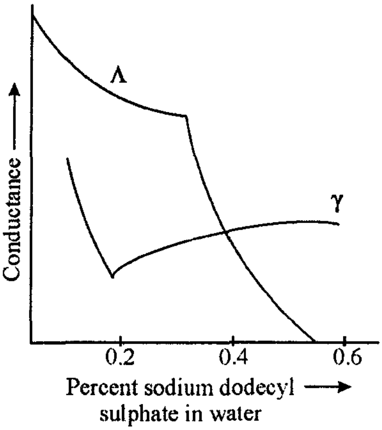


Fig. 20. The critical micelle concentration can be detected by breacks in the Λ vs c and γ vs c curves.

6·19. EMULSIONS

[I] Definition

Emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are immiscible liquids, *e.g.*, milk is an emulsion, in which particles of liquid fat are distributed in water. An emulsion according to Hotschek (1916) is a two phase liquid system consisting of *"fairly coarse dispersions of one liquid in another with which it is not miscible"*. Holmes (1934) states that emulsions are dispersion of minute drops of one liquid in another. The particles in an emulsion are comparatively larger than in sols, whereby they can be made visible even with a microscope.

Emulsions and emulsoids. Both these terms are used in colloid chemistry. They are two different things. An emulsion consists of a liquid-liquid suspension or suspension of minute drops of one liquid into another. This type of emulsion is in reality a **suspensoid.** An **emulsoid,** on the other hand, is considered to be solvated colloid like agar-agar, soaps etc. and it is characterised by a relatively high viscosity.

[II] Types of Emulsions

There are two kinds of emulsions :

(i) Water in oil type. Type in which water is the dispersed phase and its particles are distributed in oil which acts as dispersion medium, *e.g.*, butter etc. It is designated by W/O or w-in-o.

(ii) Oil in water type. Type in which oil particles (dispersed phase) are distributed in water (dispersion medium), *e.g.*, milk, vanishing creams etc. It is designated by O/W or o-in-w.

[III] Tests for Types of Emulsions

The two types of emulsions can be experimentally identified in a number of ways, which are as follows :

(i) When an oil-water mixture is vigorously shaken in the presence of an emulsifier, there are formed simultaneously oil droplets in water and water droplets in oil. Both types of droplets tend to coalesce. The type of the resulting emulsion will largely depend on two factors, *viz*, nature of emulsifier and relative rate of coalescence of the two types of droplets.

(a) Nature of the emulsifier. Hydrophilic emulsifiers dissolve better in water than in oil, so these emulsifiers promote the formation of an O/W emulsion. Hydrophobic emulsifiers dissolve better in oils than in water, so these emulsifiers promote the formation of a W/O emulsion. This is known as **Bancroft's rule.**

Griffin devised a numerical scale, known as hydrophilic-lipophilic balance (HLB) to mention the effectiveness of a particular surfactant to give a definite type of emulsion. This scale extends from 0 to 30 and a portion of it is shown in fig. (21). If the HLB number of a surfactant is in the range of 3-6, a W /O emulsion is formed and if it is in the range of 8-13, an O/W emulsion is formed.

(b) Relative rates of coalescence of droplets. The rate r_1 at which the oil droplets coalesce when dispersed in water, is given by the Arrhenius type equation, *viz.*

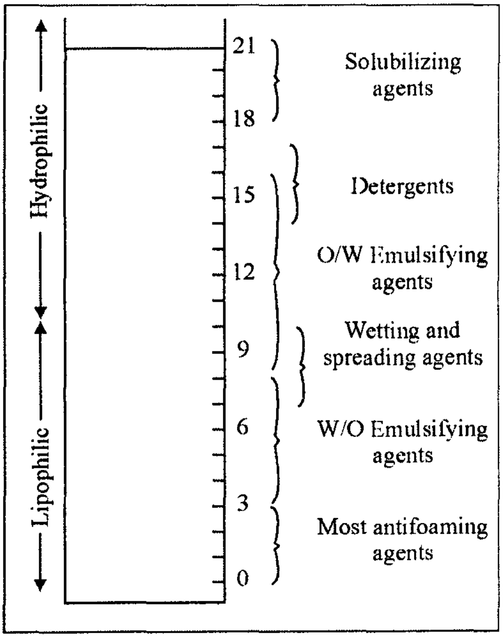


Fig. 21. The HLB scale.

$$r_1 = A_1 \exp(-E_1/RT)$$

where A_1 is collision factor which is a function of oil-water volume ratio (phase volume ratio is the relative volumes of oil and water in the emulsion, a stable emulsion has 50 : 50 oil to water ratio) divided by the viscosity of the water phase and E_1 is the energy barrier that has to be overcome before coalescence can occur. This energy barrier is composed of factors like electric potential of the oil droplets and the fraction of the surface covered by the emulsifier etc. Similarly, the rate r_2 at which the water droplets dispersed in oil coalesce is given by,

$$r_2 = A_2 \exp(-E_2/RT)$$

where A_2 is the collision factor which is a function of water-oil phase volume ratio divided by the viscosity of the oil phase and E_2 is the energy factor similar to E_1. An emulsion would be of O/W or W/O type would, however, depend on the relative magnitudes of r_1 and r_2. If $r_1 > r_2$, an W/O emulsion is formed and if $r_2 > r_1$ an O/W emulsion is formed.

(ii) Indicator method. It is due to Brailsford and Robertson and consists in adding an oil-soluble dye such as Sudan III or Fuchsin, to the emulsion. If it becomes deeply coloured, the emulsion is of the W/O type. If it remains colourless, the emulsion is of the O/W type, because the dyestuff is soluble in water and it is unable to reach the dispersed phase (oil).

(iii) Dilution method. This method is due to Briggs. A small quantity (1–2 drops) of the emulsion to be tested is placed on a microscope slide. A drop of water is added, which will result in uniform mixing when stirred, showing the presence of O/W type. If the two do not mix uniformly, it is of W/O type. But if a drop of oil is added to the emulsion, it will mix readily with the W/O type emulsion. If the two do not coalesce, the emulsion is of O/W type.

(iv) Conductivity method. This method is due to Clayton and consists in testing the conductivity of the solution by using either direct current or alternating current. If the conductivity of the emulsion is large, the emulsion is of O/W type, as these emulsions are more conducting. But if the conductivity is low, it is of W/O type, as they are less conducting.

(v) Fluorescence method. This method can be applied to those emulsions which fluoresce in ultra-violet light. A drop of emulsion to be tested is placed over a fluorescent light microscope. If the whole field fluoresces then the emulsion is of W/O type, *i.e.*, oil is the dispersion medium.

(vi) Filter paper method. This method is based on the fact that one component of the emulsion spreads over the filter paper. A drop of emulsion is kept on a piece of filter paper. If the liquid spreads easily and readily, leaving a spot at the centre, then the emulsion is of O/W type. In case the emulsion does not spread, the emulsion is of W/O type.

[IV] Preparation of Emulsions

Emulsions can be prepared by shaking or stirring the two phases with the addition of a suitable emulsifier. The types of emulsion formed, depend on the angles of contact of the two liquids with the solid emulsifier, the liquid with the smaller contact angle becomes the dispersed phase.

The liquid to be dispersed is added in small quantities to the dispersion medium, where it is spread into a thin, unstable film which spontaneously break up into droplets under the influence of surface tension. Many emulsifying machines are used, such as homogenizers used in reducing the size of globules or colloid mills due to Plauson, Day, Travis.

Stable emulsions containing about 0·1% of O/W can be made by pouring a solution of the oil in alcohol or acetone into an excess of water. Emulsion can also be prepared by using ultrasonic waves as done by Bondy and Sollner (1934–37). These waves of frequency 1,00,000 to 5,00,000 cycles per second are produced by piezo-electric quartz plate placed between two electrodes connected with a high frequency oscillator. The quartz plate and electrodes are dipped in an oil bath which also contains the vessel with the mixture to be emulsified.

A condensation method developed by Sumner is used to prepare concentrated O/W emulsions. It consists in allowing vapours of oil to pass through aqueous solution containing an emulsifying agent.

A very interesting type of emulsion known as **'chromatic emulsion'** has been presented by Holmes and Camerson by shaking equal volumes of glycerol and a 2–3% solution of dry cellulose nitrate in amyl acetate. Upon adding some CS_2 and more glycerol and shaking vigorously until the opaque emulsion becomes transparent, colours appeared which could be developed through the chromatic scale by the addition of more CS_2 and shaking. On adding amyl acetate and shaking, the colours in reverse orders are obtained.

[V] Structure of Particles in Emulsions

Langmuir (1926) said that a stable emulsion is a three component system consisting of two immiscible liquids as well as an emulsifying agent. If an oil is emulsified in water by means of soap then the lyophilic part of the sol has a greater affinity for oil. The polar head will be oriented towards the water phase. Therefore, soap molecules will be packed on the surface of the dispersed oil droplets. The hydrocarbon chain will be immersed in oil droplet while thread will be turned into water.

[VI] Properties of Emulsions

Emulsions are usually turbid, opaque, transluscent or opalescent. If the refractive indices of both the phases are nearly the same, the emulsion is nearly transparent. Many emulsions which are commercially prepared are coloured by the addition of dyes.

Since an emulsion is a colloidal system of liquid dispersed in liquid, its properties are common to that of colloidal solution. However, we will discuss the following properties.

(a) Concentration and size of the particle. In an emulsion, the amount of solid substance dissolved is very small as compared to that of the dispersion medium. In most of the emulsions, the concentration varies from 1 to 2%, but in some cases like cream, 10 to 20% fat is dispersed in water. It has been shown that if the droplets are supposed to be spheres of equal sizes then the amount of one liquid which can be dispersed in the other is 75%, but some more concentrated emulsions are also known, *e.g.*, creams used in cosmetics are jelly type systems etc.

An emulsion contains droplets of diameter 0·001–0·05 mm. Therefore, an emulsion may be regarded as coarsely dispersed system. Fat droplets can be seen in an ordinary microscope. It has been recently observed that by making use of emulsulator such as homogenizer, we can prepare stable emulsions in which the droplets are of 0·0001 mm diameter.

(b) Viscosity. Viscosity measurements of emulsions help us in elucidating the structure of emulsions. Sherman (1956) suggested that the viscosity of an emulsion is affected by the following factors :

(i) Viscosity of dispersed phase. Lieghton (1936) gave an expression connecting the viscosity (η_0) of the dispersion medium, viscosity (η_i) of the dispersed phase and the total viscosity (η) of the emulsion, which is given by :

$$\eta = \eta_0 \left[1 + 2{\cdot}5\,\phi \left(\frac{\eta_i + 0{\cdot}4\,\eta_0}{\eta_i + \eta_0} \right) \right]$$

where ϕ is the relative volume concentration of the colloidal particles.

(ii) Viscosity of dispersion medium. The viscosity (η) of the emulsion and the viscosity (η_0) of the dispersion medium is related according to the relation, $\eta = \eta_0\, x$ where x is constant depending upon other properties affecting the viscosity.

(iii) Concentration of the dispersed phase. According to Einstein and Hatschek (1910) the viscosity of an emulsion is markedly affected by the concentration of the dispersed phase.

(iv) Protecting layer and emulsifier. Several workers found that the viscosity of an emulsion is largely dependent on the nature of the protective layer surrounding the particles and also on the nature of the emulsifier.

(v) Distribution of particles. Roscoe (1951–52) gave a relation between the viscosity (η) of the emulsion and the viscosity (η_0) of the dispersion medium in terms of concentration of the dispersed phase. Accordingly,

$$\eta = \eta_0 \,/\, (1 - \phi)^{2{\cdot}5}$$

For sharply distributed emulsions, the equation reduces to :

$$\eta = \eta_0 \,/\, (1 - 2{\cdot}5\phi)^{2{\cdot}5}$$

(c) Electrical conductivity. It has been found that emulsions of O/W type are characterised by higher electrical conductivity, while emulsions of W/O type have a lower or no electrical conductivity. Lifshits and Teodorvich showed that the electrical conductivity of an emulsion increases with an increase of temperature, *e.g.*, in the case of emulsion of 50% petroleum in water, the conductivity increases to two to three folds for an increase of temperature from 30 to 90°C.

(d) Electrophoresis. Like colloidal particles, the droplets of emulsion are also electrically charged. Hence, they migrate towards the oppositely charged electrode under the influence of electric current.

(e) Dilution. On increasing the amount of dispersion medium, a separate layer is formed.

(f) Brownian motion. Just like colloidal particles, dropletes of emulsion are also in a state of constant rapid zig-zag motion.

(g) Optical properties. Droplets of emulsion scatter light to different extent, depending upon their size. However, Langlois (1953) gave the following expression in which the interfacial area and light transmission relative to clear light are inter-connected.

$$I_0/I = 1 + \beta A$$

where I is the intensity of light scattered in the case of studied emulsion, I_0 is the intensity of light scattered in a clear liquid constituting the dispersion medium, β is a constant and is equal to the ratio of the refractive indices of the dispersed phase and the dispersion medium and A is the interfacial area.

In case of certain emulsions, Tyndall effect is very weak. It may be due to fibrous particles mostly those of organic molecular colloids which scatter light to a very small extent.

(h) Electro-viscous effect. Smoluchowski (1903) observed this effect and showed that lyophobic particles bearing an electric charge would show a viscosity exceeding that of similar systems of uncharged particles. He gave the following equation,

$$\frac{\eta - \eta_0}{\eta_0} = 2{\cdot}5\,\phi\left[1 + \frac{1}{\eta_0\,\kappa\,r^2}\left(\frac{D\,\zeta^2}{2\pi}\right)\right]$$

where κ is the specific conductivity of the suspension, ζ is the zeta potential, D is the dielectric constant of the dispersion medium and r is the radius of the particle.

[VII] Reversal of Phase

The change of an emulsion of O/W type to W/O type or vice versa is known as *'reversal of phase'*. An O/W emulsion, *e.g.*, olive oil in water, containing a sodium or potassium soap as emulsifying agent, may be converted into W/O type by the addition of salts of bivalent or trivalent cations. Bancroft showed that ordinary soaps stabilize O/W type, whereas calcium and other heavy metal soaps stabilize W/O type. Clowes showed that the emulsion can be reversed by adding excess of one or other of these emulsifiers.

Mechanism of reversal of phase. The mechanism of reversal of phase is not yet clear, but Rehbinder, Goldenbery and Abe explained the mechanism. The following two factors are said to be responsible for the phenomenon in several cases.

(a) Temperature : Wellmann and Tarter suggested that the reversal of phase is due to temperature. They showed that an emulsion of water in benzene stabilized by sodium soap may be reversed by increasing the temperatue as well as on shaking. On cooling, the system reverts to its original type.

(b) Neutralisation of charges : Schulmann and Cockbain (1932) suggesed that certain emulsions, *e.g.*, oil in water type emulsions stabilized by sodium acetyl sulphate are stable due to the ionisation of emulsifier. If to this emulsion any cation such as barium or calcium is added, the system is reversed. Hence, it can be concluded that the neutralisation of charge is also responsible for the reversal of phase of an emulsion.

[VIII] Emulsifiers or Emulsifying Agents

The two types of emulsions W/O or O/W type, do not remain stable and after sometime, the two layers separate. It means that an emulsion formed by merely shaking the two liquids is unstable. But in order to get stable emulsions, it is necessary to add a third substance known as *emulsifier or emulsifying agent* in suitable quantity. By adding emulsifier, therefore, a stable emulsion of high concentration can be obtained.

It has been suggested that the emulsifier concentrates at the oil-water interface and forms a film which is sufficiently tough. This film prevents other droplets to come closer and thus prevents the separation into two layers. The function of an emulsifier is to lower the interfacial tension between the dispersed phase and the dispersion medium. Thus, in milk, casein (a protein) is known to form a strong protective multimolecular layer round the droplets of fat dispersed in water. Thus, milk is a fairly stable emulsion. The emulsifying action of non-ionogenic surfactants unlike that of ionic surfactants is not based on their ability to lower the interfacial tension between the two phases.

It must be kept in mind that an emulsitier must be soluble in both the liquid phases but only to a certain limited extent. If it is highly soluble in any one phase, it will not be adsorbed at the interface, and instead will enter the bulk of that phase. An emulsifier may also get adsorbed at the interface in the form of layer of solid particles which stabilise the emulsion. So, bentonite clay acts as an emulsifier for an oil-water emulsion. The solid particles which act as an emulsifier must be wetted by both the phases. The phase which preferentially wets the particles becomes the continuous phase. An emulsion can also be stabilised by a solid emulsifying agent only if the solid particles are smaller than the emulsion droplets. At the same time, particles that are very small and undergo strong Brownian motion do not form a protective layer. There are several types of emulsifiers, which can be classified as follows :

(i) Long chain compounds with polar groups such as soaps of various kinds, sulphonic acids and alkyl sulphates act as emulsifiers. Their function is to *lower the interfacial tension between water and oil*, so as to facilitate the mixing of the two liquids. In compounds like soap, the aliphatic portion is soluble in oil, while the end group (sulphonic acid etc.) called a polar group (because its unsymmetrical grouping contributes a dipole moment to the compound) is soluble in water. The soap molecules get concentrated at the interface between water and oil in such a way that their polar end (—COONa) and hydrocarbon chain (R^-) dip in water and oil, respectively as shown in figure (22). This allows the two liquids to come in close contact with each other.

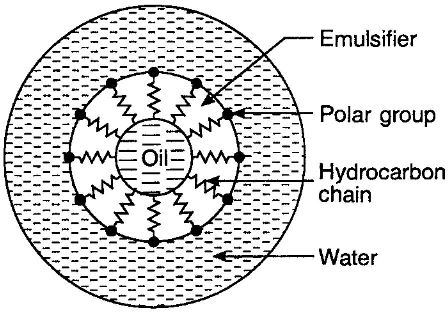


Fig. 22.

(ii) Most of the *lyophilic colloids* also act as emulsifiers such as glue, casein, starch, protein, gum arabic, dextrin, resins etc. These stabilizers form a protective layer round the globules of the dispersed phase.

(iii) Pickering showed that *certain insoluble powders* such as basic salts, clay, lime, $CaCO_3$, lamp black, gelatinous aluminium hydroxide also act as emulsifiers.

(iv) Soluble substances like iodine also act as emulsifiers, in the case of ether / water emulsion.

(*v*) Some *mixed stabilising agents* also act as emulsifiers, *e.g.*, ethyl alcohol and lycopodium powder, acetic acid and lamp black, clay and sodium oleate etc.

[IX] Theories of Emulsification

Various theories have been proposed for the phenomenon of emulsification. These are as follows :

(i) Quincke-Donnan theory or surface tension theory of emulsions. Quincke and Donnan (1888–89) suggested the formation of emulsions, due to the fact that emulsifiers lower the interfacial tension between the dispersed and continuous phase and then they concentrate at the interface. Quincke (1888) prepared emulsion of oils in solution of NaOH and showed that the interfacial tension between the oil and the solution was lower than between oil and pure water. Donnan and Fott concluded that the sodium salts of the higher fatty acids were adsorbed at the separating boundary between the oil and the solution. This is the basis of the modern theory of emulsion.

Extension of the above idea was made by Bancroft (1927) who suggested the reasons for the formation of the two types of emulsions. He said that the emulsifying film is three molecules thick; one molecule of dispersed phase, one molecule of dispersion medium and one molecule of emulsifier. The film has two surfaces, one towards the water and the other towards the oil. If the surface tension between water and emulsifier is less than that of oil and emulsifier, then the film will tend to bend so as to become convex on the water side, thereby giving an emulsion of O/W type. But in the reverse case, the film tends to bend so as to become concave on the water side or convex on the oil side, producing a W/O type emulsion.

(ii) Oriented molecular wedge hypothesis. This theory due to Harkins (1917) is based upon the theory of the relative dimensions of the head and tail ends of the soap molecules—heavy metal soaps assumed to be having several tails.

It is assumed that soap molecules consist of long hydrocarbon chains and polar end groups. At an oil-water interface, the latter will be throughout oriented towards the water, and the hydrocarbon chain towards the oil. If the cross-section of the two parts of the stabilising soap molecules is such that the polar end is larger than the hydrocarbon chain then a stable emulsion will be formed in which the area of water side of the soap film is greater than that of the oil side, *i.e.*, water will be the dispersion medium. An O/W emulsion will thus be stabilised with alkali salts of fatty acids. But if the hydrocarbon chain had a larger cross-section than the polar group, then W/O type emulsion will be stabilised. In univalent metal soap, one hydrocarbon chain is attached to each metal ion, but in multivalent metal soap there will be several chains of each cation. It is, therefore, reasonable to suggest that the hydrocarbon chains have a larger cross-section than the polyvalent cation and that this accounts for the stabilization of the W/O emulsion. This view has been experimentally supported by Hildebrand (1923) with a number of oleates and stearates.

(iii) Adsorbed film theory of emulsion. This theory was developed by Clowes who considered the system of oil and soap solutions. The soaps tend to concentrate between oil and water to form a coherent film. Soaps of monovalent cations being readily dispersed in water but not in oils form a film which is more readily wetted by water than by oil. Consequently, surface tension is lower on the water side than on oil side and the film tends to curve in such a way, so as to enclose the globules of oil in an outer phase giving an O/W type emulsion. If on the contrary, a film composed of soaps of divalent or trivalent cations, being freely dispersed in oil, but not in water is more readily wetted by oil than by water, the surface tension will become lower on the oil side than on the water side. The film thus tends to curve in such a manner, was to enclose the globules of water in an outer phase giving a W/O type emulsion.

Bhatnagar gave a generalised statement that *'all emulsifying agents which have an excess of negative ions in them and wetted by water will give* **O/W type emulsion,** *whereas all emulsifying agent, having an excess of positive ions in them and wetted by oil will give* **W/O type emulsion'.**

[X] Breaking of Emulsions

The phenomenon of breaking an emulsion into its two components is known as *'demulsification'.* Usually it has been suggested that chemical destruction of the emulsifier is a good method for carrying out demulsification, *e.g.*, the addition of an acid or bivalent cation to an emulsion, which is stabilised by soaps brings about demulsification. Sometimes, addition of ions of high valence also brings about demulsification as it reduces the zeta potential of the particles. Following are some general methods for bringing out demulsification.

(i) Mechanical method or physical method. Emulsions can be broken by heating under pressure or by distillation etc. By centrifuging, the emulsions can also be broken down. They can also be broken down by freezing. The freezing process undoubtedly destroys the globules with their protecting films just as it destroys the cells of plants and animal tissues.

(ii) Chemical method. The principle of this method is that in such cases some chemical substance is added to the emulsion which combines with the emulsifier, whereby it breaks the emulsion. If an acid is added to an emulsion stabilised by sodium oleate, then sodium oleate forms oleic acid having no emulsifying power and thus the emulsion is broken. By adding an excess of the dispersed phase, the emulsions may also be broken down. A small addition of another agent, in itself excellent emulsifier, *e.g.*, soap, suffices to break the emulsion. The addition of acids or alkalies will break a great many emulsion.

(iii) Electrical method. Demulsification is also carried out by applying a strong electrical field. The charges on the droplet account for separating emulsions by electrolysis or treating with high tension electricity as done in Cottrell process. The process has been utilised in breaking the emulsion of water/petroleum.

[XI] Uses of Emulsions

Emulsions find numerous applications in daily life, medicine, industry and cosmetics. They may be described as follows :

(i) Daily articles of life. Milk is an emulsion of fat dispersed in water stabilised by casein and as we all know is practically a complete food. Ice cream, is an emulsion, in which ice particles are dispersed in cream, stabilised by gelatin. Butter is more stable and more concentrated milk fat. When cream is agitated, fat particles coalesce and the emulsion breaks. The fat then separates in semi-solid lumps. This form which is separated from liquid by centrifugation is known as butter milk. Hence, butter may be said to be a pseudo-emulsion of W/O type. The molten butter is a true emulsion. The process of increasing the resistance of milk against creaming by mechanical treatment is known as *homogenisation.* In the process, milk is forced through fine capillaries and in dairies, this process is carried out by special types

of machines. Artificial beverages, coffee, fruit jellies are all emulsions in nature. The cleansing action of ordinary soap is due to a large extent on the production of O/W emulsion.

A number of medicines and pharmaceutical preparations are emulsions in nature. It is assumed that in this form, they are more effective. Cod-liver oil, castor oil, petroleum oil are used as medicines which are all emulsions. Asphalt emulsified in water is used for building roads, without the necessity of melting the asphalt. An important process in mining operations for concentrating the valuable part of ores, is the ore flotation. In this process, oil emulsions are added to finely divided ore and foamed in such a way that the particles of ore are carried to the surface, where they are collected. Most of the cosmetics used are emulsions, as they permit uniform spreading and promoting the penetration into the skin. Vanishing cream is an O/W type emulsion. Hair creams, cold creams are W/O type emulsions.

A variety of emulsions of oils and fats are used in leather industry to make leather soft and pliable and also to make it waterproof. About a quarter of the crude oil produced in America is pumped from the ground in the form of W/O type emulsion. These oils contain 60–70% water which can, however, be removed by further processing *e.g.*, heating, filtration, electrical heating, addition of chemicals etc. Emulsions are also used in oil and fat industry, paints and varnishes, plastic industry, adhesives, cellulose and paper industry etc.

6·20. GELS

[I] Definition

Graham applied the term gel to any coagulum from a sol, whereas according to Ostwald, a gel is a colloidal semi-solid system rich in liquid phase. The degree of sub-division of the dispersed phase varies, but in most of the cases it is within the colloidal range. The modern tendency is to consider a true gel as a solidified sol with a high degree of reversibility between the two states. According to Gortner, gel may be defined as *more* or *less rigid colloid system*. When a sol, say of gelatin, agar-agar etc. is cooled, the whole mass sets to a homogeneous semi-solid gel and the phenomenon is known as *gelation*. Gelation may be brought about by either of the methods, *(a) cooling the sol (b) evaporating the sol and (c) addition of electrolytes.*

Jelly. It is commonly known as a gel. McBain showed that there is a slight difference between a gel and a jelly. According to him, a gel is a colloidal system covering both liquids rich and rather dry systems, but a jelly is an elastic coherent dispersed system very rich in liquid phase. However, we can ascribe the same meaning to both the terms. Jellies contain 97% or even more liquid. Gelatin jellies contain 95-99% water and only 5–10% gelatin. Some jellies, like fibrin clots may contain even 99.99% water.

Xerogel. This term is used to denote a dry gel, *e.g.*, a foil of cellophane, a sheet of gelatin etc. It has been seen that xerogels contain less liquid than solid.

[II] Classification of Gels

(i) On the basis of dispersion medium. Gels produced as a result of coagulation are known as *coagels*. When the dispersion medium in the gel is either water, alcohol or benzene, then the gel formed is known as *hydrogel, alcogel or benzogel,* respectively. Gels appear to be solid, even if they contain 99% of the dispersion

medium. They may be cut, bent or broken as desired. If gels are subjected to prolonged pressure they begin to flow, assuming the shape of the containing vessel.

(ii) On the basis of chemical composition. Gels are called inorganic and organic according to their chemical composition, *e.g.*, gels containing inorganic solvents are known as inorganic gels and similarly organic gels are those gels in which organic solvents are used.

(iii) On the basis of size of particles. Gels may be colloidal or coarse depending upon whether the size of particles is small or comparatively bigger. Common jellies, agar-agar solution are colloidal gels.

(iv) Thixotropic gels. Gel which when shaken forms a sol and when kept standing re-converts into a gel is known as thixotropic gel. In such type of gels, the frame work is so weak that it is broken on standing. This phenomenon is also known as ***thixotropy***.

(v) On the basis of mechanical properties. Such gels are classified on the basis of their mechanical properties. Hence, there may be classified as elastic gels, non-elastic gels, rigid gels etc.

(a) Heat reversible type gel or elastic gel. Gel of this type is made by dissolving the substance such as gelatin, agar-agar in warm water and cooling it, till it sets. Similarly, a gel of cellulose acetate in benzyl alcohol can be prepared.

Usually, setting occurs on cooling, the greater the undercooling the slower the rate of setting, as the rate of setting has a high temperature coefficient with a positive value. Hattiangdi (1948) showed that the rate of setting of a gel is represented by an empirical equation,

$$t = ace^{-E/RT}$$

where t is the setting time, c is the concentration, E is the activation energy and a is a constant.

(b) Irreversible type gel or non-elastic gel. Sols of silicic acid or alumina set in an irreversible manner when cooled. The rigidity of the gel increases with time. The volume of a freshly prepared silicic acid gel decreases upon drying, but the decrease attains a particular limit. Beyond this limit, air takes the place of the liquid in the cavities of the gel. This volume is retained unaltered, till the gel is completely dry. The volume of the gel remains unaltered, if it again takes up liquid.

Table-7. Differences in the properties of elastic and non-elastic gels

	Property	**Elastic gels**	**Non-elastic gels**
1.	Nature	Elastic	Non-elastic or rigid.
2.	Dehydration-rehydration behaviour	Reversible, *i.e.*, dehydrated gel can be brought back into the original form by heating with water	Irreversible, *i.e.*, dehydrated gel cannot be converted into the original form by heating with water.
3.	Imbibition	When placed in water, they absorb water and swell. This phenomenon is called imbibition.	When placed in water they do not absorb water and so do not show the phenomenon of imbibition.
4.	Thixotropy	These show thixotropy, *i.e.*, undergo strinkage in volume when allowed to stand.	These also show thixotropy, *i.e.*, undergo shrinkage in volume when allowed to stand.

[III] Preparation of Gels

Gels may be easily prepared by any of the following methods.

(i) By cooling of colloidal solutions. Certain substances form gels when their hot solutions are cooled, *e.g.*, gelatin, agar-agar etc. The setting or gelation of such a solution is characteristic of :

(a) temperature of gelation, (b) time of gelation, (c) viscosity of the medium, (d) minimum concentration of the substance at which the gelation may occur.

It has been found that substances like sulphates, tartarates, acetates, citrates promote the rate of gelation, whereas certain substances like chlorides, nitrates etc. retard the rate of gelation. The gelation of proteins is retarded by acids and alkalies.

(ii) By double decomposition. The gels of some sols are prepared by the process of double decomposition. On adding water to sodium silicate we get a gel of silicic acid. During the reaction, silicic acid is prepared in the free state which rapidly sets to a gel.

(iii) By exchange of solvents. Sometimes, gelation may occur due to the exchange of solvent in which the sol is insoluble. When pure alcohol is added to the aqueous solution of calcium acetate, the whole of the salt goes into alcohol, which then sets into a gel containing the liquid.

(iv) By chemical reactions. Gels can be prepared by this method between concentrated solutions, if one product of the reaction is insoluble and if the particles have a tendency to form linear aggregates. On shaking concentrated solutions of barium thiocyanate and manganous sulphate, we get a gel of barium sulphate. Gel of aluminium hydroxide can be prepared by mixing concentrated solutions of aluminium salt and ammonium hydroxide.

(v) By coagulation or by decrease of solubility. Many gels can be prepared by the coagulation of colloidal solutions. The important properties playing an important role during this transformation are shape of the particles, concentration of the sol and degree of solvation. Sols of aluminium hydroxide or ferric hydroxide can be converted into gels when some coagulating agents are added to the colloidal solutions and provided the concentration of the sol is sufficiently high. Gelation does not necessarily take place upon coagulation or precipitation of any linear colloid, *e.g.*, if the coagulation of agar-agar is carried out with alcohol, the colloidal substance is precipitated without immobilising much of the solvent.

[IV] Conditions Affecting the Formation of Gels

The most important factors that affect gel formation are :

(a) The character of the solid used. It is probably noticed that generally a hydrophilic colloid has been used in gel formation. Although sols of hydrophobic substances have been converted into gel systems by the addition of electrolytes, even then the substance does not strictly come within our definition of a true gel.

(b) Concentration. If the concentration is too low, the fibril structure will not be continuous. With a still higher concentration, a thin jelly results and the rigidity then continues as the concentration is increased.

(c) Temperature. The temperature effect is also an important factor, because when a gel does not set, it is cooled to produce the desired result. But if the solution is too thin, cooling will not be of great assistance. Increase in temperature also increases the rate of gelation.

(d) Velocity of precipitation. It has been shown that the formation of a gelatinous precipitate is possible where the rate of precipitation is relatively high.

(e) Mechanical agitation. It is generally recognised that agitation prevents the setting of a gel, and that if it is applied after gelation, the characteristic structure will be broken and the fluidity of the mass will be increased. Some of the more unstable gels cannot be prepared unless the sol is kept at a constant temperature and may free from agitation.

(f) Presence of salts. Salts either retard or accelerate the formation of gels according to the ions present in solution and according to which of these is selectively adsorbed. The anion series for gelatin gel formation is :

$$SO_4^{2-} > \text{citrate} > \text{acetate} > Cl^- > Br^- > NO_3^- > I^-$$

The bromide, nitrate and iodide actually retard gelation. The effect of adsorbed cations as prepared by Homer is :

$$NH_4^+, K^+ > Na^+ > Li^+ > Ba^+, Sr^+, Ca^+, Mg^+$$

(g) Presence of non-electrolytes. When non-electrolytes are added to systems for gelation, there may be no effect or the process may even be accelerated or retarded. Sometimes, the addition of a third substance to the system produces very great changes.

(h) Hydrogen ion concentration. Gelation is also influenced by H^+ ions. Ostwald found that with 3% gelatin sols, only very small concentration of acid or base could be used without greatly retarding gelation. With acid or alkali concentrations of 0.05 M, the retarding effect was serious.

Loeb explained the variation of gelation with changes in pH by assuming that viscosity is affected by both ions of an acid and that whereas the H^+ ion increases the viscosity, the anion has the opposite effect.

[V] Properties of Gels

(i) Swelling of gels. Hydrophilic gels or elastic gels when placed in water absorb a definite amount of the liquid, whereby the volume increases. The process is known as ***swelling*** or ***imbibition.*** Gels differ widely in their power of imbibition from a larger amount in those that are very elastic like gelatin to a small amount in rigid type like silica gel. During an increase in volume of the gel, a considerable pressure is set up and a counter pressure known as ***'swelling pressure'*** may be applied which just prevents the increase in volume. It must be noted that although the volume of the gel increases during swelling, the total volume of the system, (gel + liquid) decreases.

Swelling is minimum at the isoelectric point, and addition of either H^+ or OH^- ions favours swelling, as shown in the case of gelatin gel by Chiari (1911). Electrolytes have also a dependence on swelling, with a maximum in the case of $NaNO_3$ or NH_4NO_3 and a maximum and then minimum with KCl. The influence of non-electrolyte on swelling must also be taken into consideration as shown by Hofmeister. Swelling is also facilitated by the increase in temperature.

(ii) Optical properties. Gels show the phenomenon of double refraction. It may be present in the gel from the start or it may be produced by pressure or tension, *e.g.*, a dry gel of gum shows double refraction like that of the glass under tension and compression. But if a swollen gel is investigated, then a quick pressure at first produces a double refraction as with a dry gel but this gradually passes into double refraction of the reverse sign, which is also immediately observed if the pressure is gradually applied. Gelatin gels in their natural state rotate the plane of polarised light.

(iii) Electrical properties. It has been seen that the electrical conductivity does not change during the transition from the sol to the gel state, as verified by Kistler (1931).

(iv) Syneresis. Syneresis is a phenomenon of the *exclusion of the liquid constituent of gels on standing, whereby the gel contracts or shrinks* [Fig. (23)]. This may be regarded as reverse of swelling. Gelatin and agar-agar show syneresis at low concentration while silicic acid shows it at high concentration. Ferguson and Applebey (1930) showed that the volume of liquid exuded during syneresis is independent of the shape and free external surface of the gel. The velocity of syneresis and the total volume of liquid exuded, increases with an increase in the concentration of the gel. Syneresis is of biological importance in the study of secretion by glands.

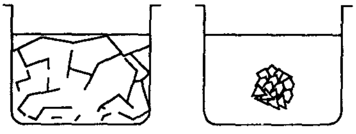


Fig. 23. Syneresis.

(v) Elastic properties. In elastic properties, gels resemble solids. It is found that if a cylinder or a strip of gel is stretched by means of a weight W suspended from it and if dl be the elongation, then the Young's modulus (Y)—the ratio between load and relative elongation in the case of longitudinal elongation—is given by,

$$Y = \frac{W}{\pi r^2} \cdot \frac{l}{dl}$$

where l is the length of the cylinder of radius r. Young's modulus depends upon the degree of swelling.

Poisson's ratio of gels—ratio of the relative lateral contraction of the relative change of length when the extension is in one direction—very largely resembles a liquid. The compressibility, flexibility, tensile strength of gels have all been studied. Rigidity is defined as the ratio of shearing stress to strain or is equal to the ratio of force per unit area to the angular deformation. It has been observed that the rigidity of jellies increases with concentration and decreases with increasing temperature. In case of gelatin jelly, the rigidity increases with square of concentration and also with the average molecular weight of the gelatin sample. Gels of low rigidity are often unstable and may be thixotropic, *i.e.*, they can be liquified on shaking and re-set on standing.

[VI] Diffusion in Gels

The soluble electrolytes and other substances diffuse into the gels, which are immersed in their solutions. Graham (1862) concluded experimentally that a solute such as NaCl diffuses into a gel of gelatin and the rate of diffusion is practically the same as that in water. Bechhold and Zeigler (1906) showed that it is only practicable in dilute gels, but in concentrated gels the rate of diffusion is comparatively low.

The difference in the diffusion of crystalloids and colloids in gel can be shown by allowing the gels of gelatin to set in half the test tube. A coloured solution is then poured into the upper part of the tube. It has been seen that while solutions of $CuSO_4$, $KMnO_4$ diffused into the gel after a certain interval of time the sols did not penetrate into the gel. This may in fact be used as a test in deciding whether a given solution is a sol or a true solution. The course of diffusion of a soluble electrolyte, *e.g.*, NaCl into a gel of gelatin can readily be followed by using a gel containing very dilute solution of $AgNO_3$ (indicator) so that white AgCl formed can confirm how far the solution has penetrated. This method was, however, subject to certain objections.

The quantitative measurement of the amount of the diffusing substance in different parts of the gels can be done by volumetric or gravimetric methods. The diffusion of a substance from an aqueous solution into a gel or from a gel into the solution follows the ***Fick's diffusion law.***

[VII] Structural Units of Gels

Gels have the following structural units :

1. Gels with unstable frame-work : These types of gel occur in ferric hydroxide, aluminium hydroxide and graphite gels. This frame-work also occurs in gels in which the structural elements are little symmetric. In such cases, the particles get joined by very weak cohesive forces or vander Waals forces of attraction. Such gels are generally thixotropic, *i.e.*, their frame-work is so weak that it gets destroyed even on shaking. The gels of linear macromolecules such as unvulcanised rubber or polystyrene belong to this group. When polystyrene is kept in a liquid, it first swells and then slowly dissolves to form a solution.

2. Gels with metastable frame-work : Metastable frame-work generally occurs in protein gels, *e.g.*, gelatin gels. These gels are characterised by the fact that they are rich in liquid elastic and get changed into liquids on heating. The structural elements are joined into a network by secondary bonds. Cohesive forces or primary valencies also exert some importance in promoting the stability of these gels. A partial orientation of the chains may occur if two or more chains are aligned into bundles and linked by hydrogen bonds or other linkages. The net work of the linear macromolecule has been shown in figure (124).

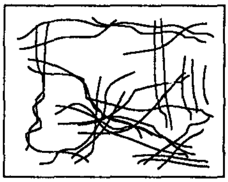


Fig. 24. Gels with metastable frame-work.

3. Gels with stable frame-work : The gels of stable frame-work are the gels of concentrated silicic acid. These gels can be obtained by adding an acid to sodium silicate solution. In the reaction, first mono-silica acid gel gets formed which then undergoes polymerisation to form space polymers. According to A.E. Alexander and P. Johnson (1949), the resulting gel is rigid and stable and cannot be changed into a liquid system. Finally, a three dimensional net work of Si-O is obtained. Vulcanised rubber is an example of cross linked xerogel. The long and twisted molecules of natural rubber do not get linked by primary valencies into a spatial frame-work but they are essentially free. Because of this reason, unvulcanised rubber swells readily and can be dissolved in a number of solvents. When heated with sulphur, the sulphur atoms react with the chains and link them together. The structure of non-vulcanised rubber is shown in figure (25).

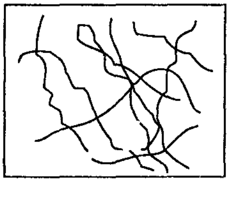


Fig. 25. Structure of non-vulcanised rubber.

[VIII] Structure of Gels

There is still a difference of opinion about the structure of gels. Various theories have, however, been proposed to explain the structure of gels.

(i) Honey-comb theory. Butschli (1897-1900) concluded as a result of investigations of gels under a microscope that many gels have fine honey-comb structure which can only be seen by using special methods. Gelatin gel after hardening with HCHO exhibited such a structure. Butschli assumed that the honey-comb walls have a thickness nearly equal to 0.2 μ–0.3 μ. This theory accounts for the rigidity of gels and the difficulty of squeezing out the water.

(ii) Martin-Fisher solvation theory. According to this theory, a gel may be regarded as a system of two components, one liquid solute and the other solid solvent. Katz studied the swelling of gels by X-ray analysis. The X-ray analysis spectrum remains unchanged during swelling. This indicates that the liquid is taken by the gel intermiscellarly and not intramolecularly, and the dimensions of crystal lattice as shown by X-ray spectra remains constant. This proves that the structure of gels is miscellar in nature.

(iii) Zsigmondy's theory. Zsigmondy and his co-workers as a result of ultra-microscopical observations with gelatin gel could not confirm the honey-comb structure and suggested that the structure of the gel is much finer than that assumed by Butschli. This view of the structure of the gel was supported by Bachmann's experiments. Therefore, according to Zsigmondy and Bachmann, gels have granular fine structure. This theory is also supported by experiments of diffusion of electrolytes into gels.

(iv) Fibrillar theory. It may also be assumed that in gelatin, the particles arrange themselves into fibres, which are then inter-twined. These threads cause the cohesion and great elasticity of gels. The experiments of Zsigmondy and Flade on gels of soap and barium malonate can be interpreted in this way.

(v) von Wiemarn's theory. According to von Wiemarn's concept, gels may be classified according to the degree of dispersion of their primary structural elements. The examination of a large number of photomicrographs of a hydrated strontium sulphate gel taken at different intervals of their formation throws light on the structure of gels. According to the above examination, it is revealed that the tissue of gel is composed of bundles of thin crystalline needles. In each bundle, the needles spread radially from the centre and the ends of the needles of different bundles are interwoven, thus producing a continuous structure.

(vi) Thomas-Sibi theory. Thomas and Sibi (1928–30) conducted experiments and suggested views close to von Wiemarn's theory. They assumed that sol on cooling forms cluster of needles which interpenetrate to give a firm mass. They further showed that units of structure may be intertwining hair instead of straight needles.

[IX] Applications of Gels

The process of gel formation is used in the following ways :

(1) Gelatin and agar-agar gels are employed in laboratories for making liquid junctions.

(2) Silica gel is used in laboratory as a dehydrating agent and in dessicator.

(3) Silica gel is employed in industry and also used as a catalyst. It also acts as a resistance to catalytic poisoning during the manufacturing from contact process.

(4) Boot polishes and animal tissues have gel structures.

(5) Solidified alcohol (a gel) is used as a fuel in picnic stoves and is made from alcohol and calcium acetate.

[X] Chemical Reactions in Gels

The study of chemical reactions in gels has become a matter of great importance. These reactions can be studied as follows :

Mix a 10% sol of gelatin or other suitable colloid with an equal volume of a dilute solution of one of the reactants. Pour it in different test tubes, so that they are 2/3rd full. Allow it to set to form a gel. Then pour a more concentrated solution of other reactant into the upper part of the tube. It is then observed that it takes several hours or even days to form a precipitate of a few cm length. The precipitate formed has four types of structures :

(i) Continuous structure. *It consists of small particles uniformly distributed, so that the whole mass appears to be homogeneous.*

(ii) Discrete structure. *It consists of particles of relatively large size separated by considerable space as in silicic acid gel.*

(iii) Cellular structure. *It consists of a network of honeycomb like cells of precipitate enclosing the gel.*

(iv) Periodic structure. *It may contain definite bands or rings of precipitate separated by space, e.g., Liesegang ring phenomenon.*

6·21. SOL-GEL TRANSFORMATION

Sol-gel transformation is a phenomenon in which a gel is formed from a sol. Fernau and Pauli showed that a freshly prepared sol of CeO_2 containing about 10 g per litre was transformed into a gel by coagulation with electrolyte. But if the sol of CeO_2 was kept for 200–300 days, then it lost its power and gave a precipitate instead of a gel, by the addition of electrolytes. But in the case of some lyophilic sols, such as gelatin in water, agar in water, the sol-gel transformation is well known and the transformation is reversible within certain limits. For example, if a gelatin sol (of not too low concentration) is prepared by heating gelatin with water upto 70°C, and it is then cooled, it is seen that the sol sets to a gel at low temperature. If the gel is again warmed, it liquefies to a sol. This process can be repeated as and when desired. It appears that an irreversible chemical reaction is continuously taking place in gelatin sol, which can be easily recognised. If a gelatin sol is kept at a high temperature at which it does not gelatinise, the viscosity decreases continuously and reaches a considerable lower end value than its original value. The sol thus formed loses the property of gelatinizing and the gelatin thus transformed is known as *β-glutin or galactose.* In other words, the sol $\rightleftharpoons$ gel transformation is actually reversible, as long as the temperature 65–70° is not exceeded.

This sol-gel transformation proceeds perfectly continuously, because there are no singular points or rapid changes in the temperature-time curve.

[I] Physical Changes Occurring in Sol-Gel Transformation

(i) Thermal. The cooling curves of solutions of substances having low molecular weight show usually pronounced breaks or arrest points when solute begins to separate. With sols the onset of gelation produces a small break, showing that the sol-gel transformation is accompanied by the liberation of heat. Similar behaviour is seen with soap sol when it is changed into gel.

(ii) Optical. Arsiz (1915) showed that there is a complete continuous change in the Tyndall cone of light during the sol-gel transformation. A gelatin sol in water containing glycerine, shows a weak Tyndall cone at 70°C. But as the sol is cooled, the Tyndall cone becomes stronger, and which becomes weaker on warming again. It alters in its intensity during the sol-gel transformation taking place at constant temperature. In other words, the Tyndall light increases and decreases with the viscosity of the solution.

(iii) Electrical conductivity. No change is observed in the electrical conductivity during the sol-gel transformation. If the sols contain electrolytes, a slight increase in conductivity is observed, which may be ascribed to secondary effects during the transformation.

(iv) Viscosity. Viscosity is the property which changes remarkably during the sol-gel transformation. The relationships are clear and well defined in the case of glycero-sols of gelatin as studied and examined by Arsiz.

A sol of gelatin is prepared by heating it below 70°C. It is then cooled from a temperature t_1 to temperature t_2 [Figure (26)]. The viscosity then follows the curve aa'. If now the sol is kept at a temperature t_2 the viscosity gradually increases corresponding to $a'b'$ and finally reaches the equilibrium state, b. If conversely, the gel at temperature t_2 is rapidly heated to t_1 the viscosity changes from b' to b. When kept at temperature t_1, the viscosity decreases from b to c, which is the equilibrium state. The critical viscosity at which this transformation has taken place is shown by dotted curve. The equilibrium values of the viscosity, lying upon the KK′ curve change entirely continuously with temperature. The changes are shown in the graph of figure (26).

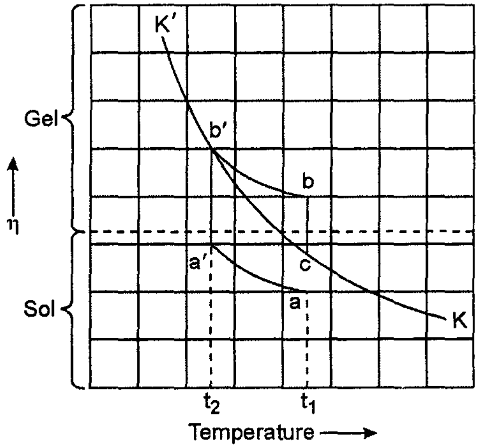


Fig. 26

(v) Diffusion. It has been found that the rate of diffusion of substances having low molecular weights is similar to the rate of diffusion of pure solvent.

(vi) Volume. During the sol-gel transformation a change in volume occurs. It was found that in some cases expansion of volume takes place, as in the case of methyl cellulose-water system, while in some cases contraction of volume takes place, *e.g.*, gelatin-water system. In the gelation of 9% sol of ferric hydroxide, no change in volume was observed. The change in volume can be ascribed to either the process of crystallisation or dissolution.

(vii) Other properties. As regards a number of other properties, sols and gels appear to be exactly alike, *e.g.*, in refractive index, vapour pressure etc.

[II] Influence of Dissolved Substances on the Sol-Gel Transformation

Dissolved substances have a marked effect on the sol-gel transformation. Paschels (1890–1900) examined the changes in the solidifying point of gelatin sols in presence of some substances. The effect of anions appears to be in the order of SO_4 > tartarate > acetate > halogens > thiocyanates. The first three groups favour gelatinization and thereby raise the solidifying point and thus shortens the time of gelatinization. The rest of the groups lower the solidifying point and thereby lengthen the time of gelatinization.

Non-electrolytes also influence the time of gelatinization. Lewites found that substances such as sugar, polyhydric alcohols etc. shorten the time of gelatinization and substances like urea, urethane, thiourea etc., lengthen the time of gelatinization.

[III] Theories of Sol-Gel Transformation

Various theories have been put forward to explain the sol-gel transformation, but the most explanatory theory is based on the reversal of phase as seen in emulsions. If we take two immiscible liquids A and B and disperse A in B, we get an emulsion. If we coagulate this emulsion by some electrolytes, then B becomes the dispersed phase and A becomes the dispersion medium. So, one of the theories is that when a sol is converted into a gel, the dispersed phase becomes the continuous medium. But this theory is untenable, because when there will be a reversal of phase, there will be short changes in physical properties, and so if sol and gel transformations were similar, there must have been a sudden variation in all the physical properties. In no case, *e.g.*, in refractive index, conductivity, viscosity etc. one could find a sharp change during the sol-gel transformation.

6·19. THIXOTROPY

[I] Introduction

When suitable quantities of electrolytes are added to a concentrated sol like $Fe(OH)_3$, Al_2O_3, V_2O_5, ZrO_2, SnO_2 etc. a pasty gel is formed which has a remarkable property of being liquefied when shaken, only to set again to gel state, on standing. So, in many cases, gels can be liquefied either by shaking or any other mechanical action, but returns to the gel state more or less rapidly as soon as the disturbing action is stopped. Peterfi (1927) suggested the name of *'thixotropy'* (change by touch) for this type of phenomenon. It is also known as *'isothermal reversible sol-gel transformation'*. Systematic observations on thixotropy were made by Szegvari and Shalek (1923), when they studied sols of Fe_2O_3 and many dilute sols of high polymers.

Goodeve and Whitfield (1837–39) studied the equilibrium between the spontaneous building of an internal structure and its breakdown. The apparent viscosity of thixotropic system was measured at different rates of shear. If η_a, η_r represent the apparent viscosity and extrapolated residual viscosity, respectively, then we have,

$$\eta_a = \eta_r + \frac{\theta}{S}$$

where θ is the coefficient of thixotropy and S is the shearing force.

If η_a and $1/S$ are plotted as ordinate and abscissa, we get curves of different types. The intercept on the Y-axis will give the value of η_r, *i.e.*, resistance of flow at extremely high shear ratio. It has been observed that thixotropy of carbon black dispersion is reduced on adding 3% linoleic acid. These curves also show the effect of thixotropy in the absence and presence of linoleic acid.

[II] Theories of Thixotropy

Several theories have been proposed to account for thixotropy which are given below :

(i) Solvation or hydration theory. According to this theory, thick envelopes called lyospheres of oriented water molecules are formed round the colloidal particles and these eventually become so large that freedom of movement is lost and the system becomes a gel. It is also regarded that lyospheres are destroyed on shaking, but partially, so that the gel is then liquefied. It is seen that finely divided inorganic substances suspended in inorganic solvents, also exhibit thixotropy. This fact goes against this theory.

(ii) Oriented coagulation theory. According to this theory, the particles of sol capable of forming a thixotropic system are believed to be *anisotropic* and *anisometric* or both, so that the electrical charge and water of hydration, if any, are unequally distributed. When the correct amount of electrolyte is added to reduce the zeta potential to a sufficient extent, the particles tend to coalesce, but owing to their shape they can form a stable gel only if correctly oriented. The extent of the surfaces of the particle in contact is probably limited, and as a consequence, any stress will tend to reduce this and destroy the gel structure. It is interesting to note in connection with this theory, that nearly all thixotropic sols show marked streaming double refraction, so that the particles are probably anisotropic or anisometric.

(iii) Three dimensional theory. This theory is based on the hypothesis of three dimensional gel structure as already described before. It is supposed that when a gel is thixotropic, shaking is only sufficient to break the cross linking, thus re-forming the sol. The particles would then be linear, thus accounting for the double refraction of flow suggested in the second theory.

[III] Measurement of Thixotropy

No comprehensive method is available for determining thixotropy, but the feature of the property of thixotropy can be determined by the rate of solidification. We know that

$$\eta_a = \eta_r + \theta/S$$

where η_a is the apparent viscosity, η_r is the residual viscosity, S is the shearing force and θ is the coefficient of thixotropy. For determining viscosity, a number of viscometers are available. In a method devised by Jones (1934), the rotating Couette viscometer as shown in figure (27) is used. It consists of a cylindrical shaped container C_1 which contains the sol. A small cylinder C_2 hangs into it. In the upper portion, there is a mirror which reflects a beam of light onto a scale. The vessel

C_1 is rotated by means of an electric motor. As a result of this, the sol moves and through it, motion is transferred to cylinder C_2. At constant speed of C_1, the viscosity is proportional to the angle ϕ through which C_2 is rotated. We have

$$\eta = k_1\phi/\omega \text{ and } \eta = k_1/\phi$$

The value of k_1 depends upon the radius and height of the cylinder. The angular velocity ω of C_1 produces a shear stress which corresponds to a pressure p of the capillary viscometer. This viscometer has the advantage that it allows the shear stress to be changed within appreciable limits.

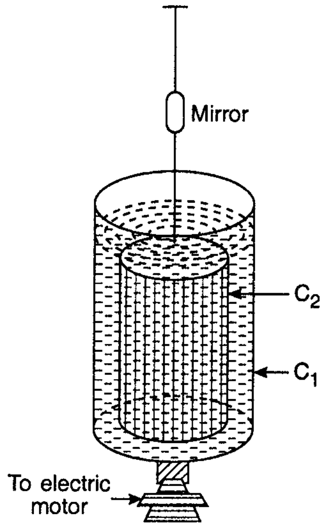


Fig. 27. Rotating couette viscometer

[IV] Influence of Foreign Substances on Thixotropy

Thixotropic gelation may be considered as a form of flocculation and is sensitive to all kinds of additions. The time of solidification (T) is strongly dependent on the concentration (c) of the electrolyte, as seen in the empirical equation given by Schalek and Szegvari (1923).

$$\log T = A - B \cdot c$$

It has been shown that thixotropic gelation is a slow coagulation. Time of solidification is also changed with a change in the pH of the solution as mentioned by Freundlich. It is seen that alcohol promotes the thixotropic gelation and after evaporating the alcohol, the sol returns to the gel state.

[V] Influence of Temperature on Thixotropy

As seen from Schalek and Szegvari's experiments, an increase of temperature decreases the time of solidification.

[VI] Applications of Thixotropy

The phenomenon of thixotropy has found several applications in biological fields, technology and in articles of daily use. Protoplasm has thixotropic properties. Myosin sols are known to form strongly thixotropic gels, which might indicate that thixotropy has a significance for muscular action. Most of the quick-sands are thixotropic in nature. The application of thixotropy is much used in *drilling muds* used in drilling oil wells. Drilling muds always contain a certain amount of plastic clays responsible for its thixotropy. Paints, varnishes and printing inks are all thixotropic in nature. A paint having a greater time of solidification is considered to be its good property. A suspension of graphite in a mineral oil shows a thixotropic gelation.

Rheopexy. It has been seen that some thixotropic systems increase in consistency more rapidly, even by very slow stirring than at complete rest. Such a phenomenon is known as rheopexy. McBain showed that a system of sodium laurate may be kept in the form of a gel for a long time, but it sets to a solid jelly even on light stirring.

6·23. GENERAL APPLICATIONS OF COLLOIDS

The applications of colloids can broadly be divided into three types :

(i) Natural applications, (ii) Technical applications, (iii) Analytical applications.

[I] Natural Applications

(i) Rain. Cloud is a colloidal system in which water particles are distributed in air. When air which has become saturated with water vapours, reaches the cooler part of the atmosphere, cloud is formed as a result of condensation. Further cooling and condensation form bigger drops of water which fall due to gravity in the form of rain.

(ii) Blue colour of the sky. As there are dust particles along with water in the sky, which scatter blue light, the sky, therefore, appears blue. If there were no scattering, the sky would have appeared totally black [Figure (28)].

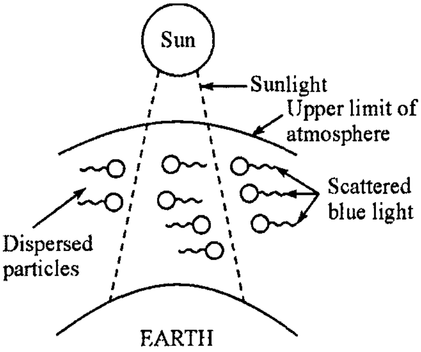


Fig. 28. Blue colour of sky.

(iii) Blood. Blood is a colloidal system, having albuminoid substance as the dispersed phase carrying a negative charge. The stoppage of bleeding by the application of alum or ferric chloride can be explained on the basis of coagulation, as in this case Al^{3+} acts as active ion for the coagulation of negatively charged albuminoid particles.

(iv) Articles of daily use. Milk which is a complete food is an emulsion of oil in water (O/W) type stabilised by casein. Butter is an emulsion of water dispersed in fat and is of W/O type. Fruit juice is a colloidal system having juice dispersed in the solid tissue of the fruit. Ice cream is ice particles dispersed in cream.

(v) Tails of comets. Comets are members of the solar system which have highly eccentric orbits around the sun. When they approach the sun, their velocity increases enormously and a trail of gaseous matter is formed behind. This trail has colloidal matter in it and this scatters sun's rays, making a visible tail behind. When the comets have gone away from the sun on their highly eccentric paths, they slow down and the trail disappears.

(vi) Formation of deltas. When river water, carrying sand, dust and other suspended matter in colloidal form meets sea water at its mouth, the salts present in sea water bring about coagulation of the colloidal matter. This is the mechanism of the formation of deltas which are triangular in shape [Figure (29)]. River deltas, being thus rich in organic matter, form excellent production soils. Sundarbans (West Bengal) is the largest delta in the world, having an area of 8,000 sq. miles.

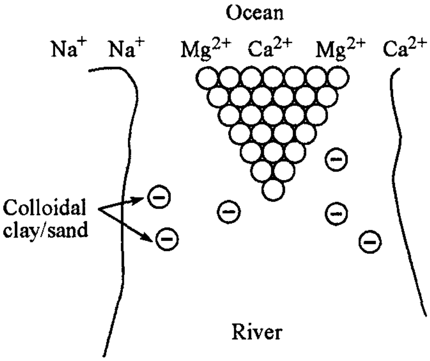


Fig. 29. Delta formation.

[II] Technical Applications

There are numerous technical applications of colloids, but we shall list only the important ones.

(i) Rubber industry. Rubber is obtained from the sap of certain trees. The sap—also known as latex—is a colloidal system of caoutchouc* particles dispersed in water, stabilised by protein contents. On coagulating the latex by various methods, colloidal gel, known as rubber is obtained. When rubber is heated with sulphur a product known as vulcanised rubber is obtained used in cycle and motor tyres etc. For soft rubber, the amount of sulphur varies from 2-10%, while for hard rubber the amount varies from 30-35%.

The rubber particles carry a negative charge. When rubber is to be deposited on any material, then two electrodes are made, the anode is made of that substance on which rubber has to be deposited. On passing an electric current, rubber thus deposits on it by this principle.

(ii) Tanning of leather. Both hide and leather are colloidal substances possessing the gel structures. When hide is soaked in any tanning agent which consists of tannin (a sol containing negatively charged particles), mutual coagulation of the two takes place due to opposite charges. This process is known as tanning and the hide becomes more and more leather-like, imparting hardness to it.

Chrome tanning is a process in which chromium salts are the tanning agents for the precipitation of hide.

(iii) Soils and clays. The value of a soil, *i.e.*, its ability to retain moisture is dependent on the colloidal properties of ***humus***—an important constituent of the soil. When soil is completely saturated with H^+ ions, it is known as *'clayic acid'* and the salts derived from this acid as *'clayates'*. There are colloids, *e.g.*, $Fe(OH)_3$, $Al(OH)_3$, amorphous silicates and bacteria which are present in soils.

The humus in the soil acts as protective colloid and brings about greater dispersion, imparting stability to the soil. The soil does not permit the percolation of water and remains wet for an inconveniently long periods. In presence of calcium salts, humus brings about coagulation of clay particles. The soil thus retains water, permitting the excess to percolate through. The dispersion coefficient or percentage of clay is the amount which passes into suspension on being left in contact with water. All good soils have a comparatively low dispersion coefficient and all barren alkali soils have a high value, having a low rate of percolation in to water. Highly acid soils have a low dispersion coefficient and very high rate of percolation.

(iv) Purification of sewage and water. Sewage consists of impure particles dispersed in water and is thus colloidal in nature carrying a negative charge. The dirt particles carrying a negative charge are coagulated on the oppositely charged positive electrode and are thus removed. [Figure (30)]. The deposit is then used as manure. The method for sewage purification is known as *'activated sludge process'*.

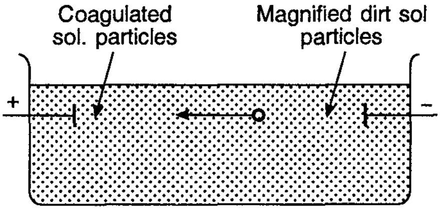


Fig. 30. Purification of sewage.

Impure water consists of negatively charged particles of clay and organic colloidal matter bacteria. This water can be purified by the addition of alum which gives Al^{3+} ions. These Al^{3+} ions coagulate

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*Caoutchouc is a polymer of C_5H_{10}.

the negatively charged particles and cause them to settle down. Some of the impurities such as Pb from lead pipes are adsorbed and removed. The clear water can then be filtered through decantation.

(v) Photography. Photographic plates are thin glass plates coated with a fine suspension of silver bromide and gelatin. Silver bromide dispersed in gelatin gel forms a photographic emulsion. The AgBr sol may be produced by mixing gelatin solution containing dilute solution of $AgNO_3$ with dilute alkali bromide, whereby insoluble AgBr is formed in the form of a fine suspension. It is stabilised by gelatin which is then painted on thin glass plates.

(vi) Metallurgy of alloys. The technical property of an alloy depends upon the size of the subdivided particles in it. Thus, alloys which are brittle and non-elastic have a coarse structure. As the degree of dispersion is increased, the hardness of the alloy is also increased. Ageing, distortion, fatigue in alloys decrease the degree of dispersion, making the alloys less strong.

(vii) Colours of various materials. The colour of various meterials is due to colloid metal and colloid metallic compound. The red colour of ruby glass is due to colloidal gold. Yellow glass owes its colour to colloidal silver. Colloidal chromium imparts colour to artificial rubies.

(viii) Dyeing. Cotton, silk and wool are all colloidal in nature having a gel structure. The dyestuffs include a number of substances having different properties, their degree of dispersion is colloidal. Dyeing process involves the phenomenon of adsorption. Mordants which are also colloids are used for fast dyeing. These mordants are adsorbed very rapidly by the fibre, *e.g.*, $Al(OH)_3$, $SnCl_2$, tannin, etc.

(ix) Smoke and fumes precipitation. Smoke is a system in which carbon particles are dispersed in air carrying a negative charge. In large industrial cities smoke comes out from the chimney and the carbon particles present in it are very injurious to human health. So, to remove carbon particles, use is made of *'Cottrell electrical precipitator'* [Fig. (31)]. In it the smoke is made to pass through a positively charged anode in the chimney, when carbon particles settle down. According to a modern method, the smoke is led to a chamber fitted with a metallic knob charged to a very high positive potential (20,000 volts). The gases free from smoke, pass from the top of the chimney.

(x) Medicines. Most of the medicines which are used are colloidal in nature. They are more effective due to their easy assimilation and adsorption by the human system. *Colloidal antimony* is effective in curing *kalazar. Colloidal sulphur* is effective in curing *skin diseases* and in *killing germs. Colloidal calcium* and *gold* are used as *intramuscular injections*, to increase the vitality of human system in serious diseases. *Colloidal silver or argyrol* is used for curing granulations. *Milk of magnesia*, an emulsion, is used for stomach troubles.

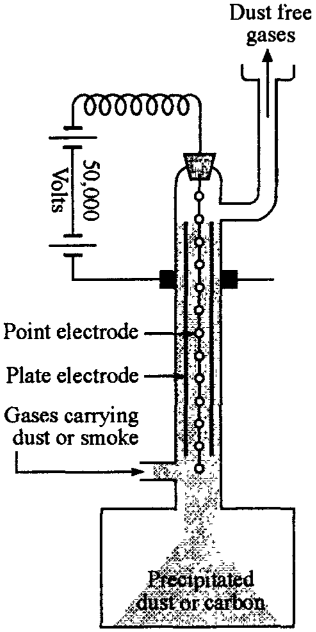


Fig. 31. Cottrell electrical precipitator.

[III] Analytical Applications

(i) Qualitative and quantitative analysis. A knowledge of the behaviour of colloids and their mode of formation play an important role in analytical problems.

Before starting qualitative analysis, organic matter should be destroyed, otherwise they will form protective colloid and prevent the precipitation of various precipitates. One of the functions of NH_4Cl is to aid the precipitation of the otherwise colloidal metallic sulphides of the fourth group. The solubility of $Zn(OH)_2$ in an excess of NaOH in the separation of Zn from Mn is almost a case of peptization of a sol, and when sodium zincate solution is passed through an ultrafilter, the $Zn(OH)_2$ is retained. Similarly, the dissolution of $Cr(OH)_3$ by NaOH solution is due to peptization which is re-precipitated on boiling the sol.

In volumetric analysis, hydrophilic colloids alter the end point, *e.g.*, in a titration of HCl and NaOH, the amount of deviation in the end point is increased with increasing amounts of colloids. In the volumetric estimation of silver by Mohr's method, the phenomenon of adsorption comes into being.

In gravimetric analysis, definite crystalline precipitates are desired and the procedure thus adopted aims to get sufficiently bigger particles, because extremely small particles may pass through the filter paper. To prevent adsorption of the undesirable molecules with the desired precipitate, it is necessary to precipitate the solution at the boiling point. To achieve this a fairly dilute solution is used.

(ii) Detection of natural honey from artificial honey. Ley's test for detecting the natural honey from artificial honey consists in treating few drops of the honey with an ammonical silver salt solution. If the honey is natural or pure, then the metallic silver produced assumes a reddish yellow colour due to the traces of albumin or ethereal oils, which act as protective colloids and maintain the colloidal silver in a high degree of dispersion. A dark yellow or greenish precipitate is formed with artificial honey.

(iii) Identification of traces of noble metals. Noble metals when present in the colloidal form produce very bright and intense colours. Cassius purple test indicates the presence of colloidal gold. Donnan showed that dilute solutions of noble metals are reduced in the common borax beads to form solid sols. The colour of the bead differs with the degree of dispersion of the metal and character of the metal. In case of dilute $AuCl_3$ solution, a rose coloured bead is obtained, but the presence of violet or blue bead is observed with concentrated acids. Silver salts and platinum salts give blue yellow, violet beads, respectively. This method is a very sensitive test, more sensitive than the spectro-analytical methods.

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. Explain the terms colloids and crystalloids. How would you separate one from the other ?
2. What is the size range of colloidal particles ? Carefully distinguish between a molecular solution, a colloidal dispersion and a coarse dispersion.
3. What do you understand by the terms colloidal solution ? In what respects do the physical properties of a colloidal solution differ from those of a molecular solution ?

4. Comment on the statement "Colloidal solutions are two-phase systems". Explain the terms : sol, alcosol, benzosol and organosol.
5. What are lyophilic and lyophobic sols? Discuss the essential differences between lyophilic and lyophobic sols.
6. Discuss the various methods for the preparation of colloidal solutions.
7. How would you prepare colloidal solutions of (i) gold (ii) ferric hydroxide and (iii) arsenic sulphide ? Give an account of the varous methods employed for the purification of colloidal solutions.
8. Explain the use of (a) dialysis (b) electro-dialysis and (e) ultrafiltration in the purification of colloidal solutions.
9. How do you conclude that colloidal particles are often electrically charged ? Are all colloidal solutions electrically charged ?
10. Discuss the optical properties shown by colloids.
11. Describe the preparation of two different types of colloidal solutions.
12. Classify the various types of colloidal solutions. Discuss the electrical properties of colloidal solutions and explain the action of electrolytes on them.
13. Discuss the origin of charge on collodal particles. What is meant by electrical double layer ?
14. Describe different methods of determining the size of colloidal particles.
15. What are emulsions? Describe the methods used in finding the type of an emulsion. How are emulsions prepared ?
16. What are gels ? How are they classified ? Describe the various methods for the preparation of gels.

[II] Short Answer and Very Short Answer Type Questions

1. What is meant by the colloidal state of matter ?
2. (a) How are colloidal solutions freed from soluble impurities ?
   (b) How could you show that colloidal particles carry electrical charge ?
   (c) How does the charge originate ?
3. What are colloids?
4. How are colloids classified ?
5. Explain what happens when a colloidal solutions of gold is treated as follows :
   (i) A beam of light is passed through it,
   (ii) An electrolyte is added, and
   (iii) If it is brought under the influence of an electric field.
6. Explain the following :
   (a) A sulphur sol is coagulated by adding a little electrolyte, whereas a gelatin sol is apparently unaffected.
   (b) A colloidal solution is stabilised by adding gelatin.
   (c) Presence of H_2S is essential in As_2S_2 sol, H_2S ionizes and should precipitate the sol.
7. Define the terms : sol, gel, lyophilic colloids, electrophoresis, Brownian movement, Tyndall effect and coagulation as applied to colloidal solution.
8. Explain why :
   (i) Deltas are formed at a place where the rivers pour their water into the sea?
   (ii) Potash alum is used for removing impurities from water?
   (iii) In many factories the smoke before it comes out from the chimney is led to charged metallic plate?

9. How does :
  (i) Electrophoresis provide information about thc sign of charge on a particle ?
  (ii) A ferric hydroxide sol is coagulated which has been stabilized by adsorption of H^+ ions?

10. Explain, why?
  (a) The precipitation of a colloidal solution is not easy in the presence of gelatin?
  (b) A colloidal solution contains electrically charged particles?
  (c) Alum is used in town water supply?
  (d) What happens when a strong beam of light passes through a dilution of colloidal gold ?

11. How can detergent action of colloids be explained ?

12. Define "gold number". Gold numbers for gelatin, haemoglobin and sodium oleate are 0·005, 0·05 and 0·07 respectively. Which has the greatest protective action?

13. Define emulsion. Give two examples.

14. Define protective action and protective colloids.

15. How will you prepare colloidal solution of ferric hydroxide, arsenious sulphide, sulphur, carbon iodine, mastic, silicic acid and gold ? In what respects do the properties of a colloidal solution (e.g., ferric hydroxide) differ from those of true solution (e.g., aqueous solution of ferric chloride) ?

16. Distinguish between true solution and colloidal solution.

17. How may the sign of charge on colloidal particles be determined ? Classify the following sols according to their charge :
Gold sol, ferric hydroxide, gelatin, blood, sulphur, arsenious sulphide.

18. What is the origin and significance of charge on a colloidal particle ?

19. What is meant by the term coagulation of colloidal solutions ? Bring out clearly the role of electrolytes in causing flocculation of colloidal solutions.

20. Explain the term : flocculation value of an electrolyte.

21. What are protective colloids? Explain how a lyophilic colloid can stabilise a lyophobic colloid.

22. How is colloidal solution of As_2S_2 or gold prepared ?

23. How is a colloidal solution purified ?

24. (a) Given a red coloured liquid, how could you show whether or not it is a sol.
  (b) How will you show that colloidal particles are charged ? How will you determine the nature of charge on them ?

25. Write short notes on the following :
  (a) Stability of colloids.
  (b) Hardy-Schulze law.
  (c) Principle involved in the extraction of juice from beet root.
  (d) Reversible or protective colloids.
  (e) Dialysis.
  (f) Gold number
  (g) Tyndall effect.
  (h) Brownian movement.
  (i) Cataphoresis.
  (j) Peptization.
  (k) Emulsions.
  (l) Coagulation.

(m) Origin of charge on colloidal particles.
(n) Optical properties of colloids.
(o) Isoelectric point.
(p) Ultra-microscope.
(q) Electro-osmosis.
(r) Sol-gel transformation.
(s) Protection.
(t) Special electrical properties of colloids.
(u) Applications of colloids.
(v) Electrical double layer.
(w) Zeta potential
(x) Lyophilic and lyophobic colloids.
(y) Thixotropy.

26. Describe Bredig's arc method for the preparation of colloidal solutions.
27. How can detergent action of soap be explained ?
28. How can lyophobic colloids be prepared ?
29. Define zeta potential. How it is helpful in explaining the stability of sols ?
30. What is Hardy-Schulze law ?
31. Define gold number.

[III] Multiple Choice Questions

1. The following will have the maximum coagulating power :
(i) Na^+ (ii) Sn^{4+} (iii) Ba^{2+} (iv) Al^{3+}.

2. Milk is :
(i) Gel (ii) Sol (iii) Aerosol (iv) Emulsion

3. The size of colloid particles is :
(i) $> 0.1\ \mu$ (ii) $1\ m\mu - 0.1\ \mu$ (iii) $> 1\ m\mu$ (iv) $> 5000\ m\mu$

4. A freshly prepared precipitate of SnO_2 peptised by HCl will carry the following charge :
(i) Neutral (ii) Positive (iii) Negative (iv) Amphoteric

5. Every colloid system is :
(i) Homogeneous (ii) Heterogeneous
(iii) Contains one phase (iv) Homogeneous and heterogeneous

6. The following is a hydrophobic colloid :
(i) Gelatin (ii) Gum (iii) Starch (iv) Sulphur

7. Gold sol prepared by different methods will have different colours. It is due to :
(i) Difference in size of colloid particles
(ii) Gold shows variable valency
(iii) Different concentrations of gold
(iv) Presence of impurities.

8. Following is an emulsifier :
(i) Oil (ii) Water (iii) NaCl (iv) Soap

9. The sky appears blue. It is due to :
(i) Reflection (ii) Absorption (iii) Scattering (iv) Refraction

10. Which of the following reaction will give colloidal solution :
(i) $Cu + HgCl_2 \rightarrow Hg + CuCl_2$
(ii) $Cu + CuCl_2 \rightarrow Cu_2Cl_2$

(iii) $2Mg + CO_2 \rightarrow 2MgO + C$

(iv) $2HNO_3 + 3H_2S \rightarrow 3S + 4H_2O + 2NO$

11. Fat is :

(i) Emulsion (ii) Gel (iii) Colloidal solution (iv) Solid sol

12. Colloidal solutions cannot be purified by :

(i) Dialysis (ii) Electrodialysis

(iii) Ultrafiltration (iv) Electrophoresis

13. The charge on As_2S_3 sol is due to the adsorption of :

(i) H^+ (ii) OH^- (iii) S^{2-} (iv) O_2^-

14. Surface tension of lyophilic sols is :

(i) Lower than water (ii) More than water

(iii) Equal to water (iv) Sometimes lower and sometimes more than water

15. On addition of 1.0 ml of 10% NaCl to 10 ml gold sol in the presence of 0.0250 gm of starch, the coagulation is just stopped. The gold number of starch is :

(i) 0.025 (ii) 2.5 (iii) 2.5 (iv) 25.0

16. Which of the following is a lyophilic colloid ?

(i) Milk (ii) Fog (iii) Blood (iv) Gelatin

17. At critical micelle concentration, the surfactant molecules undergo :

(i) Association (ii) Aggregation

(iii) Micelle formation (iv) All the above

18. Which of the following electrolytes is least effective in causing coagulation of $Fe(OH)_3$ sol ?

(i) $K_3Fe(CN)_6$ (ii) K_2SO_4 (iii) KCl (iv) K_2CrO_4

19. The ability of an ion to bring about coagulation of a given colloid depends on :

(i) Its charge (ii) Sign of the charge only

(iii) Magnitude of charge (iv) Both charge and magnitude

20. Which of the following statement is not true ?

(i) Elastic gels undergo imbibition

(ii) Non-elastic gels are reversible in nature

(iii) Inorganic gels usually exude solvent on standing

(iv) Both elastic and non-elastic gels show thixotropy.

[IV] Fill in the Blanks

1. True solutions are .... systems.

2. In a colloidal system .... phases are present.

3. In aerosol .... is the dispersed phase and .... is the dispersion medium.

4. Hair cream is an example of .... system.

5. The process of converting a fresh precipitate into a colloidal solution is known as ....

6. Tyndall effect is due to .... of light

7. When placed in water .... gels .... This phenomenon is called ....

8. Breaking of emulsions is also known as ....

9. The emulsifier in milk is ....

10. Formation of deltas is an example of ....

[V] True or False

State whether the following statements are true (T) or false (F) ?

1. The lower the gold number, the better is the protective power of a protective colloid.
2. Lyophobic sols are irreversible in nature.
3. Smoke is an emulsion.
4. Colloidal system is biphasic in nature.
5. Colloidal solutions exhibit Brownian motion.
6. The soap may be considered as a surfactant.
7. Blood carries a positive charge.
8. Lyophilic colloids can act as protective colloids
9. The role of an emulsifier is to increase the surface tension between the two phases.
10. Elastic gels are reversible in nature.
11. The process of reversible sol-gel transformation is called thixotropy.
12. The colour of a colloidal solution depends on the shape and size of the particles.
13. Avogadro's number can be determined with the help of Brownian motion.
14. Out of NaCl, $BaCl_2$, $AlCl_3$ solutions, the coagulating power of NaCl is maximum for coagulating a As_2S_3 sol.
15. The difference in potential between the fixed and diffuse layers of an electrical double layer is called streaming potential.

ANSWERS

[III] Multiple Choice Questions

1. (b) **2.** (d) **3.** (b) **4.** (b) **5.** (b)
6. (d) **7.** (a) **8.** (d) **9.** (c) **10.** (d)
11. (a) **12.** (d) **13.** (c) **14.** (a) **15.** (d)
16. (d) **17.** (d) **18.** (c) **19.** (d) **20.** (b)

[IV] Fill in the Blanks

1. Homogeneous **2.** two **3.** liquid, solid **4.** emulsion **5.** peptization
6. Scattering **7.** elastic, swell, imbibition **8.** demulsification
9. casein **10.** coagulation

[V] True or False

1. (T) **2.** (F) **3.** (F) **4.** (T) **5.** (T)
6. (T) **7.** (F) **8.** (T) **9.** (F) **10.** (T)
11. (T) **12.** (T) **13.** (T) **14.** (F) **15.** (F).

Chapter 7

CHEMICAL KINETICS

7·1. INTRODUCTION

Chemical kinetics is that branch of chemistry which deals with the study of the rate of chemical reactions and the mechanism by which they occur. In other words, it deals with how fast and through what mechanism a particular chemical reaction occurs.

The chemical reactions can be classified into the following categories on the basis of their speeds :

(a) ***Instantaneous or fast reactions*** which proceed at a very fast speed and it is practically impossible to measure the speed of such reactions. Typical examples of fast reactions include (i) several ionic reactions, i.e., neutralisation of acids and bases, (ii) organic substitution reactions, (iii) reactions of biological importance and (iv) explosive reactions of oxygen with hydrogen and hydrocarbons. The rates of such reactions can be measured by using special methods.

(b) ***Extremely slow reactions*** which proceed at a very slow speed and the speed is so slow that it is again not possible to measure the speed of such reactions.

(c) ***Reactions which proceed at a measurable speed.*** Reactions involving organic substances belong to this category, *e.g.*, inversion of cane sugar, saponification of ethyl acetate etc.

Reactions belonging to the above third category, *viz.*, (c) are utilised in the study of chemical kinetics.

7·2. REACTION VELOCITY

Reaction velocity is different at different intervals of time and hence it cannot be determined by dividing the quantity of the substance transformed by time. Reaction velocity is, therefore, defined as,

"the rate at which the concentration of a reactant changes with time."

Reaction velocity is represented by $\left(-\frac{dc}{dt}\right)$; where dc is the concentration of the reactant left behind after a short interval of time dt. The negative sign implies that the concentration of the reactants decreases with time or the reaction velocity decreases with time.

The velocity of a reaction is also represented by dx/dt, where dx is the amount of the reactants changed during a small interval of time dt.

[I] Relation Between Reaction Velocity and Time

Guldberg and Waage (1867) emphasised the dynamic nature of chemical equilibrium. According to them, *"the rate of a chemical reaction is directly* *proportional to the product of the acive masses or molecular concentrations of the reactants."* As the chemical reaction proceeds, the reactants are consumed, whereby their molecular concentrations decrease. Therefore, the rate of the chemical reaction will also decrease with time. If a graph is plotted between reaction velocity and time, it is seen that the reaction velocity falls rapidly in the initial stages of the reaction and after sometime the curve becomes asymptotic to the time axis [Fig. (1)] It can, therefore, be easily concluded that the reaction velocity is maximum to start with, which then falls gradually with time. It the later stages, the reaction velocity becomes so low that it takes a very long time for it to become zero, *i.e.*, for the reaction to be completed. It can, therefore, be safely assumed that in the later stages, the reaction is nearly complete.

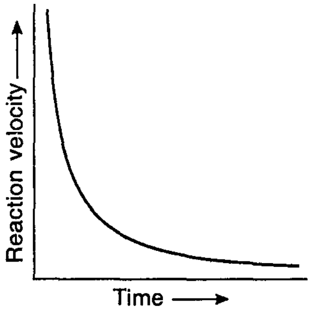


Fig. 1.

Consider the reacion,

$$aA + bB \rightleftharpoons cC + dD$$

In it, *a* moles of A react with *b* moles of B to form *c* moles of C and *d* moles of D. The rate of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole. Thus, we can write as follows :

$$r = \frac{-d\,C_A}{d\,t} \times \frac{1}{a} = k\,C_A^a\,C_B^b \qquad \text{...(1)}$$

$$r = \frac{-d\,C_B}{d\,t} \times \frac{1}{b} = k\,C_A^a\,C_B^b \qquad \text{...(2)}$$

$$r = \frac{+d\,C_C}{d\,t} \times \frac{1}{c} = k\,C_A^a\,C_B^b \qquad \text{...(3)}$$

$$r = \frac{+d\,C_D}{d\,t} \times \frac{1}{d} = k\,C_A^a\,C_B^b \qquad \text{...(4)}$$

From equations (1), (2), (3) and (4), we get,

$$r = \frac{-d\,C_A}{d\,t} \times \frac{1}{a} = \frac{-d\,C_B}{d\,t} \times \frac{1}{b} = \frac{+d\,C_C}{d\,t} \times \frac{1}{c} = \frac{+d\,C_D}{d\,t} \times \frac{1}{d}$$

The unit of reaction rate or reaction velocity is expressed in mole per litre per unit time, *i.e.*, mol L^{-1} time^{-1}.

[II] Factors Affecting Reaction Velocity

A number of factors affect the rate of reaction, the most significant of them are as follows:

(a) ***Effect of concentration of reactants.*** The rate of a chemical reaction is influenced by the number of collisions per second between the reacting molecules. On increasing the concentration of the reactants, the number of collisions and hence the rate of reaction also increases and vice versa.

(b) ***Effect of nature of reactants.*** Reactions between polar or ionic molecules occur almost instantaneously. Those reactions in which the bonds are arranged or electrons are transferred take a comparatively longer time than the former ones. For example, reactions involving neutralisation or double displacement are very fast, while the oxidation-reduction reaction (involving electron transfer) are slower.

(c) ***Effect of catalyst.*** A catalyst can increase or decrease the rate of chemical reaction, *e.g.*, the combination of hydrogen and oxygen to form water is slow at ordinary temperatures, while it proceeds rapidly in presence of platinum *(positive catalysis)*. Similarly, the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen becomes slow in presence of ethyl alcohol (*negative catalysis*).

(d) ***Effect of surface area of reactants.*** Surface area of reactants is of importance only for heterogeneous reactions. As particle size decreases, surface area for the same mass increases. The smaller particles thus react more rapidly than the larger particles. For example, burning of coal dust in air takes place more rapidly than that of large lumps of coal.

(e) ***Effect of temperature.*** With the exception of few reactions, the rate of a reaction is increased considerably with an increase in temperature. Generally, the rate of a reaction is almost doubled or trebled by an increase of 10°C in temperature.

The ***temperature coefficient*** (denoted by γ) of a reaction is, however, defined as the *ratio of the specific rate constants at two temperatures separated by 10°C, usually 25°C and 35°C, i.e.,*

$$\text{Temperature coefficient, } \gamma = \frac{k_{t+10}}{k_t}$$

In most of the homogeneous gaseous reactions the values of γ lies beteen 2 and 3. The average value of this coefficient is three. Consequently, when the temperature changes by 10°C the rate of reaction changes 3 times. Similarly, for the change of temperature by 100°C, the rate of reaction is found to change by 3^{10} (= 59049) times.

Rate constant at a temperature T K is given by

$$k_T = A \,.\, e^{-E/RT}$$

At $(T + 10)$ the rate constant is given by

$$k_{(T+10)} = A \,.\, e^{-E/R(T+10)}$$

If E and A are assumed to be constant over this small range of temperature, then

$$\gamma = \frac{k_{(T+10)}}{k_T} = \frac{A \,.\, e^{-E/R\,(T+10)}}{A \,.\, e^{-E/RT}}$$

$$\gamma = e^{[-E/R(T+10)\,+\,E/RT]}$$

$$= e^{[10E/RT(T+10)]}$$

$$\gamma = \exp\left[\frac{10E}{RT\,(T+10)}\right]$$

At room temperature say 27°C (300 K) and taking the value of $E = 85$ kJ mole^{-1}

$$\gamma = \exp\left[\frac{10 \times 85 \times 1000}{8.314 \times 300 \times 310}\right]$$

$$\approx 2.7$$

It has been observed that for most of the reactions γ lies between 2 and 3, *i.e.*, for every 10 degree rise in temperature, the reaction rate nearly doubles up.

(f) ***Effect of nature of light.*** Sometimes, visible or ultraviolet light enhances the rate of a chemical reaction, *e.g.*, the reaction between hydrogen and chlorine takes place only in sunlight.

7·3. VELOCITY OR RATE CONSTANT

If we consider the reaction $A + B \rightarrow$ Products and if C_A, C_B be the molar concentrations of reactants, A and B at any time t, then the rate

$$\frac{dx}{dt} = kC_A\,C_B$$

where k = velocity or rate constant.

If $C_A = 1$ and $C_B = 1$, then $k = \frac{dx}{dt}$. So, velocity constant is defined as the *rate of the reaction when the molar concentration of each reactant is unity.* It is also known as *specific reaction rate.*

Unit of Rate Constant

Let us consider the following general reaction :

$$aA + bB + \ldots\ldots\ldots \rightarrow \text{Products}$$

The rate of reaction is given by, $r = \frac{dx}{dt} = kC_A^a\,C_B^b$ ...(1)

The unit of r is mol L^{-1} s^{-1} and that of C_A and C_B is mol L^{-1}. So, from equation (1),

$$\text{mol}\,L^{-1}\,s^{-1} = k\,(\text{mol}\,L^{-1})^a \times (\text{mol}\,L^{-1})^b \times \ldots$$

$$\therefore \qquad k = [(L\,\text{mol}^{-1})^{(a+b+\ldots)-1}] \times s^{-1}$$

Problem 1. ***Decomposition of*** N_2O_5 ***occurs in the following manner :***

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Write various formulae expressing the rate of the reaction. How the rate constant in the various rate equations are related to one another?

Solution: The rate can be expressed in the following ways :

(i) $$\frac{1}{2}\frac{-d[N_2O_5]}{dt} = k\,[N_2O_5]$$

(ii) $$\frac{1}{4}\frac{d[NO_2]}{dt} = k_1\,[N_2O_5]$$

(iii) $$\frac{d[O_2]}{dt} = k_2\,[N_2O_5]$$

From the equation representing the reaction, we see that two moles of NO_2 are formed for every mole of N_2O_5 that decomposes. Therefore,

$$k_1 = 2k$$

Similarly, $k_2 = \left(\frac{1}{2}\right)k$, because half mole of O_2 is formed for every mole of N_2O_5 that reacts.

7·4. ORDER OF REACTION

In chemical kinetics, the reactions are generally classified in terms of their order. Order of a reaction is defined as follows :

'The order of reaction is given by the number of atoms or molecules whose concentration changes during a chemical reaction'.

Or

'The order of reaction is given by the number of concentration terms of atoms or molecules which determine the rate law'.

A reaction is said to be of ***first order***, if its rate, r (or dx/dt) is given by the following expression,

$$r = \frac{dx}{dt} = kC_A$$

The reaction is of ***second order*** and ***third order*** if its rate is given by expressions (1) and (2), respectively.

$$\frac{dx}{dt} = k\,C_A^2 \quad \text{or} \quad k\,C_A \cdot C_B \qquad \text{...(1)}$$

$$\frac{dx}{dt} = k\,C_A^3 \quad \text{or} \quad k\,C_A^2 \cdot C_B \quad \text{or} \quad k\,C_A \cdot C_B^2 \qquad \text{...(2)}$$

The subscripts A, B and C stand for various reactants A, B and C, respectively. When the rate of a reaction is given by

$$\frac{dx}{dt} = kC_A^{n_1} \cdot C_B^{n_2} \cdot C_C^{n_3} \ldots\ldots$$

where k is a constant, the reaction orders of the individual constituents are n_1, n_2, n_3, etc., and the order of the reaction as a whole, n, is given by

$$n = n_1 + n_2 + n_3 + \ldots$$

So, order of reaction may also be defined as, *'the sum of the powers to which the concentration (or pressure) terms of the reactants are raised in order to express the reaction rate.*

7·5. MOLECULARITY

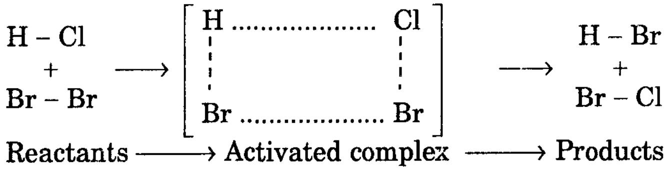
Many chemical reactions are not kinetically simple, they proceed through a number of steps between initial reactants and final products. Each of the individual steps is called an *elementary reaction*. Complex reactions are made up of a sequence of elementary reactions.

In the earlier literature, the terms unimolecular, bimolecular and trimolecular were used to express reactions of the first, second and third orders. We now apply the concept of molecularity only to elementary reactions. The molecularity shows how many molecules of reactants are involved in the elementary reaction. For example, consider the reaction $NO + O_3 = NO_2 + O_2$. When an NO molecule strikes an O_3 molecule with sufficient kinetic energy, it can capture an O atom, thus completing the reaction. This elementary reaction involves two molecules and it is, therefore, called a *bimolecular reaction.*

At the molecular level, a chemical reaction is a rearrangement of the chemical bonds of reactant molecules to form the chemical bonds of product molecules. It is necessary to change the energy state of a reactant molecule to allow the original bonds to change over to the new bonds. Consider the reaction,

$$HCl + Br_2 = HBr + BrCl$$

One H – Cl bond and one Br – Br bond are changed into one H – Br bond and one Br – Cl bond.



The transition state between reactants and products is called the *activated complex.*

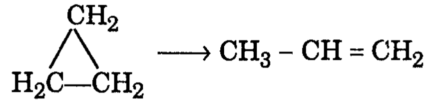
The molecularity of a reaction can be defined as the '*number of molecules of reactants that are used to form the* ***activated complex.***' The word molecule is used in its general sense to include atoms and ions also. In other words, molecularity of a reaction is defined as the ***number of atoms or molecules which collide together at one and the same time for the reaction to occur.***

In the examples of $NO + O_3$ and $HCl + Br_2$, the complex is formed from two molecules and the reactions are bimolecular. Clearly, the molecularity of a reaction must be a whole number, and in fact, is always found to be one, two or occassionally three. Experimental measurements show that the rate law for the reaction of NO with O_3 is

$$\frac{-d[NO]}{dt} = k_2 [NO] [O_3].$$

This reaction is, therefore, second order. All bimolecular reactions are second order, but the converse is not true; many second order reactions are not bimolecular.

Similarly, chemical reactions that are unimolecular are either isomerisations or decompositions. The isomerisation of cyclopropane to propene in the gas phase is one of the most carefully studied unimolecular reactions.



Experimental results show that the rate law for the above reaction is,

$$\frac{-d\,[\text{cyclopropane}]}{dt} = k_1\,[\text{cyclopropane}]$$

This reaction is, therefore, first order. All the unimolecular reactions are first order, but the converse is not true, some first order reactions are not unimolecular.

[I] Differences Between Order of Reaction and Molecularity

(1) For simple reactions. Earlier, no distinction was made between molecularity and order of a reaction. Reactions of first, second and third orders were called unimolecular, bimolecular, trimolecular reactions. This practice is, however, not followed now.

In several reactions, the order of reaction is different from molecularity, particularly when one of the reactants is in large excess, *e.g.*, inversion of cane sugar, hydrolysis of methyl acetate etc.

(i) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(Excess)}]{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(ii) $CH_3COOCH_3 + H_2O \xrightarrow[\text{(Excess)}]{H^+} CH_3COOH + CH_3OH$

Both the reactions are bimolecular but the order of reaction is 1, as it is found from experimental data that the rate of reaction is directly proportional to concentration of cane sugar in the first case and that of ester in the second case. This is explained due to the fact that water is present in large excess and its concentration does not change during the course of the reaction.

Moreover, molecularity of any process can only be small positive integers, while order of reaction can have zero as well as fractional values.

We thus conclude that in ***elementary reactions***, the molecularity of the reaction is given by the number of molecules of the reactant or reactants appearing in the stoichiometric equation for the reaction, while the order of reaction is given by the number of concentration terms of the reactant or reactants on which the rate of reaction depends.

Table-1. Differences between order of reaction and molecularity

	Molecularity		Order of reaction
1.	It is equal to the number of molecules of reactants which take part in a single step chemical reaction.	1.	It is equal to the sum of the powers of the molar concentrations of the reactants in the rate expression.
2.	It is a theoretical concept which depends on the rate determining step in the reaction mechanism.	2.	It is an experimentally determined quantity which is obtained from the rate for the overall reaction.
3.	It is always a whole number.	3.	It may be whole number, zero or fractional value.
4.	It is obtained from a single balanced chemical equation.	4.	It cannot be obtained from a balanced chemical equation.
5.	It reveals some basic facts about reaction mechanism.	5.	It does not reveal anything about reaction mechanism.

(2) For complex reactions. Those reactions which occur in two or more steps are termed as complex reactions, from the point of view of chemical kinetics. Each step of it is a simple reaction, *i.e.*, an elementary reaction has its own molecularity depending upon the number of molecules of the reactant or reactants taking part in that simple reaction.

Consider a complex reaction, in general,

$$2A + 3B \longrightarrow X + Y$$

Suppose that the reaction occurs through the following steps :

(i) $$A + B \xrightarrow{\text{Slow}} M + N$$

(ii) $$B + M \xrightarrow{\text{Fast}} BM$$

(iii) $$BM + A \xrightarrow{\text{Fast}} X + Z$$

(iv) $$B + N + Z \xrightarrow{\text{Fast}} Y$$

The complex reaction $2A + 3B \rightarrow X + Y$ takes place in four steps, the rates of every elementary reaction differs from one another. Suppose the first elementary reaction is the slowest. The rate of the overall reaction cannot be faster than the rate of the slowest reaction. In other words, *the rate of the overall reaction will be exactly equal to the rate of the slowest reaction. Thus, we can conclude that the slowest step in the sequence of various steps is the rate determining step of the overall reaction.* So, step (i) is the rate determining step.

The rate of reaction of step (i), which is the slowest, will be given by,

$$\text{Rate} = -\frac{d\,C_A}{d\,t} = -\frac{d\,C_B}{d\,t} = k\,[A]\,[B]$$

The rate of the overall reaction will evidently be given by the above expression. The order of the slowest reaction and, therefore, the order of the overall reaction will also be 2. The molecularity of the slowest reaction, *viz*, step (i) is also 2. However, the molecularity of the other succeeding steps is 2, 2 and 3. Consider the reduction of bromic acid to hydrobromic acid by hydroiodic acid. It occurs as follows :

$$HBrO_3 + 6HI \longrightarrow HBr + 3H_2O + 3I_2$$

The reaction involves seven molecules, yet it is of second order. The order of reaction is justified by the following mechanism :

(i) $HBrO_3 + HI \rightarrow HBrO_2 + HIO$ [Slow]

(ii) $HBrO_2 + 4HI \rightarrow HBr + 2H_2O + 2I_2$ [Fast]

(iii) $HIO + HI \rightarrow + H_2O + I_2$ [Fast]

As the first step is slow, it means that the reaction is of second order. In elementary steps involved in the complex reaction each has its own molecularity. The molecularities of steps (i), (ii) and (iii) are 2, 5 and 2, respectively.

We thus conclude that the order of a complex reaction is given by the order of the slowest step involved in the reaction. The molecularity of such a complex reaction has thus no significance. Each step or reaction involved has its own value of molecularity. It is given by the number of molecules of reactant or reactants involved in that particular step of the overall reaction. *The molecularity of the slowest step gives the order of the overall reaction.*

Why reactions of the higher orders are rare?

From the balanced chemical equation of the overall reaction, we can neither predict the order nor the molecularity of a reaction. For example, in the reaction $2A + 3B \rightarrow$ products, neither the molecularity nor the order of reaction is $2 + 3 = 5$. This also follows from probability considerations, as the chances of five molecules to collide simultaneously are remote. In fact, the chances for even three molecules to collide simultaneously are not high, whereas the chances for one or two molecules to collide simultaneously are high. *This is the reason why reactions of third and higher orders are very rare and most of the reactions are of first and second order.*

Problem 1. ***For the decompositon of*** **N_2O_5** ***dissolved in*** **CCl_4** ***which occurs as follows :***

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

The following data at 303 K are obtained :

Reactant concentrations $[N_2O_5]$	Rate of decompositon, $\frac{-d[N_2O_5]}{dt}$
0.170 mole lit^{-1}	0.05 mle lit^{-1}hr^{-1}
0.340 mole lit^{-1}	0.10 mole lit^{-1} hr–1
0.680 mole lit^{-1}	0.20 mole lit^{-1} hr–1

(i) Write the rate equation for the reaction. What is the order of reaction ?

(ii) Calculate the rate constant for the reaction at 303 K.

(iii) Calculate the decomposition at the instant when $[N_2O_5]$ is 0.54 mole lit^{-1}.

Solution : (i) It is observed from the data that the rate of decomposition of N_2O_5 is proportional to the concentration of N_2O_5. The rate becomes twice when the concentration is doubled and becomes four times when the concentration is made four times. Mathematically, we can write

$$\frac{-d\,[N_2O_5]}{dt} \propto [N_2O_5]$$

∴ Order of reaction = 1.

The rate equation is,

$$\frac{-d\,[N_2O_5]}{dt} = k\,[N_2O_5]. \qquad \text{... (i)}$$

(ii) The rate constant,

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{0{\cdot}05}{0.17} = 0.2941\ \text{hr}^{-1}.$$

(iii) By substituting the values of k and $[N_2O_5] = 0.54$ mole lit^{-1} in equation (i), we get,

Rate of decompositon $= 0.2941 \times 0.54$

$= \mathbf{0.1588\ mole\ lit^{-1}\ hour^{-1}}$.

7·6. PSEUDO-MOLECULAR REACTIONS

There are several reactions which obey a first order rate equation although in reality they are bi-or tri-molecular. For example, consider the hydrolysis of methyl acetate (ester) in presence of an acid.

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{Acid}} CH_3COOH + CH_3OH$$

According to the law of mass action, this reaction should be of second order, with the rate dependent on the concentration of both ester and water. Actually, however, the rate is found to be of first order with respect to the ester and independent of water. Reactions showing such behaviour are termed ***pseudo-molecular reactions*** (*pseudo = false*).

The pseudo-unimolecular nature of this reaction is explainable by the fact that water is present in such excess that its concentration remains practically constant during the course of the reaction. Pseudo-molecular reactions are encountered whenever concentrations of one or more reactants remain constant during the course of the reaction.

7·7. ZERO ORDER REACTIONS

[I] Definition of Zero Order Reactions

Reactions in which the concentrations of the reactants do not change with time and the reaction rates remain constant throughout, are said to be zero order reactions.

[II] Rate Equation of Zero Order Reactions

Consider the following reaction,

$$\begin{array}{ccl} A & \rightarrow & B \\ a & & 0 \quad \text{Initially} \end{array}$$

For a zero order reaction, the reaction velocity at any time t is given by

$$\frac{dx}{dt} = k \text{ (constant)},$$

or $$dx = k\,dt \qquad \text{... (1)}$$

On integrating equation (1), we get

$$\int dx = \int k\,dt$$

or $$x = kt + I \qquad \text{(where } I = \text{integration constant)}$$

When $t = 0, x = 0$ then $I = 0$

$\therefore$ $$x = kt \qquad \text{...(2)}$$

Equation (2) is the general rate equation for a zero order reaction.

[III] Characteristics of Zero Order Reactions

(i) The unit of zero order rate constant (k) is that of concentration × time^{-1}. If concentration is expressed is mole lit^{-1}, then unit of k will be mole lit^{-1} time^{-1}.

(ii) The concentration of the product increases linearly with time. So, a plot of x against time (t) will be a straight line passing through the origin.

[IV] Examples of Zero Order Reactions

The photochemical reaction of H_2 and Cl_2 over water (saturated with HCl) surface is of zero order. Some heterogeneous reactions like the thermal decomposition of HI on gold surface, enzyme reactions etc., obey first order kinetics.

7·8. FIRST ORDER REACTIONS

[I] Definition of First Order Reactions

A first order reaction is that in which the reaction rate is determined by the change of one concentration term of reactant only.

[II] Rate Equation of First Order Reactions

Consider a first order reaction,

$$\begin{array}{cccl} A & \rightarrow B & + C & \\ a & 0 & 0 & \text{(Initially)} \\ a-x & x & x & \text{(After time } t) \end{array}$$

Suppose the initial concentration of the reactant A be a mole/litre. Let x mole/litre of A decomposes after time t, leaving behind $(a - x)$ mole/litre of A. The amounts of B and C formed will be x mole/litre each.

The rate for a first order reaction is proportional to the concentration of A at any particular time. Therefore,

$$\frac{dx}{dt} = k\,C_A$$

where k = rate constant or velocity constant.

$\therefore$ $$\frac{dx}{dt} = k\,(a - x) \qquad \text{...(3)}$$

or $$\frac{dx}{(a - x)} = k\,dt \qquad \text{...(4)}$$

Integrating equation (4), we get

$$-\log_e (a - x) = kt + I \qquad \text{...(5)}$$

where I is integration constant.

When $t = 0, x = 0$; then

$$I = -\log_e a$$

Hence, equation (5) becomes

$$-\log_e (a - x) = kt - \log_e a$$

$$k = \frac{1}{t} \log_e \frac{a}{a - x} \qquad ...(6)$$

$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a - x} \qquad ....(7)$$

If $\log_{10}\left(\frac{a}{a - x}\right)$ is plotted against time t, a straight line passing through the origin is obtained with a slope of 2.303/k.

Equations (6) and (7) are known as ***first order rate equations***. Equation (6) can also be written as

$$\log_e \frac{a}{a - x} = k\,t$$

$$\frac{a - x}{a} = e^{-k\,t}$$

or

$$x = a\,(1 - e^{-kt}) \qquad ...(8)$$

If equation (4) is integrated between proper limits, we have

$$\int_{x = x_1}^{x = x_2} \frac{d\,x}{a - x} = \int_{t = t_1}^{t = t_2} k\,d\,t$$

or

$$k = \frac{1}{(t_2 - t_1)} \log \frac{a - x_2}{a - x_1} \qquad ...(9)$$

From equation (9), it is possible to calculate the rate constant from any pair of concentration measurements.

[III] Characteristics of First Order Reactions

(i) The unit of velocity constant (k) will be time^{-1}, because

$$k = \frac{1}{t} \log_e \frac{a}{a - x}$$

$$= \frac{1}{\text{time}} \cdot \frac{\text{mole/litre}}{\text{mole/litre}} = \frac{1}{\text{time}}$$

If time is expressed in hour, minute or second then k will be expressed in hour^{-1}, minute^{-1} or second^{-1}, respectively.

(ii) ***The value of velocity constant is independent of the units of concentration chosen.*** If unit of concentration is changed to n times its original value, then equation (7) becomes

$$k = \frac{2.303}{t} \log_{10} \frac{n\,a}{n\,a - n\,x}$$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

This equation is the same as equation (7).

(iii) ***The time taken to complete a certain fraction of a reaction is independent of the initial concentration of the reactant.*** Suppose $t_{0.5}$ is the time taken to reduce the concentration of A from a to $a/2$. Thus, $x = a/2$. So, from equation (7),

$$k = \frac{2.303}{t_{0{\cdot}5}} \log \frac{a}{a-(a/2)}$$

$$t_{0{\cdot}5} = \frac{2.303}{k} \log 2 = \frac{0{\cdot}693}{k} \qquad \text{...(10)}$$

Equation (10) is thus independent of a.

[IV] Examples of First Order Reactions

(i) Inversion of cane sugar. The reaction takes place in presence of an acid which acts as a catalyst and is represented by the equation.

$$\underset{\text{(Dextro rotatory)}}{C_{12}H_{22}O_{11} + H_2O} \xrightarrow{H^+ \text{ ions}} \underbrace{\underset{\substack{\text{Glucose}\\ \text{(Dextro)}}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ \text{(Laevo)}}}{C_6H_{12}O_6}}_{\text{(Laevo rotatory)}}$$

The reaction is bimolecular, but as the concentration of water remains almost constant, the reaction obeys the first order rate expression. Both cane sugar and glucose are dextro rotatory, *i.e.*, rotate the plane of polarisation to the right, but fructose is laevo rotatory, *i.e.*, rotates the plane of polarisation to the left. The laevo rotation of fructose is −92° which more than counteracts the dextro rotation of glucose which is +52.5°. So, as the reaction proceeds the plane of polarisation changes. The rotation of plane of polarised light is measured at different intervals of time with the help of a polarimeter.

The initial rotation of the plane of polarised light is due to cane sugar solution and will be to the right. Let it be r_0. As the reaction proceeds, fructose is formed and so the rotation due to sugar and glucose will go on falling due to laevo rotation of fructose. This fall in the rotation will correspond to the quantity of fructose produced. Let the rotation after a certain interval of time be r_1. After a long time, when the reaction is completed the rotation will correspond to the total inversion of cane sugar. Let it be r_∞. We thus have :

$r_0 - r_\infty$ = Initial concentration of cane sugar (a)

$r_t - r_\infty$ = Concentration of cane sugar at time t [after taking proper sign]

Substituting these values in equation (7), we get

$$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

From the above equation, the values of k come out to be constant at different time intervals.

(2) Hydrolysis of methyl acetate. The hydrolysis of methyl acetate is catalysed by hydrogen ions and takes place as follows :

$$CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + CH_3OH$$

It is a pseudo-unimolecular reaction, since the active mass of water remains constant. As acetic acid is produced in the chemical change, the reaction kinetics is followed by titrating the reaction mixture with standard solution of an alkali.

Let freshly distilled methyl acetate and $N/2$ hydrochloric acid stand in separate bottles in a thermostat for half an hour. When they had acquired the temperature of the bath, mix 5 ml of methyl acetate in 100 ml of $N/2$ HCl. Immediately withdraw 5 ml of the reaction mixture with the help of a pipette and add a few pieces of ice to *freeze the equilibrium*. Now titrate the solution by adding $N/50$ solution of NaOH from the burette using phenolphthalein as an indicator. Similarly, again pipette out 5 ml of the reaction mixture after five minutes and repeat the above procedure. Repeat the procedure by withdrawing 5 ml of the reaction mixture after 10, 15, 20, 30, 45 minutes and finally at the end of 24 hours.

The amount of NaOH used is equivalent to the amount of HCl present originally and the amount of acetic acid produced in the reaction. The amount of HCl present originally can be determined by titrating against the same alkali before the start of the reaction. The amount of acetic acid produced after different intervals of time t can be determined.

The amount of acetic acid formed at the end of the reaction is equivalent to the initial amount (a) of methyl acetate. Suppose V_0, V_t and V_∞ are the volumes of $N/50$ NaOH solution used at zero, t and infinite time, respectively.

The amount of acetic acid produced after time t, *i.e*,, value of x is proportional to $(V_t - V_0)$. The initial concentration of methyl acetate, *i.e.*, value of a is proportional to $(V_\infty - V_0)$. Therefore, amount of ester present at time t, *i.e*,

$$(a - x) \propto (V_\infty - V_0) - (V_t - V_0)$$

$$\propto V_\infty - V_t$$

Hence, from first order rate equation, we have

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

The value of k comes out to be consant showing the reaction to be of the first order.

(3) Decay of thorium emanation. Practically, all radioactive transformations are first order reactions. Rutherford and Soddy (1893) investigated the decay of thorium-X with time. The data for the rate of decay of isolated thorium–X (deposited on a platinum wire, say) was obtained, omitting the initial part of the process. All the units used were arbitrary. Similarly, decay of radium emanation is a first order reaction.

The rate of decay of a radioactive nucleus is proportional to the number of nuclei that can decay. If n is the number of radioactive nuclei at time t, then

$$-\frac{dn}{dt} = k_1 n. (11)$$

If n and n_0 are the number of atoms after time t and initially, respectively, then according to equation (8), we have

$$a - x = n \text{ and } a = n_0$$

Therefore, $$n = n_0 . e^{-kt}$$

On the other hand, if I_0 be the initial activity, measured by the magnitude of the saturation current in an electrometer and I be the activity after time t, then we have

$$I = I_0 \, e^{-kt},$$

or
$$k = \frac{1}{t} \log \frac{I_0}{I} \qquad \text{...(12)}$$

(4) Decomposition of hydrogen peroxide in aqueous solution. The reaction may be written as :

$$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$$

The reaction is catalysed by the addition of platinum. The progress of the reaction is followed by measuring the volume of oxygen evolved after different intervals of time. This can be done by withdrawing a small amount of the solution and determining the concentration of H_2O_2 left behind by titrating against $KMnO_4$ after different intervals of time.

If same volume of the solution is withdrawn and same solution of $KMnO_4$ is used during the experiment, the concentration of H_2O_2 left behind at any instant, *i.e.*, $(a - x)$ is given directly by the volume of $KMnO_4$ solution used. The volume of $KMnO_4$ used before the start of the reaction, *i.e.*, at zero time gives the initial concentration of H_2O_2, *i.e.*, a.

(5) Decompositon of ammonium nitrite in aqueous solution. An aqueous solution of ammonium nitrite decomposes readily as follows :

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

The rate of reaction can be determined by collecting and measuring the volume of N_2 evolved after different intervals of time. In this case, the volume of N_2 collected after a given time gives the measure of the quantity of ammonium nitrite decomposed during that interval of time, *i.e.*, gives the value of x. The total volume of N_2 collected at the end of the reaction gives a measure of the total concentration of ammonium nitrite taken initially, *i.e.*, a. If V_∞ is the volume of N_2 collected at the end of reaction and V_t is the volume of N_2 collected after time t, then the concentration of ammonium nitrite at any time t, *i.e*, $(a - x)$ will be given by $(V_\infty - V_t)$. The rate constant is then represented as :

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Problem 1. ***The optical rotation of sucrose in presence of dil. HCl at various intervals is given in the following table :***

t (min.)	**0**	**10**	**20**	**40**	**90**	**100**	**∞**
Rotation (degree)	**32.4**	**28.8**	**25.5**	**19.6**	**10.3**	**6.1**	**– 14.1**

Show that the reaction is of the first order and find when the solution is optically inactive?

Solution : Initial concentration of sucrose $(a) \propto r_0 - r_\infty$

$$(a - x) \propto r_t - r_\infty$$

For a first order reactions :

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x} = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$$k_{10} = \frac{2{\cdot}303}{10}\log_{10}\frac{32{\cdot}4-(-14{\cdot}1)}{28{\cdot}8-(-14{\cdot}1)} = \frac{2{\cdot}303}{10}\log\frac{46{\cdot}5}{42{\cdot}9} = \mathbf{0{\cdot}00807\ min^{-1}}$$

$$k_{20} = \frac{2{\cdot}303}{20}\log\frac{46{\cdot}5}{39{\cdot}6} = \mathbf{0{\cdot}008137\ min^{-1}}$$

$$k_{40} = \frac{2{\cdot}303}{40}\log\frac{46{\cdot}5}{33{\cdot}7} = \mathbf{0{\cdot}00805\ min^{-1}}$$

$$k_{90} = \frac{2{\cdot}303}{90}\log\frac{46{\cdot}5}{24{\cdot}4} = \mathbf{0{\cdot}007167\ min^{-1}}$$

$$k_{100} = \frac{2{\cdot}303}{100}\log\frac{46{\cdot}5}{20{\cdot}8} = \mathbf{0{\cdot}008040\ min^{-1}}$$

From the calculations, it is clear that the reaction is of the first order and average value of k is **0.007890 min^{-1}**.

(b) When $r_t = 0$, $(a-x) \propto (0 - r_\infty) \propto (+14.1)$

$$t = \frac{2{\cdot}303}{0{\cdot}000789}\log\frac{46{\cdot}5}{14{\cdot}1}$$

$$= \mathbf{150.8\ min}$$

Problem 2. ***A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?***

Solution : For a first order reaction :

$$k = \frac{2{\cdot}303}{t}\log_{10}\frac{a}{a-x}$$

So $$\frac{2{\cdot}303}{t_1}\log\frac{a_1}{a_1-x_1} = \frac{2{\cdot}303}{t_2}\log\frac{a_2}{a_2-x_2}$$

We have, $$x_1 = \frac{15}{100}a_1\ ;\ t_1 = 20\ ;\ x_2 = \frac{60}{100}a_2\ ;\ t_2 = ?$$

$$\frac{2{\cdot}303}{20}\log\frac{a_1}{\left(a_1 - \frac{15}{100}a_1\right)} = \frac{2{\cdot}303}{t_2}\log\frac{a_2}{\left(a_2 - \frac{60}{100}a_2\right)}$$

or $$\frac{1}{20}\log\frac{100}{85} = \frac{1}{t_2}\log\frac{100}{40}$$

or $$t_2 = \frac{20\log\frac{100}{40}}{\log\frac{100}{85}} = \mathbf{112{\cdot}7\ secs.}$$

Problem 3. ***The first order rate constant for the pyrolysis of t-butyl chloroacetate follows the equation:***

$$\mathbf{\log_{10} k\left(min^{-1}\right) = 33{\cdot}91 - \frac{36{\cdot}300}{RT}}$$

Calculate : (a) The pre-exponential factor, A, if $k = Ae^{-E/RT}$. (b) How long it will take for 1 mole to decompose 25% at 227°C ?

Solution : (a) We have

$$k = Ae^{-E/RT}$$

or $$\log_e k = \log_e A - \frac{E}{RT}$$

or $$\log_{10} k = \log_{10} A - \frac{E}{2{\cdot}303\,RT}$$

Comparing the coefficients, we have

$$\log_{10} A = 33{\cdot}91$$

or
$$A = \mathbf{81.28 \times 10^{32}}$$

(b) At 227°C or 500K, we have

$$\log_{10} k = 33{\cdot}31 - \frac{36{\cdot}300}{0{\cdot}002 \times 500} \qquad (\because\ R = 0.002 \text{ k cal. deg}^{-1} \text{ mole}^{-1})$$
$$= -2.39$$

or
$$k = 0.004074 \text{ min}^{-1}$$

Now for a first order reaction

$$k = \frac{2{\cdot}303}{t} \log \frac{a}{a-x}$$

$$0{\cdot}004074 = \frac{2{\cdot}303}{t} \log \frac{a}{a - 0{\cdot}25\,a}$$

$$= \frac{2{\cdot}303 \times 0{\cdot}1249}{0{\cdot}004074} = \mathbf{70{\cdot}60 \text{ min.}}$$

Problem 4. ***If the half life of C^{14} is 5600 years, how many atoms of C^{14} are required to produce an average of five beta emissions per minute ?***

Solution : Since $t_{0{\cdot}5} = 5600 \times 365 \times 24 \times 60$ min., it follows from equation (10) that

$$k = \frac{0{\cdot}693}{2{\cdot}95 \times 10^9} = 2{\cdot}35 \times 10^{-10} \text{ min}^{-1}$$

If $-\Delta n / \Delta t = 5 \text{ min}^{-1}$, then from equation (11),

$$n = \frac{-(\Delta n / \Delta t)}{k} = \frac{5{\cdot}00}{2{\cdot}35 \times 10^{-10}} = \mathbf{2{\cdot}13 \times 10^{10} \text{ atoms.}}$$

Problem 5. ***The rate of reaction $2NO + Cl_2 \rightarrow 2NOCl$ is doubled when the concentration of Cl_2 is doubled. When the concentrations of both the reactants are doubled the rate becomes eight times. What is the order of reaction with respect to NO and with respect to Cl_2 ? What is the total order ?***

Solution : As the reaction rate is doubled, when the concentration of Cl_2 is doubled, *i.e.*, rate $\propto Cl_2$ or order of reaction with respect to Cl_2 is one.

The rate becomes eight times on doubling the concentrations of both NO and Cl_2. This shows that the rate would become four times if only concentration of NO is doubled, *i.e.*, rate $\propto [NO]_2$ or order of reaction with respect to NO is two.

The total order of reaction = 1 + 2 = **3**.

Problem 6. ***A reaction $A_2 + 2B \rightarrow 2AB$ is first order with respect to both A_2 and B. Derive the rate equation in terms of a, b, x, t and k, where a and b are initial concentrations of A_2 and B, respectively, x is the concentration of AB at any time t and k is the specific reaction rate (at $t = 0, x = 0$.).***

Solution : As the order with respect to A_2 and B is one, so according to law of mass action, the rate equation is

$$\frac{dx}{dt} = k\,[A_2]\,[B] \qquad \text{...(i)}$$

At time t, [AB] = x, so from stoichiometry of the reaction

$$[A_2] = \left(a - \frac{x}{2}\right),\ [B] = (b - x)$$

Substituting the values of $[A_2]$ and [B] in equation (i), we get the required rate equation of the reaction which is as follows :

$$\frac{dx}{dt} = k\left(a - \frac{x}{2}\right)(b - x)$$

7·9. SECOND ORDER REACTIONS

[I] Definition of Second Order Readions

A reaction is said to be of second order if its reaction rate is determined by the change of two concentration terms of reactants.

[II] Rate Equation of Second Order Reactions

It can be represented as,

$$\frac{dx}{dt} = k\,C_A^2 \qquad \text{(For 2A} \rightarrow \text{Products)}$$

$$\frac{dx}{dt} = k\,C_A \cdot C_B \qquad \text{(For A + B} \rightarrow \text{Products)}$$

(a) Rate expression when concentrations of both reactants are equal. Suppose, we start with equal concentrations of both the reactants, say a mole. Let x mole of each be transformed during an interval of time t. The velocity of the reaction will then be given by

$$\frac{dx}{dt} \propto (a - x)(a - x)$$

or
$$\frac{dx}{dt} = k\,(a - x)^2$$

or
$$\frac{dx}{(a - x)^2} = k\,dt$$

or
$$\int \frac{dx}{(a - x)^2} = \int k\,dt$$

or
$$\frac{1}{a - x} = k\,t + I \qquad \text{...(13)}$$

where I = integration constant.

When $t = 0, x = 0$, we have from equation (13),

$$\frac{1}{a} = I$$

Substituting the value of I in equation (13), we get

$$\frac{1}{a - x} = k\,t + \frac{1}{a}$$

or
$$k = \frac{1}{t}\left[\frac{1}{a - x} - \frac{1}{a}\right]$$

$$= \frac{1}{t} \cdot \frac{x}{a(a - x)} \qquad \text{...(14)}$$

Equation (14) is the rate equation for a second order reaction when concentrations of both the reactants are equal.

(b) Rate expression when the concentrations of the reactants are not equal. Suppose a and b represent the initial concentrations of the reactants and

$(a-x)$ and $(b-x)$ be their respective concentrations after time t. The reaction rate will be given by

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

$$= k(a-x)(b-x)$$

or

$$\frac{dx}{(a-x)(b-x)} = k\,dt$$

Splitting into partial fractions, we get

$$\frac{1}{(a-b)}\left\{\frac{dx}{(b-x)} - \frac{dx}{(a-x)}\right\} = k\,dt$$

Integrating it we get

$$\frac{1}{(a-b)}[-\log(b-x) + \log(a-x)] = kt + I \qquad \text{...(15)}$$

where $I =$ integration constant.

When $t = 0, x = 0$ then from equation (15), we have

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

Substituting the value of I in equation (15), we get,

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

or

$$k = \frac{1}{t(a-b)}\log\frac{b(a-x)}{a(b-x)} \qquad \text{...(16)}$$

Converting it to logarithm to the base 10,

$$k = \frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)} \qquad \text{...(17)}$$

Equations (16) and (17) are the general rate equations for a second order reaction.

[III] Characteristics of Second Order Reactions

(1) As in equation (14) or (16) there is one concentration term in the numerator and two concentration terms in the denominator, ***the numerical value of k will change with the change in the units in which the concentration is expressed.***

(2) The unit of k is given by (time)$^{-1}$ × (concentration)$^{-1}$ or (mole/litre)$^{-1}$ sec^{-1}, if time is expressed in second and concentration in mole lit^{-1}.

From equation (14), we have

$$k = \frac{1}{t}\frac{x}{a(a-x)}$$

$$= \frac{1}{\text{sec.}}\cdot\frac{\text{mole/litre}}{(\text{mole/litre})(\text{mole/litre})} = \frac{1}{\text{sec}}\cdot\frac{1}{\text{mole/litre}}$$

So, unit of k will be (mol L^{-1}) sec^{-1} or mol^{-1} L sec^{-1}.

(3) The time required to complete a certain fraction of the reaction is inversely proportional to the initial concentration of the reactants.

Let $t_{0.5}$ be the time required for the completion of half the reaction. Its value can be calculated by substituting $x = a/2$ in equation (13). Therefore, we have,

$$k = \frac{1}{t_{0.5}} \cdot \frac{\frac{a}{2}}{a\left(a - \frac{a}{2}\right)}$$

$$= \frac{1}{t_{0.5}} \cdot \frac{\frac{a}{2}}{a \cdot \frac{a}{2}}$$

or $$t_{0.5} = \frac{1}{k} \cdot \frac{1}{a}$$

or $$t_{0.5} \propto \frac{1}{a}$$

(4) When one of the reactants is present in large excess, the second order rate expression becomes a first order rate expression.

From equation (16) we have

$$k = \frac{1}{t\,(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)}$$

Suppose the value of a is much larger than b, then the values of b and x can be neglected in comparison to a, so we have

$$k = \frac{1}{t\,.\,a} \log \frac{b\,.\,a}{a\,(b-x)} \quad \text{or} \quad k\,.\,a = \frac{1}{t} \log \frac{b}{(b-x)}$$

or $$k' = \frac{1}{t} \log \frac{b}{b-x} \qquad \text{...(18)}$$

Equation (18) is of the same form as given for a first order reaction.

[IV] Examples of Second Order Reactions

(i) Saponification of esters. The reaction between ethyl acetate and alkali is of second order and takes place as follows :

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

The reaction kinetics may be studied as follows :

Take 50 ml of 0.01M ester solution and 50 ml of 0.01M NaOH solutions in two separate flasks and keep them in a water bath to attain the same temperature. When the flasks have acquired the same temperature, the alkali is poured as rapidly as possible into the ester solution. Immediately pipette out 10 ml of the reaction mixture into a conical flask. The mixture is titrated against a standard acid. 10 ml reaction mixture is then taken out of the reaction vessel after 10, 20, 30, 40 minutes. These solutions are then titrated against standard acid solution as before. The infinite reading is taken after 24 hours. Let the titre values at the beginning of the experiment, *i.e.*, at zero time, at any time t and infinite time be V_0, V_t and V_∞, respectively.

Volume of standard acid solution used at the beginning of the experiment, *i.e.*, at zero time (V_0) $\propto$ Initial concentration of NaOH (a), *i.e.*, $a \propto V_0$.

Volume of standard acid solution used at any instant of time t, *i.e.*, $V_t \propto$ Concentration of NaOH at that instant, *i.e.*, $(a - x)$. So, $(a - x) \propto V_t$.

From the above equations, we can have

$$x \propto V_0 - V_t$$

The second order rate expression is given by

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)}$$

Substituting the values of a, x and $(a-x)$ in terms of volume we get

or $$k = \frac{1}{t} \cdot \frac{(V_0 - V_t)}{V_0 \cdot V_t}.$$

(ii) Reaction between persulphate and iodide ions. In a second order reaction, it is not necessary that number of reactants should be only two. As a matter of fact, there may be only one reactant and the velocity may be proportional to the square of its concentration or there may be more than two reactants, but the reaction velocity may be proportional to the product of concentrations of only two reactants.

The reaction between persulphate and iodide is represented as

$$K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$$

The reaction seems to be of third order. Actually, the rate of the reaction is given by

$$\frac{dx}{dt} = k.\ [I^-]\ [S_2O_8^{2-}]$$

Hence, the order of the reaction is two and not three. The mechanism suggested is :

First stage : $S_2O_8^{2-} \rightleftharpoons 2\,SO_4^{-1}$

Second stage : $SO_4^{-1} + I^{-1} \rightarrow SO_4^{2-} + I$

Third stage : $I + I \rightarrow I_2$

The first and third stages are fast,whilst the second stage is slow. So, the second stage determines the order of the reaction.

Problem 1. ***For a second order reaction***

$$\mathbf{CH_3COOC_2H_5 + OH^- \rightarrow CH_3COO^- + C_2H_5OH}$$

at 25°C, $k = 6.21 \times 10^{-3}$ litre mole^{-1} sec^{-1}. Calculate the time for the hydrolysis of 90% ester, if the initial concentration of the reactants in the reaction mixture are :

***(a)* 0.05 *M* ester + 0.10 *M* NaOH. *and (b)* 0.05 *M* ester + 0.05 *M* NaOH.**

Solution : **(a)** For a second order reaction when the initial concentration of the reactants are not equal, we have

$$k = \frac{2{\cdot}303}{t\,(a-b)} \log_{10} \frac{b\,(a-x)}{a\,(b-x)}$$

or $$t = \frac{2{\cdot}303}{k\,(a-b)} \log_{10} \frac{b\,(a-x)}{a\,(b-x)}$$

$a = 0.1\text{M}$; $b = 0.05\text{M}$; $x = 0.05 \times 90/100 = 0.045$ M.

Therefore,

$$t = \frac{2{\cdot}303}{0.0062 \times (0{\cdot}1 - 0{\cdot}05)} \log_{10} \frac{0{\cdot}05\,(0{\cdot}1 - 0{\cdot}045)}{0{\cdot}1 \times (0{\cdot}05 - 0{\cdot}045)}$$

$$= \mathbf{5.5 \times 10^3\ sec}$$

(b) For a second order reaction, when the initial concentrations of the reactants are equal, we have

$$k = \frac{1}{a\,t}\cdot\frac{x}{a-x}$$

Therefore, $$a = 0{\cdot}1\text{ M};\ x = 0{\cdot}1\times\frac{99}{100} = 0.09\text{ M}$$

$$t = \frac{1}{a\,.\,k}\cdot\frac{x}{a-x}$$

$$= \frac{1}{0{\cdot}1\times 0{\cdot}00621}\cdot\frac{0{\cdot}09}{(0{\cdot}1-0{\cdot}09)} = \mathbf{14{\cdot}3\times 10^3\ sec}$$

Problem 2. ***In a first order reaction it takes 100 sec for half the reaction to complete. How long will it take for the 99% change ? What will this time be if the reaction is of the second order and involves only one reactant ?***

Solution : For half the reaction, $x = a/2$, then

$$k = \frac{2{\cdot}303}{t_{0\cdot5}}\log_{10}\frac{a}{a-\left(\frac{1}{2}\right)} = \frac{2{\cdot}303}{t_{0\cdot5}}\log_{10} 2 \qquad \text{...(i)}$$

For 99% change, $x = 0.99a$

or $$k = \frac{2{\cdot}303}{t}\log_{10}\frac{a}{a-0{\cdot}99a} = \frac{2{\cdot}303}{t}\log 100 \qquad \text{...(ii)}$$

From equations (i) and (ii), we get

$$\frac{2{\cdot}303}{t_{0\cdot5}}\log 2 = \frac{2{\cdot}303}{t}\log 100$$

or $$\frac{2.303}{100}\log 2 = \frac{2{\cdot}303}{t}\log 100$$

or $$t = 100\cdot\frac{\log 100}{\log 2} = \frac{200}{0{\cdot}3010} = \mathbf{664\ sec.}$$

For second order reaction involving one reactant,

$$k = \frac{1}{a\,t}\cdot\frac{x}{a-x}$$

or $$\frac{1}{a_1 t_1}\cdot\frac{x_1}{a_1-x_1} = \frac{1}{a_1 t_2}\cdot\frac{x_2}{a_1-x_2}$$

or $$\frac{1}{t_1}\cdot\frac{x_1}{a_1-x_1} = \frac{1}{t_2}\cdot\frac{x_2}{a_1-x_2}$$

∴ $$\frac{1}{100}\cdot\frac{\frac{a_1}{2}}{a_1-\frac{a_1}{2}} = \frac{1}{t_2}\cdot\frac{\frac{99a_1}{100}}{a_1-\frac{99a_1}{100}}$$

$$\frac{1}{100} = \frac{1}{t_2}\times 99$$

or $$t_2 = 99\times 100 = \mathbf{9900\ sec.}$$

Problem 3. ***At 298 K, the specific rate constant for the hydrolysis of ethyl acetate by sodium hydroxide is 6.36 lit mole^{-1} min^{-1}. Starting with concentrations of base and ester of 0.01 mole lit^{-1}, what proportion of ester will be hydrolysed in 20 minutes ?***

Solution : From the given data

$$a = 0.01\text{ mole lit}^{-1}$$

and $$t = 20\text{ min.}$$

$$k = 6{\cdot}36 \text{ lit mole}^{-1} \text{ min}^{-1}$$

Let $x = fa$, where f is the fraction decomposed. The second order rate expression is given by

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)}$$

Substituting the values, we get,

$$k = \frac{1}{t} \cdot \frac{fa}{a\,(a-fa)} = \frac{1}{t \cdot a} : \frac{f}{1-f}$$

or $$6.36 = \frac{1}{20 \times 0.01} \cdot \frac{f}{1-f}$$

or $$\frac{f}{1-f} = 6.36 \times 20 \times 0.01 = 1.272$$

or $$f = 0{\cdot}56 \text{ or } \mathbf{56\%}$$

7·10. THIRD ORDER REACTIONS

[I] Definition of Third Order Reactions

A reaction is said to be of third order if its reaction rate is determined by the change of three concentration terms of reactants.

Reactions of third and higher orders are rare, but there are in fact reactions which are definitely of third and sometimes of higher order. This is due to the fact that the probability of three modecules coming to a single point simultaneously, *i.e.*, probability of trimolecular collisions is much less as compared to unimolecular or bimolecular collisions.

[II] Rate Equation of Third Order Reactions

For a third order reaction :

$$A + B + C \rightarrow \text{Products}$$

The reaction rate is given by,

$$\frac{dx}{dt} = k\,(a-x)\,(b-x)\,(c-x)$$

where a, b and c are the initial concentrations of reactants A, B and C and x is the concentration of each reactant decomposed in time t.

[I] Case I. When $a = b = c$ **(Integrated rate law)**

$$\frac{dx}{dt} = k\,(a-x)^3$$

$$\frac{dx}{(a-x)^3} = k\,dt$$

On integration, we get

$$\int \frac{dt}{(a-x)^3} = \int k\,dt$$

$$\frac{1}{2\,(a-x)^2} = kt + I \qquad \dots (1)$$

where I = integration constant.

When $t = 0, x = 0$, we then have

$$\frac{1}{2\,a^2} = I$$

Substituing the value of I in equation (1), we get

$$\frac{1}{2\,(a-x)^2} = k\,t + \frac{1}{2a^2}$$

$$k\,t = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

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

$$k = \frac{1}{2t}\cdot\frac{x\,(2a-x)}{a^2\,(a-x)^2} \qquad \text{...(2)}$$

[II] Case II. When $a \neq b \neq c$ **(Integrated rate law)**

$$\therefore \qquad \frac{dx}{dt} = k\,(a-x)\,(b-x)\,(c-x)$$

or

$$\frac{dx}{(a-x)\,(b-x)\,(c-x)} = k\,dt \qquad \text{...(3)}$$

Let

$$\frac{1}{(a-x)\,(b-x)\,(c-x)} = \frac{p}{(a-x)} + \frac{q}{(b-x)} + \frac{z}{(c-x)} \qquad \text{...(4)}$$

Multiplying by $(a-x)\,(b-x)\,(c-x)$ we get

or $\quad 1 = p\,(b-x)\,(c-x) + q\,(a-x)\,(c-x) + z\,(a-x)\,(b-x)$

Putting $x = a$, b and c, respectively in equation (4), we get

$$p = \frac{1}{(b-a)\,(c-a)} \qquad \text{...(5)}$$

$$q = \frac{1}{(a-b)\,(c-b)} \qquad \text{...(6)}$$

$$z = \frac{1}{(a-c)\,(b-c)} \qquad \text{...(7)}$$

Substituting the values of p, q and z from equations (5), (6) and (7) in equation (4) and rearrangement, we get a differential equation which is equivalent to equation (2).

$$-\frac{1}{(a-b)\,.\,(c-a)}\cdot\frac{dx}{(a-x)} - \frac{1}{(a-b)\,(b-c)}\cdot\frac{dx}{(b-x)} - \frac{1}{(b-c)\,.\,(c-a)}\cdot\frac{dx}{(c-x)} = k\,dt$$

On integrating both the sides, we get

$$\frac{1}{(a-b)\,(c-a)}\log_e(a-x) + \frac{1}{(a-b)\,(b-c)}\log_e(b-x) + \frac{1}{(b-c)\,(c-a)}\log_e(c-x)$$

$$= k\,t + I \qquad \text{...(8)}$$

where I = integration constant.

When $t = 0$, $x = 0$, we get from equation (8),

$$\frac{1}{(a-b)\,(c-a)}\log_e a + \frac{1}{(a-b)\,(b-c)}\log_e b + \frac{1}{(b-c)\,(c-a)}\log_e c = I$$

Substituting the value of I in equation (8), we get

$$\frac{1}{(a-b)\,(c-a)}\log_e(a-x) + \frac{1}{(a-b)\,(b-c)}\log_e(b-x) + \frac{1}{(b-c)(c-a)}\log_e(c-x)$$

$$= kt + \left[\frac{1}{(a-b)(c-a)}\log_e a + \frac{1}{(a-b)(b-c)}\log_e b + \frac{1}{(b-c)(c-a)}\log_e c\right]$$

or $$\left[\frac{1}{(a-b)(c-a)}\log_e\frac{a-x}{a}+\frac{1}{(a-b)(b-c)}\log_e\frac{b-x}{b}+\frac{1}{(b-c)(c-a)}\log_e\frac{c-x}{c}\right]=k\,t$$

or $$k=\frac{1}{t}\left[\frac{(b-c)\log_e\frac{a-x}{a}+(c-a)\log_e\frac{b-x}{b}+(a-b)\log_e\frac{c-x}{c}}{(a-b)(b-c)(c-a)}\right] \quad \ldots(9)$$

[III] Case III. *When two of the molecules are identical and third is different* (Integrated rate law)

$$2A \quad + \quad B \longrightarrow \text{Products}$$

Concentration when $t = 0$ $\quad a \quad b$

Concentration when $t = t$ $\quad (a-2x) \quad (b-x)$

$$\frac{dx}{dt}=k\,(a-2x)^2\,(b-x)$$

or $$\frac{dx}{(a-2x)^2\,(b-x)}=kdt \quad \ldots(10)$$

Breaking into partial fractions, we get

$$\frac{1}{(a-2x)^2\,(b-x)}=\frac{px+q}{(a-2x)^2}+\frac{z}{(b-x)} \quad \ldots(11)$$

or $$1=(px+q)\,(b-x)+z(a-2x)^2$$

or $$1=(qb+za^2)+(pb-q-4za)\,x+(4z-p)\,x^2 \quad \ldots(12)$$

Equating coefficients of x^2, x and constant on both sides of equation (12), we get

$$4z-p=0 \text{ or } p=4z \quad \ldots(13)$$

and $$pb-q-4za=0 \quad \ldots(14)$$

and $$qb+za^2=1$$

$\therefore$ $$q=\frac{1-za^2}{b} \quad \ldots(15)$$

Putting values of p and q from equations (13) and (15) in equation (14),

$$4zb-\frac{(1-za^2)}{b}-4za=0$$

or $$4zb^2-1+za^2-4abz=0$$

or $$4zb^2+za^2-4abz=1$$

or $$z\,(4b^2+a^2-4ab)=1$$

or $$z\,(2b-a)^2=1$$

$\therefore$ $$z=\frac{1}{(2b-a)^2} \quad \ldots(16)$$

Integrating equation (10), we get

Now $$\int\frac{dx}{(a-2x)^2\,(b-x)}=k\int_0^t dt$$

or $$\int_0^x\frac{px+q}{(a-2x)^2}\,dx+\int_0^x\frac{z}{(b-x)}\,dx=k\int_0^t dt \quad \text{(From equation 11)}$$

Substituting the values of p, q and z, we get

$$\int_0^x \frac{\left[\frac{4x}{(2b-a)^2}\right]+\left[4(b-a)/(2b-a)^2\right]}{(a-2x)^2}\,dx+\int_0^t \frac{[1/(2b-a)^2]}{(b-x)}\,dx=k\int_0^t dt$$

$$\int_0^x \frac{4xdx}{(2b-a)^2(a-2x)^2}+\int_0^x \frac{4(b-a)}{(2b-a)^2(a-2x)^2}\,dx+\int_0^x \frac{dx}{(2b-a)^2(b-x)}=k\int_0^t dt$$

Multiplying both sides by $(2b-a)^2$

$$\int_0^t \frac{4xdx}{(a-2x)^2}+\int_0^x \frac{4(b-a)\,dx}{(a-2x)^2}+\int_0^x \frac{dx}{(b-x)}=(2b-a)^2\,k\int_0^t dt$$

or
$$-\int \frac{2xd\,(a-2x)}{(a-2x)^2}-(b-a)\int_0^x \frac{2d\,(a-2x)}{(a-2x)^2}-\int_0^x \frac{d\,(b-x)}{(b-x)}=(2b-a^2)\,k\int_0^t dt$$

$$\log\left(\frac{a-2x}{a}\right)+\frac{2ax}{a\,(a-2x)}+\frac{4x\,(b-a)}{a\,(a-2x)}+\log\left(\frac{b}{b-x}\right)=(2b-a)^2\,kt$$

or
$$\ln\left[\frac{b\,(a-2x)}{a\,(b-x)}\right]+\left[\frac{2ax+4x\,(b-a)}{a\,(a-2x)}\right]=(2b-a)^2\,kt$$

$$\log\left[\frac{b\,(a-2x)}{a\,(b-x)}\right]+\left[\frac{2x\,(2b-a)}{a\,(a-2x)}\right]=(2b-a)^2\,kt$$

$$\therefore \quad k=\frac{1}{t(2b-a)^2}\left[\frac{2x\,(2b-a)}{a\,(a-2x)}+\log\left[\frac{b\,(a-2x)}{a\,(b-x)}\right]\right] \qquad \text{...(17)}$$

Equation (17) is kinetic equation for the above type of third order reaction.

The kinetics of the nitric oxide reactions mentioned below have actually been observed to obey equation (17). All these reactions take place in gas-phase.

(a) $2NO + H_2 \longrightarrow N_2O + H_2O$

(b) $2NO + O_2 \longrightarrow 2NO_2$

(c) $2NO + Cl_2 \longrightarrow 2NOCl$

(d) $2NO + Br_2 \longrightarrow 2NOBr$

[III] Characteristics of Third Order Reactions

(1) From equation (2), we have

$$k=\frac{1}{\text{time}}\cdot\frac{(\text{concentration}\times\text{concentration})}{(\text{concentration})^2\times(\text{concentration})^2}$$

$$=\frac{1}{\text{time}}\times\frac{1}{(\text{concentration})^2}.$$

The unit of k will be ***(time)***$^{-1}$ ***(concentration)***$^{-2}$. If concentration is expressed in mole/litre and time in second then k will be expressed in $(\text{sec})^{-1}$ $(\text{mole/litre})^{-2}$ *i.e.*, $(\text{mol L}^{-1})^{-2}\ \text{sec}^{-1}$ or $\text{mol}^{-2}\ \text{L}^2\ \text{sec.}^{-1}$.

(2) ***The time taken to complete a certain fraction of a reaction is inversely proportional to the square of the initial concentration of the reactants.***

The time ($t_{0.5}$) taken for the completion of half the reaction is given by $x = a/2$. Therefore,

$$k = \frac{1}{2t_{0.5}} \frac{a/2\,(2a - a/2)}{a^2\,(a - a/2)}$$

or
$$t_{0.5} = \frac{1}{2t} \cdot \frac{a/2.\,3a/2}{a^2.a^2/4} = \frac{3}{2k} \cdot \frac{1}{a^2}$$

i.e.
$$t_{0.5} \propto \frac{1}{a^2}$$

[IV] Examples of Third Order Reactions

(i) Reaction between *p*-nitro benzoyl chloride and *n*-butyl alcohol.

(ii) Reaction between silver acetate and sodium formate.

$$HCOONa + 2CH_3COOAg \longrightarrow 2Ag + CO_2 + CH_3COOH + CH_3COONa$$

7·11. HALF LIFE OF SYSTEMS INVOLVING MORE THAN ONE REACTANT

We have seen that the half life of one reactant system of n^{th} order is inversely proportional to $(n-1)^{th}$ power of initial concentration of the reactant, *i.e.*, $t_{0.5} \propto 1/a^{(n-1)}$, where a = initial concentration of one reactant system. *But in more than one reactant system, the half life is decided by the reactant present in the smallest amount, i.e., it is the time for half of the reactant present in the smallest amount.* This fundamental concept is made clear by taking the following problem.

Problem 1. ***The reaction***

$$2A + B \longrightarrow C + D$$

goes to completion and follows the following rate law

$$-\frac{d\,[A]}{dt} = k\,[A]^2\,[B]$$

Fill the gaps left in the following information :

Set	$[A]_0 \times 10^6$ (*mole dm*$^{-3}$)	$[B]_0 \times 10^6$ (*mole dm*$^{-3}$)	***Half time*** ($t_{0.5}$)
1	300	40	62.6
2	300	60	—
3	5	300	625
4	10	300	—

Solution : In more than one reactant system, the half life is the time for half of the reactant present in small amount.

Sets 1 and 2. In set 1, B is in small amount, the half life is for reactant B. Further the reaction is of first order w.r.t. B so the half life is independent of initial concentration. Therefore, for same values of $[A]_0$, the $t_{0.5}$ corresponding to $[B]_0 = 60$ will be the same as in set 1.

So, missing data in set 2 is 62.6 seconds.

Sets 3 and 4. The reactant, A is present in small amount, hence $t_{0.5}$ will depend upon A. According to rate law expression the order w.r.t. A is 2, *i.e.*,

$$t_{0.5} = \frac{1}{ka} = \frac{1}{k\,[A]_0}$$

or $$\ln t_{0.5} = \ln\left[\frac{1}{A}\left(\frac{2^{(n-1)}-1}{(n-1)\,a^{(n-1)}}\right)\right] + \frac{E_a}{RT}$$

or $$\ln t_{0.5} = \ln A' + \frac{E_a}{RT} \qquad \text{...(5)}$$

where $A' = \frac{1}{A}\left(\frac{2^{(n-1)}-1}{(n-1)\,a^{(n-1)}}\right)$

The relation (5) shows the dependence of $t_{0.5}$ on temperature. This equation shows that increase of temperature decreases the half life period. Further, plot of $\ln t_{0.5}$ against $\frac{1}{T}$ is a straight line with slope equal to E_a/R. [Fig. (2)].

Therefore, $E_a = R\,.\,\text{slope} = R\,.\,\tan\theta$.

If at two temperatures T_1 and T_2, the half life periods of a reaction are, respectively $(t_{0.5})_1$ and $(t_{0.5})_2$, then from equation (5),

$$\log\left[\frac{(t_{0.5})_2}{(t_{0.5})_1}\right] = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right)$$

Equation (5) enables us to calculate E_a.

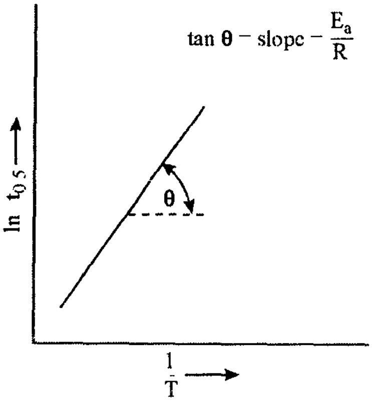


Fig. 2

7·12. NEGATIVE ORDER REACTIONS

Sometimes, the reaction rate decreases as the concentration of one of its substances is increased. For example, the conversion of ozone into oxygen, *i.e.*,

$$2O_3 \longrightarrow 3O_2$$

follows the rate law,

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

So, the order of reaction with respect to O_2 is -1.

It may be noted that negative orders like zero and fractional orders are obtained, whenever the desired reaction does not occur as written, *i.e.*, in a single step conversion, but involves more complicated reaction mechanism consisting of two or more elementary steps.

7·13. DETERMINATION OF ORDER OF REACTION

Different methods for determining the order of reaction are discussed below:

[I] Integration Method

In this method, the initial concentration of all the reactants taking part are determined. The concentration of the reacting substance is then determined at different intervals of time. The different values of a and x are thus determined. These values are substituted in various order rate expressions, and the equation which gives the most constant values of velocity constant for a series of intervals of time gives the order of the reaction. The method, therefore, involves the trial of one equation after another till the correct one is found.

$$\therefore \quad \frac{(t_{0.5})_3}{(t_{0.5})_4} = \frac{[A]_{0\,(4)}}{[A]_{0\,(3)}}$$

$$\frac{625}{(t_{0.5})_4} = \frac{10}{5} = 2$$

$$\therefore \quad (t_{0.5})_4 = \frac{625}{2} = 312.5 \text{ sec.}$$

So, missing data in set 4 is 312.5 sec.

For the ***pseudo-order reaction*** the half life is always defined with respect to the concentration of species present in small amounts.

[I] Relation Between Half Life Period and Temperature

The relationship between half life period ($t_{0.5}$) and temperature (T) for a reaction can be obtained with the help of Arrhenius equation. The Arrhenius equation is,

$$k = A.\, e^{-E_a/RT}$$

where A = Pre-exponential factor or frequency factor

k = Rate constant at temperature T

E_a = Energy of activation of the reaction

Taking the logarithm to the base '*e*', we get

$$k = \ln A - \frac{E_a}{RT} \qquad \text{...(1)}$$

Now, for one component system, *i.e.*,

$$n\text{A} \longrightarrow \text{Products},$$

the half-life period, $t_{0.5}$ is related to its initial concentration by equation (2) except $n = 1$, *i.e.*,

$$t_{0.5} = \frac{2^{(n-1)} - 1}{(n-1)\, a^{(n-1)} \,.\, k} \qquad \text{...(2)}$$

where a = Initial concentration of the reactant

n = Order of reaction

k = Rate constant

For $n = 1$, we have

$$t_{0.5} = \frac{0.693}{k}$$

If the reaction is of pseudo-order, the half life is always defined with respect to the concentration of species present in small amounts.

Taking logarithm of equation (2), base being '*e*', we get

$$\ln t_{0.5} = \ln\left[\frac{2^{(n-1)} - 1}{(n-1)\, a^{(n-1)}}\right] - \ln k \qquad \text{...(3)}$$

Combining equations (1) and (3), we get

$$\ln t_{0.5} = \ln\left[\frac{2^{(n-1)} - 1}{(n-1)\, a^{(n-1)}}\right] - \ln A + \frac{E_a}{RT} \qquad \text{...(4)}$$

[II] Fractional Change Method or Half Life Method

As discussed before, the time taken to complete one half of the reaction is independent of initial concentration of the reactant for a first order reaction, inversely proportional to the initial concentration of the reactant for a second order reaction, inversely proportional to the square of the initial concentration of the reactant for a third order reaction. This is so, provided the reactants are all taken at the same initial concentration. Thus, in general, for a reaction of n^{th} order,

$$t_{0.5} \propto \frac{1}{a^{n-1}}$$

Suppose we start with two independent reactions with initial concentrations a_1 and a_2. Let the corresponding times be t_1 and t_2, respectively, then

$$t_1 \propto \frac{1}{a_1^{n-1}}$$

and $$t_2 \propto \frac{1}{a_2^{n-1}}$$

or $$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

or $$\log\frac{t_1}{t_2} = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

or $$n = 1 + \frac{\log(t_1 / t_2)}{\log(a_2 / a_1)}$$

From this equation the order of reaction, n can be calculated.

In case of gaseous reactions, the initial pressure (p) can be taken instead of initial concentration (a), so that,

$$n = 1 + \frac{\log(t_1 / t_2)}{\log(p_2 / p_1)}$$

[III] Isolation Method

This method was given by Ostwald in 1902. In this method, the concentration of all reactants except one is taken in excess and the order of reaction is then determined by any method with respect to that reactant which is not taken in excess. The reactant which is not taken in excess, is said to be ***isolated*** from other reactants which are taken in excess. Then in another separate experiment, the concentration of any other reactant is not taken in excess, keeping that of all the others in excess. The order of reaction is again determined. The total order of reaction will be the sum of the order of all isolated reactions.

Consider the reaction

$$a_1\,\mathrm{A} + n_2\mathrm{B} + n_3\mathrm{C} \longrightarrow \text{Products}$$

The reaction velocity is given as follows :

$$\frac{dx}{dt} = k.\,C_{\mathrm{A}}^{n_1}\,.\,C_{\mathrm{B}}^{n_2}\,.\,C_{\mathrm{C}}^{n_3}$$

Let the order of reaction be n_1 when A is isolated, n_2 when B is isolated, and n_3 when C is isolated. The order of reaction as a whole will then be given by $n_1 + n_2 + n_3$.

The advantage of this method is that the mode of action of each component can be determined separately and disturbing effects can be traced to the origin.

[IV] Van't Hoff Differential Method

In different method, the initial rate of reaction is measured when the concentration of one of the reactant is varied and that of all others are kept constant. Initial reaction rates are determined by measuring the slopes of concentration-time curves at zero time. These initial rates are related to the concentration of the reactants through the expression

$$\left(\frac{dx}{dt}\right)_0 = k.\ [A]_0^x\ [B]_0^y$$

When [B] is kept constant,

$$\left(\frac{dx}{dt}\right)_0 = k'\ [A]_0^x$$

where $k' = k\ [B]_0^y$

or
$$\ln\left(\frac{dx}{dt}\right)_0 = \ln k' + x \ln [A]_0$$

So, if we measure the initial reaction rates while varying the initial concentration of one reactant, and keeping that of the others constant. A plot of ln $(dx/dt)_0$ against ln $(A)_0$ gives a straight line whose slope gives the value of x, the order of reaction with respect to A.

Similarly, the order of reaction with respect to the other reactant may be determined by measuring the initial reaction rates with varying concentration of B, at constant [A].

In several cases, (dx/dt) may be replaced by $(\Delta x/\Delta t)_0$, where, Δt is the time required to convert the initial concentration of the reactant by a small amount Δx. One of the reactions where such a conversion can be easily carried out is the reaction between persulphate and iodide ions. The experiment is called ***iodine clock experiment***. The involved reaction is

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

The reaction mixture besides containing $S_2O_8^{2-}$ and I^- also contains the known volumes of very dilute solutions of sodium thiosulphate and starch. In the beginning the produced iodine reacts with $Na_2S_2O_3$ present in the solution. When the whole amount of $Na_2S_2O_3$ is consumed, the produced iodine gives blue colour with starch. The strength of hypo solution is so adjusted that the blue colour appears in a very small interval of time, say, within 30 to 40 seconds, when the experiment is carried out with the largest concentrations of $S_2O_8^{2-}$ and I^- ions. The different sets of solutions may be prepared as shown in the table–2.

Table-2. Different sets of solutions for iodine clock experiment

	Flask-1		Flask-2			
	Volume of 0.1 M $S_2O_8^{2-}$ V/cm^3	**Volume of water V/cm^3**	**Volume of 0.1 M I^- V/cm^3**	**Volume of water V/cm^3**	**Volume of $Na_2S_2O_3$ solution V/cm^3**	**Volume of starch solution V/cm^3**
Set 1	10.0	0.0	10.0	0.0	5.0	3.0
	8.0	2.0	10.0	0.0	5.0	3.0
	6.0	4.0	10.0	0.0	5.0	3.0
	4.0	6.0	10.0	0.0	5.0	3.0
Set-2	10.0	0.0	8.0	2.0	5.0	3.0
	10.0	0.0	6.0	4.0	5.0	3.0
	10.0	0.0	4.0	6.0	5.0	3.0

In set-1, the volume of $S_2O_8^{2-}$ is varied keeping the volume of I^- constant, while in set-2 the volume of I^- is varied keeping the volume of $S_2O_8^{2-}$ constant. This gives us different initial concentrations of $S_2O_8^{2-}$ and I^-. The two flasks are mixed and the times are noted till the blue colour appears. The different times so obtained may be analysed as follows.

The rate equation of $S_2O_8^{2-} - I^-$ reaction may be written as

$$\frac{dx}{dt} = k\,[S_2O_8^{2-}]^m\,[I^-]^n \qquad \ldots (1)$$

For set-1, equation (1) reduces to

$$\frac{dx}{dt} = k'\,[S_2O_8^{2-}]^m$$

Now $\left(\frac{dx}{dt}\right)_0$ may be replaced by $(\Delta x)_0/(\Delta t)_0$, where $(\Delta x)_0$ represents the small amount of iodine produced in a small interval of time $(\Delta t)_0$. So, we have

$$\left(\frac{\Delta x}{\Delta t}\right)_0 = k'\,[S_2O_8^{2-}]_0^m$$

or

$$\frac{1}{(\Delta t)_0} = \frac{k'}{(\Delta x)_0}\cdot[S_2O_8^{2-}]_0^m$$

Now since $[S_2O_8^{2-}]_0^m$ will be proportional to its volume, we may thus write

$$\frac{1}{(\Delta t)_0} = k''\,\{V(S_2O_8^{2-})\}_0^m$$

Taking logarithm, we get

$$\log\{(\Delta t)_0/\text{sec}\} = -\log k'' - m\log\{V(S_2O_8^{2-})/\text{lit}\}_0 \qquad \ldots (2)$$

So, a plot of $\log\{(\Delta t)_0/\text{sec}\}$ versus $\log\{V(S_2O_8^{2-})/\text{lit}\}_0$ will give a straight line of slope equal to $-m$, *i.e.*, order with respect to $S_2O_8^{2-}$. For set-2, equation (2) can be

$$\log\{(\Delta t)_0/\text{sec}\} = -\log k''' - n\log\{V\,[I]\,/\text{lit}\}_0 \qquad \ldots (3)$$

So, the order n with respect to I^- can be obtained from the plot of $\log\{(\Delta t)_0/\text{sec}\}$ versus $\log\{V\,[I^-]/\text{lit}\}_0$. The total order of reaction will be given by $(m + n)$.

(V) Graphical Method

As discussed before, the reaction velocity in a first order reaction varies as one concentration term, while in a second order reaction, the reaction velocity is dependent on two concentration terms and so on. Mathematically, we can express the reaction velocity for a reaction of n^{th} order as

$$\frac{dx}{dt} = k\,(a-x)^n \qquad \ldots(4)$$

where a is the initial concentration and x is the amount of reactant at time t.

If a straight line is obtained by plotting dx/dt and $(a-x)^n$, then the reaction is of the n^{th} order. In the case of zero order reaction, a straight line is obtained by plotting x against t. For a first order reaction, a straight line is obtained by ploting $\frac{dx}{dt}$ against $(a-x)$ (Figure (3)]. Similarly, for a second order reaction, a straight line is obtained by plotting $\frac{dx}{dt}$ against $(a-x)^2$ [Figure (4)].

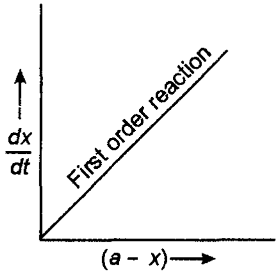


Fig. 3.

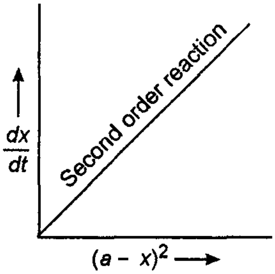


Fig. 4.

The values of dx/dt at different intervals of time can be determined by plotting a curve between x (the amount of the substance decomposed) and time t. The value of dx/dt at a particular time corresponding to a particular value of $(a-x)$ is given by the slope of the curve at that point [Fig. (5)]. On taking logarithm of equation (4), we get

$$\log \frac{dx}{dt} = \log k + n \log (a-x)$$

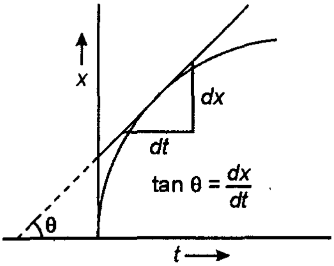


Fig. 5.

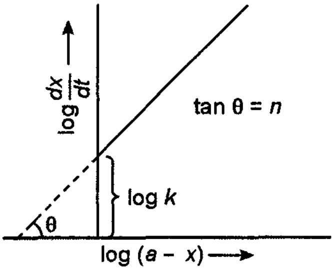


Fig. 6.

A curve when plotted beteen log dx/dt and log $(a-x)$ will give a straight line, the slope of which will give the value of n, *i.e.*, the order of reaction [Fig. (6)]. The intercept on the axis of Y will give the value of log k.

(VI) Method of Ratio Variation

A complex reaction involving different substances may be studied by appreciably increasing the concentration of the reactant, one at a time and observing the reaction rates over a period in which the change in composition is not over 10%. Consider the reaction,

$$A + B \longrightarrow \text{Products}$$

The rate of this reaction is given by,

$$\frac{dx}{dt} = k\,[A]^m\,[B]^n$$

The index m can be determined by doubling [A], while keeping [B] constant and determining experimentally the change in the rate $\Delta x/\Delta t$, since

$$\frac{(\Delta x\,/\,\Delta t)_2}{(\Delta x\,/\,\Delta t)_1} = \frac{k\,[A]^m\,2^m\,[B]^n}{k\,[A]^m\,[B]^n} = 2^m$$

where the subscripts 2 and 1 refer to concentrations [2A] and [A], respectively. The same procedure is adopted for evaluating n. The overall order of reaction $= (m + n)$.

Problem 1. ***In the reaction*** $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$, ***a molecular mixture of gases at 336 mm Hg initial pressure, was half changed in 108 sec and when the initial pressure was 288 mm Hg, it was half changed in 147 sec. Determine the order of reaction.***

Solution : We know that

$$\frac{(t_{0.5})_1}{(t_{0.5})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad \text{...(i)}$$

$a_1 \propto 336/2$ mm Hg, *i.e.*, 168 mm Hg

$a_2 \propto 288/2$ mm Hg, *i.e.*, 144 mm Hg

From equation (i) we have,

$$\frac{108}{147} = \left(\frac{144}{168}\right)^{n-1}$$

$$\log\frac{108}{147} = (n-1)\log\left(\frac{144}{168}\right)$$

$$(n-1) = \frac{\log\frac{108}{147}}{\log\frac{144}{168}} = \frac{0.1337}{0.6070} = 2.0$$

$$\therefore \qquad n = 2 + 1 = 3$$

Hence the **reaction is of the third order.**

Problem 2. ***From the following data of initial concentration and rate, calculate the order of the reaction*** $aA \rightarrow$ ***Products, and its rate constant*** k.

[A] (mole L^{-1})	**0·1**	**0·2**	**0·4**
r (mole L^{-1} s^{-1})	**9×10^{-5}**	**36×10^{-5}**	**144×10^{-5}**

Solution : Let the order of reaction be n, and k be the rate constant. The rate equation $r = k[A]^n$ for various data may be written as

$r_1 = k\,(0{\cdot}1 \text{ mol } L^{-1})^n = 9 \times 10^{-5} \text{ mol } L^{-1}\,s^{-1}$

$r_2 = k\,(0{\cdot}2 \text{ mol } L^{-1})^n = 36 \times 10^{-5} \text{ mol } L^{-1}\,s^{-1}$

$r_3 = k\,(0{\cdot}4 \text{ mol } L^{-1})^n = 144 \times 10^{-5} \text{ mol } L^{-1}\,s^{-1}$

$$\frac{r_1}{r_2} = \frac{k\,(0{\cdot}1)^n}{k\,(0{\cdot}2)^n} = \frac{9 \times 10^{-5}}{36 \times 10^{-5}} = \frac{1}{4}$$

$$\left(\frac{1}{2}\right)^n = \frac{1}{4} = \left(\frac{1}{2}\right)^2$$

$n = 2 =$ order of the reaction.

Similarly, $$\frac{r_3}{r_1} = \frac{(0{\cdot}4)^n}{(0{\cdot}1)^n} = \frac{144 \times 10^{-5}}{9 \times 10^{-5}} = 16$$

i.e., $$(4)^n = 16 = (4)^2$$

$$n = 2 = \text{order of the reaction}$$

$$\text{Rate constant, } k = \frac{\text{Rate}}{[\text{A}]^n} = \frac{r_v}{[\text{A}]^2}$$

Substituting the known values in the above equation, we get,

(i) $$k = \frac{9 \times 10^{-5}\ \text{mol L}^{-1}\ s^{-1}}{(0{\cdot}1\ \text{mol L}^{-1})^2} = \mathbf{9 \times 10^{-3}\ L\ mol^{-1}}\ \text{s}^{-1}$$

(ii) $$k = \frac{36 \times 10^{-5}\ \text{mol L}^{-1}\ s^{-1}}{(0{\cdot}2\ \text{mol L}^{-1})^2} = \mathbf{9 \times 10^{-3}\ L\ mol^{-1}}\ \text{s}^{-1}$$

(iii) $$k = \frac{144 \times 10^{-5}\ \text{mol L}^{-1}\ s^{-1}}{(0{\cdot}4\ \text{mol L}^{-1})^2} = \mathbf{9 \times 10^{-3}\ L\ mol^{-1}}\ \text{s}^{-1}$$

Problem 3. ***For a first order reaction* A $\longrightarrow$ B, *compute the rate for each of the following initial concentrations.***

(i) 0·1 mol L^{-1}, (ii) 0·05 mol L^{-1}, (iii) 0·2 mol L^{-1}, (iv) 0·3 mol L^{-1}. If r = 4 × 10^{-3} mol L^{-1} s^{-1} when the initial concentration is 0·1 mol L^{-1}, what is the rate constant ?

Solution : From the given information, we have

$$r = 4 \times 10^{-3}\ \text{mol L}^{-1}\ s^{-1} \text{ when } [\text{A}] = 0{\cdot}1\ \text{mol L}^{-1}$$

Since the order of the reaction is 1, the rate equation becomes

$$r = k\ [\text{A}]^n = k\ [\text{A}]$$

$$4 \times 10^{-3}\ \text{mol L}^{-1}\ s^{-1} = k \times 0{\cdot}1\ \text{mol L}^{-1}$$

$$k = \frac{r}{[\text{A}]} = \frac{4 \times 10^{-3}\ \text{mol L}^{-1}\ s^{-1}}{0{\cdot}1\ \text{mol L}^{-1}} = \mathbf{4 \times 10^{-2}}\ \boldsymbol{s}^{-1}$$

(i) $r_1 = (4 \times 10^{-2}\ s^{-1})\ (0{\cdot}01\ \text{mol L}^{-1}) = 4 \times 10^{-4}\ \text{mol L}^{-1}\ s^{-1}$

(ii) $r_2 = (4 \times 10^{-2}\ s^{-1})\ (0{\cdot}05\ \text{mol L}^{-1}) = 2 \times 10^{-3}\ \text{mol L}^{-1}\ s^{-1}$

(iii) $r_3 = (4 \times 10^{-2}\ s^{-1})\ (0{\cdot}2\ \text{mol L}^{-1}) = 8 \times 10^{-3}\ \text{mol L}^{-1}\ s^{-1}$

(iv) $r_4 = (4 \times 10^{-2}\ s^{-1})\ (0{\cdot}3\ \text{mol L}^{-1}) = 1{\cdot}2 \times 10^{-2}\ \text{mol L}^{-1}\ s^{-1}$

Problem 4. ***The reaction* 2NO + O$_2$ $\longrightarrow$ NO$_2$ *follows the rate law* $r = k\ [\text{NO}]^2\ [\text{O}_2]$. *If* $k = 2{\cdot}0 \times 10^{-6}\ \text{s}^{-1}\ \text{mol}^{-2}\ \text{L}^2$, *what is the rate of the reaction when* [NO] = 0·04 mol L^{-1} *and* [O$_2$] = 0·2 mol L^{-1} *?***

Solution. On substituting the given values in the rate equation :

$$r = k\ [\text{NO}]^2[\text{O}_2],$$

we get, $$r = (2{\cdot}0 \times 10^{-6}\ s^{-1}\ \text{mol}^{-2}\ \text{L}^2)\ (0{\cdot}04\ \text{mol L}^{-1})^2\ (0{\cdot}2\ \text{mol L}^{-1})$$

$$= \mathbf{6{\cdot}4 \times 10^{-10}\ mol\ L^{-1}}\ \boldsymbol{s}^{-1}$$

Problem 5. ***For a reaction* aA + bB $\longrightarrow$ mM + nN, *the rate is given as* r = k[A]^x [B]^y. *Compute the order of the reaction and rate constant from the given initial concentrations and the corresponding rates.***

[A] mol L^{-1}	**0·1**	**0·1**	**0·2**
[B] mol L^{-1}	**0·2**	**0·4**	**0·2**
r mol L^{-1} s^{-1}	**4 × 10^4**	**16 × 10^4**	**8 × 10^4**

Solution : On substituting the known data in the rate equation $r = k\ [A]^x\ [B]^y$ we shall have

$$r_1 = 4 \times 10^4 \text{ mol L}^{-1} s^{-1} = k\ (0{\cdot}1 \text{ mol L}^{-1})^x\ (0{\cdot}2 \text{ mol L}^{-1})^y$$

$$r_2 = 16 \times 10^4 \text{ mol L}^{-1} s^{-1} = k\ (0{\cdot}1 \text{ mol L}^{-1})^x\ (0{\cdot}4 \text{ mol L}^{-1})^y$$

$$r_3 = 8 \times 10^4 \text{ mol L}^{-1} s^{-1} = k\ (0{\cdot}2 \text{ mol L}^{-1})^x\ (0{\cdot}2 \text{ mol L}^{-1})^y$$

$$\frac{r_1}{r_2} = \frac{4 \times 10^4}{16 \times 10^4} = \frac{k\ (0{\cdot}1)^x\ (0{\cdot}2)^y}{k\ (0{\cdot}2)^x\ (0{\cdot}4)^y} = \left(\frac{1}{2}\right)^y$$

$$\therefore \quad \left(\frac{1}{2}\right)^y = \frac{1}{4} = \left(\frac{1}{2}\right)^2$$

$\therefore\ y = 2 =$ order with respect to B

$$\frac{r_1}{r_3} = \frac{4 \times 10^4}{8 \times 10^4} = \frac{k\ (0{\cdot}1)^x\ (0{\cdot}2)^y}{k\ (0{\cdot}2)^x\ (0{\cdot}2)^y}$$

$$\therefore \quad \left(\frac{1}{2}\right)^x = \left(\frac{1}{2}\right)^1$$

$\therefore\ x = 1 =$ order with respect to A

Overall order of reaction $= x + y = 1 + 2 = 3$

$$\text{Rate constant, } k = \frac{\text{Rate}}{[A]^x\ [B]^y} = \frac{r}{[A]\ [B]^2}$$

Substituting the known values in the above equation, we get :

$$k = \frac{4 \times 10^4 \text{ mol L}^{-1} s^{-1}}{(0{\cdot}1 \text{ mol L}^{-1})\ (0{\cdot}2 \text{ mol L}^{-1})^2} = \mathbf{1{\cdot}0 \times 10^7\ L^2\ mol^{-2}\ s^{-1}}$$

$$k = \frac{16 \times 10^4 \text{ mol L}^{-1} s^{-1}}{(0{\cdot}1 \text{ mol L}^{-1})\ (0{\cdot}4 \text{ mol L}^{-1})^2} = \mathbf{1{\cdot}0 \times 10^7\ L^2\ mol^{-2}\ s^{-1}}$$

$$k = \frac{8 \times 10^4 \text{ mol L}^{-1} s^{-1}}{(0{\cdot}2 \text{ mol L}^{-1})\ (0{\cdot}2 \text{ mol L}^{-1})^2} = \mathbf{1{\cdot}0 \times 10^7\ L^2\ mol^{-2}\ s^{-1}}$$

7·14. EXPERIMENTAL METHODS TO STUDY REACTION KINETICS

The kinetics of reactions can be studied by different methods. Some of them are as follows :

(1) By polarimetric method. Reactions such as inversion of cane sugar can be followed polarimetrically without the reaction mixture being disturbed. (For details, see article 7.8)

(2) By potentiometric or spectrophotometric method. The concentration of a reactant or product at different time intervals can be carried out by potentiometry and spectrophotometry etc. In spectrophotometric determination, the principle underlying the method is Beer's law, according to which we have

$$\log \frac{I_0}{I} = \varepsilon\, cx$$

where I_0 is the intensity of incident radiation, I is the intensity of the radiation after passing through a solution of concentration c of a light absorbing substance, x is thickness of the cell in which the solution is kept and ε is the molar absorptivity. The latter is a function of the wavelength of radiation and the absorbing material.

So, if we choose a wavelength for which ε is larger for the chemical species, $\log (I_0/I)$ will be proportional to the concentration of that substance. If the substance is either a reactant or product we can determine how its concentration changes from the plot of $\log I_0/I$ versus time.

Once the data on concentration versus time is known, the order of reaction and its reaction rate constant may be determined by any of the known methods.

(3) By conductometric method. If in a reaction, the ions are consumed or produced or one ion is replaced by the other, the concentration of reaction species at different time intervals may be determined conductometrically. For example, in the saponification of ethyl acetate, the fast conducting OH^- ions are replaced by acetate ions. The change in conductivity will be directly proportional to the amount of OH^- ions consumed or acetate ions produced. Suppose κ_0, κ_t and κ_t are the conductivities of the reaction at the start of reaction, at time t after the reaction has started and at the end of the reaction, respectively. Therefore, we may write,

$$[OH^-]_0 \propto \kappa_0 - \kappa_\infty$$

$$[OH^-]_t \propto \kappa_t - \kappa_\infty$$

and

$$x \propto \kappa_0 - \kappa_t$$

where x is the extent of reaction per unit volume at time t.

In order to relate conductivity directly to concentration, a table or graph of conductivity may be made using solutions of known concentrations of the ions of interest. For first order reactiions, one may substitute

$$[A]_0 \propto \kappa_0 - \kappa_\infty$$

$$[A]_0 - x \propto \kappa_t - \kappa_\infty$$

So,

$$\log_e \frac{[A]_0}{[A]_t} = \log_e \frac{a}{a-x} = \log_e \left(\frac{\kappa_0 - \kappa_\infty}{\kappa_t - \kappa_\infty} \right) = k_1 t.$$

7·15. COMPOSITE REACTIONS (COMPLEX REACTIONS)

Composite reactions occur from the intervention of many simple reactions which act either simultaneously (opposing and parallel reactions) or sucessively (sucessive or consecutive reactions).

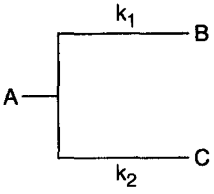
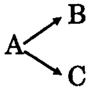


Fig. 7.

[I] Side Reactions, Parallel Reactions or Concurrent Reactions

In such reactions, the reacting substances, instead of proceeding along one path to yield a given set of products, also follow one or more other paths to give different products, such as  where, B and C may not have any chemical affinity for one another.

Let a be the initial concentration of A and x be the amount transformed in time t. If y and z be the amounts of B and C formed in time t, then we have the rates of formation of B and C given by dy/dt and dz/dt, respectively. Since both B and C are formed from A, we have

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt} \qquad ...(1)$$

If the reaction is unimolecular and k_1 is the velocity constant for the formation of B from A, then

$$\frac{dy}{dt} = k_1 (a - x)$$

Similarly, the rate of formation of C is given by

$$\frac{dz}{dt} = k_1 (a - x)$$

where k_2 = velocity constant for the formation of C from A. Hence, from equation (1), we have

$$\frac{dx}{dt} = k_1 (a - x) + k_2 (a - x) = (k_1 + k_2)(a - x)$$

On integration, we have

$$k_1 + k_2 = K \text{ (say)} = \frac{1}{t} \log \frac{a}{a - x} \qquad ...(2)$$

Now in order to evaluate k_1 and k_2 separately, we must know some relationship between them. The amounts of B and C formed at any time will depend upon the rates of the two reactions, *i.e.*,

$$\frac{\text{Amount of B at any stage}}{\text{Amount of C at any stage}} = \frac{dy/dt}{dz/dt} = \frac{k_1 (a - x)}{k_2 (a - x)} = \frac{k_1}{k_2} = K' \text{ (say)} \qquad ...(3)$$

The relative amounts of B and C can be determined at the end of the reaction, and the ratio of the relative amounts give the value of K'. The values of k_1 and k_2 can be calculated separately from equations (2) and (3) in terms of K and K' which are directly measurable quantities. We have

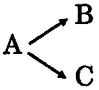
$$k_1 + k_2 = K \quad \text{and} \quad k_1 / k_2 = K'$$

Therefore, $$K = K'k_2 + k_2 = k_2 (1 + K')$$

or $$k_2 = \frac{K}{1 + K'}$$

Similarly, $$k_1 = \frac{KK'}{1 + K'}$$

(1) Wegscheider's test for side reactions. Wegscheider's principle states that, ***the ratio between the amounts of the substances formed in two side reactions is independent of time.*** It distinguishes side reactions from opposing or consecutive reactions.

In the reaction  $A \genfrac{}{}{0pt}{}{\nearrow B}{\searrow C}$, in which both side reactions were unimolecular, it has already been shown that,

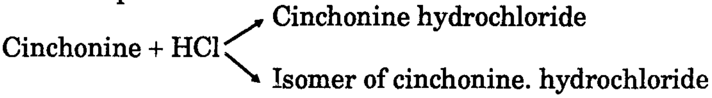
$$\frac{\text{Rate of formation of B}}{\text{Rate of formation of C}} = \frac{\text{Amount of B at any stage}}{\text{Amount of C at any stage}}$$

$$\frac{k_1 (a - x)}{k_2 (a - x)} = \frac{k_1}{k_2} = K' . \qquad ... (4)$$

The constant K' is independent of time.

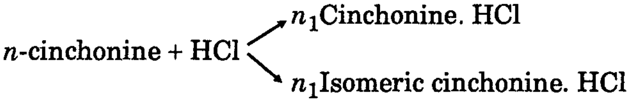
Application of Wegscheider's test. Skraup showed that the reaction between cinchonine and hydrochloric acid forms cinchonine hydrochloride. At the same time an isomeric form of cinchonine hydrochloride is also formed. Skraup considered the reactions to be consecutive—ordinary cinchonine hydrochloide being formed first, from which the isomeric form is formed in turn afterwards. On applying Wegscheider's test the reactions were considered to be side reactions and not consecutive reactions.

The reactions can be represented as



$$\text{Cinchonine} + \text{HCl} \begin{array}{l} \nearrow \text{Cinchonine hydrochloride} \\ \searrow \text{Isomer of cinchonine. hydrochloride} \end{array}$$

In general,

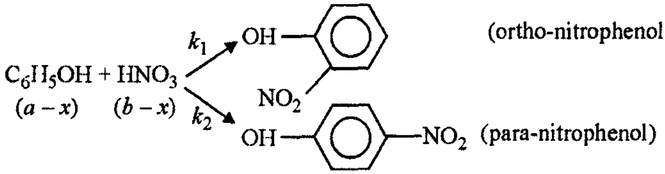


$$n\text{-cinchonine} + \text{HCl} \begin{array}{l} \nearrow n_1\text{Cinchonine. HCl} \\ \searrow n_1\text{Isomeric cinchonine. HCl} \end{array}$$

The value of $n = 1$.

If different number of molecules of cinchonine would have combined with HCl to form ordinary and isomeric cinchonine hydrochloride, the reactions still would have been side reactions, but in that case Wegscheider's test would have failed.

Phenol on nitration gives two products namely, ortho and para nitrophenols.



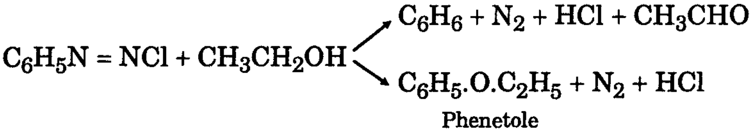
$$\frac{\text{Amount of } x}{\text{Amount of } y} = \frac{\text{Rate of formation of } o\text{- product}}{\text{Rate of formation of } p\text{- product}}$$

$$\frac{dx/dt}{dy/dt} = \frac{k_1(a-x)(b-x)}{k_2(a-x)(b-x)} = \frac{k_1}{k_2} = K \text{ (Constant)}$$

Thus, Wegscheider's test holds good.

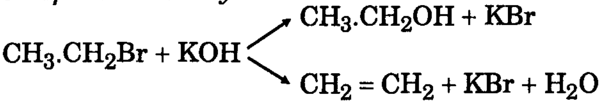
(2) Examples of side reactions

(1) Reaction between dry benzene diazonium chloride and ethyl alcohol.



$$C_6H_5N = NCl + CH_3CH_2OH \begin{array}{l} \nearrow C_6H_6 + N_2 + HCl + CH_3CHO \\ \searrow \underset{\text{Phenetole}}{C_6H_5.O.C_2H_5} + N_2 + HCl \end{array}$$

(2) Action of KOH on ethyl bromide.



$$CH_3.CH_2Br + KOH \begin{array}{l} \nearrow CH_3.CH_2OH + KBr \\ \searrow CH_2 = CH_2 + KBr + H_2O \end{array}$$

[II] Opposing or Reversible Reactions

Opposing reactions result in chemical equilibrium. In many cases the equilibrium is so much on the product side at the experimental temperature and pressure that for all practical purposes it can be said that the reaction is complete, as in the dissociation of N_2O_5. But there are other systems in which the equilibrium remains on the reactants side, *e.g.*, the hydrolysis of ethyl acetate in water.

$$CH_3COOC_2H_5 + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COOH + C_2H_5OH$$

a	b	0	0	(Initially)
$a-x$	$b-x$	x	x	(At equilibrium)

The correct expression for the rate of change is given by

$$\frac{dx}{dt} = k_1 (a-x)(b-x) - k_2 x^2,$$

and not by

$$\frac{dx}{dt} = k_1 (a-x)(b-x)$$

It means that the rate of decrease of ester is not characterised by a factor k_1 but by $(k_1 - k_2)$.

(i) When both the reactions are of first order.

The simplest case of opposing reactions is that in which both the forward and backward reactions are of the first order, *i.e.*,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

a	b	(Initially)
$a-x$	$b+x$	(At equilibrium)

where k_1 and k_2 are rate constants for forward and backward reactions.

Let the initial concentrations of A and B be a and b, respectively. If after time t, x mole/litre of A changes into B, then, concentrations of A and B will be $(a-x)$ and $(b+x)$, respectively.

The different rate expression is thus given by

$$\frac{dx}{dt} = k_1 (a-x) - k_2 (b+x). \qquad ...(5)$$

At equilibrium, the net rate is zero, *i.e.*, $dx/dt = 0$, then

$$k_1 (a - x_e) = k_2 (b + x_e) \qquad ...(6)$$

where x_e is the value of x at equilibrium.

From equation (6), we get $(b + x_e) = \frac{k_1}{k_2} . (a - x_e)$

or $$b = \frac{k_1}{k_2} . (a - x_e) - x_e$$

Substituting the value of b in equation (5), we get

$$\frac{dx}{dt} = k_1 (a-x) - k_2 \left[\frac{k_1}{k_2}(a - x_e) - x_e + x \right]$$

$$= (k_1 + k_2)(x_e - x)$$

or $$\frac{dx}{x_e - x} = (k_1 + k_2)\, dt$$

or $$\int_{x_0}^{x} \frac{dx}{x_e - x} = \int_0^t (k_1 + k_2)\, dt$$

or $$\log \frac{x_e - x_0}{x_e - x} = (k_1 + k_2)\, t$$

or $$k_1 + k_2 = \frac{1}{t} \cdot \ln \frac{x_e - x_0}{x_e - x} \qquad ...(7)$$

Equation (7) is similar to the first order rate expression, except that the measured rate constant is now the sum of the forward and reverse rate constants. Examples of such reactions are mutarotation of π-bromonitro camphors, conversion of ammonium thiocyanate into urea etc.

Problem 1. ***Mutarotation of α-glucose in solution is partially transformed into β-glucose according to an equilibrium reaction. This causes a variation of the specific rotation [α], of polarised light. The following data was obtained, from which calculate the value of $(k_1 + k_2)$ in $\mathbf{min^{-1}}$.***

Time	**0**	**4**	**∞**
[α]	**110**	**74.6**	**52.6**

Solution : Although the specific rotation of β-glucose is not given, it will be recalled that the difference from the initial value is proportional to the fraction of the substance transformed. Thus,

$$\frac{x}{x_e} = \frac{110 - 74{\cdot}6}{110 - 52{\cdot}6} = 0{\cdot}616$$

$$(k_1 + k_2) \cdot 4 = 2{\cdot}303 \log \frac{x_e}{x_e - x} = 2{\cdot}303 \log \frac{1}{1 - (x/x_e)}$$

or $$k_1 + k_2 = \frac{2{\cdot}303}{4} \log \frac{1}{1 - 0.616} \text{ hour}^{-1}$$

or $$k_1 + k_2 = \frac{2{\cdot}303}{4 \times 60} \log \frac{1}{0.384} = \mathbf{0.004\ min^{-1}}$$

(ii) When a first order reaction is opposed by a second order reaction.

Consider the reaction :

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \quad + \quad \mathrm{C}$$

$$\begin{array}{cccl} a & 0 & 0 & \text{(Initially)} \\ a - x & x & x & \text{(At any time } t\text{)} \end{array}$$

The rate of reaction at any time t is given by

$$\frac{dx}{dt} = k_1 (a - x) - k_2 x^2 \qquad ...(8)$$

$$= k_1 a - k_2 \left\{ x^2 + \frac{k_1}{k_2} \cdot x \right\}$$

The square is completed by adding and substracting $k_1^2/4k_2$, and the resulting square is then divided by k_2. Then

$$\frac{1}{k_2} \cdot \frac{dx}{dt} = \left\{ \frac{k_1}{k_2} \cdot a + \frac{1}{4} \left(\frac{k_1}{k_2} \right)^2 \right\} - \left(x + \frac{1}{2} \frac{k_1}{k_2} \right)$$

or $$\frac{1}{k_2} \cdot \frac{dx}{dt} = \alpha^2 - \left(x + \frac{1}{2} \cdot \frac{k_1}{k_2} \right)^2$$

where $$\alpha = \left\{ \frac{k_1}{k_2} . a + \frac{1}{4}\left(\frac{k_1}{k_2}\right)^2 \right\}^{1/2}$$

We thus have,

$$\frac{dx}{\left\{\alpha - \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)\right\}\left\{\alpha + \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)\right\}} = k_2 \, dt$$

$$\frac{dx}{\left\{\alpha - \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)\right\}} + \frac{dx}{\left\{\alpha + \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)\right\}} = 2\,\alpha\, k_2 \cdot dt$$

or $$\int \frac{dx}{\alpha - \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)} + \int \frac{dx}{\alpha + \left(x + \frac{1}{2}\frac{k_1}{k_2}\right)} = 2\,\alpha\, k_2 \cdot \int dt$$

or $$\log\left\{\alpha - \left(x + \frac{1}{2}\cdot\frac{k_1}{k_2}\right)\right\} + \log\left\{\alpha + \left(x + \frac{1}{2}\cdot\frac{k_1}{k_2}\right)\right\} = 2\,\alpha\, k_2 t + I$$

where I is the integration constant.

When $t = 0$, $x = 0$, hence

$$k_2 = \frac{1}{2\,\alpha\, t} \log \frac{a + x\left(\frac{k_2}{k_1}\alpha - \frac{1}{2}\right)}{a - x\left(\frac{k_2}{k_1}\alpha + \frac{1}{2}\right)}$$

The fractional factor may be written in the form

$$\frac{x}{a} = \left\{\frac{1}{2} + \frac{k_2}{k_1} . \alpha \coth\,(k_2\,\alpha\, t)\right\}^{-1}$$

At $t = \infty$, $\coth\,(k_2\,\alpha\, t) \to 1$,

$$\left(\frac{x}{a}\right)_{t\to\infty} = \left(\frac{1}{2} + \frac{k_2}{k_1} . \alpha\right)^{-1}$$

On squaring and rearranging, we get

$$\left(\frac{x}{a}\right)_{t\to\infty} = \frac{k_1}{k_2} = K \qquad \text{...(9)}$$

At equilibrium $x = x_e$, hence on substituting the value of k_2 from equation (9) in (8), and integrating it after splitting into partial fractions, we have

$$k_1 = \frac{x_e}{t\,(2a - x_e)} \log \frac{a x_e + x\,(a - x_e)}{a\,(x_e - x)}$$

Examples of this type are decomposition of phosphorous pentachloride into phosphorus trichloride and chlorine, hydrolysis of ethyl acetate in presence of acid etc.

(iii) When a second order reaction is opposed by a first order reaction.

Consider the following reaction :

$$\mathrm{A + B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C}$$

a	a	0	(Initially)
$a - x$	$a - x$	x	(At any time t)

We have $$\frac{dx}{dt} = k_1 (a - x)^2 - k_2 x \qquad \text{...(10)}$$

At equilibrium, $$k_1 (a - x_e)^2 = k_2 x_e \qquad \text{...(11)}$$

Substituting the value of k_2 from equation (11) in (10) and integrating after splitting it into partial fractions, we have

$$k_1 = \frac{x_e}{t\,(a^2 - x_e^2)} \log \frac{x_e\,(a - x x_e)}{(a^2 x_e - x)}$$

Examples of this type are synthesis of NH_3 by Haber's process, reaction between ethyl alcohol and acetic acid etc.

(iv) When a second order reaction is opposed by one of the same order.

Consider the following reaction :

$$\underset{(a-x)}{\mathrm{A}} + \underset{(b-x)}{\mathrm{B}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{x}{\mathrm{C}} + \underset{x}{\mathrm{D}}$$

Thus, $$\frac{dx}{dt} = (k_1 - k_2) \left\{ x^2 + \frac{k_2 (a + b)}{k_1 - k_2} . x + \frac{k_1 a b}{k_1 - k_2} \right\}$$

or $$\frac{dx}{dt} = k_1 (a - x)(b - x) - k_2 x^2.$$

Remember that $k_2 / k_1 = K'$ and at equilibrium $x = x_e$, we have after splitting into partial fractions and integrating

$$k_1 = \frac{1}{2(1 - K')\beta t} \log \frac{1 - \left(\dfrac{x}{\alpha + \beta} \right)}{1 - \left(\dfrac{x}{\alpha - \beta} \right)}$$

where, $$\alpha = \frac{1}{2} \frac{k_1 (a + b)}{(k_1 - k_2)} = \frac{1}{2} \cdot \frac{a + b}{1 - K'}$$

$$\beta = \frac{1}{2} \cdot \frac{k_1}{k_1 - k_2} \cdot \left\{ (a - b)^2 + \frac{4k_2}{k_1} a\, b \right\}^{1/2}$$

Examples of this type are saponification of ethyl acetate by alkali, decomposition of HI etc.

(v) When a third order reaction is opposed by one of the second order.

Consider the following reaction,

$$\underset{(a-x)}{\mathrm{A}} + \underset{(b-2x)}{2\mathrm{B}} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{2x}{2\mathrm{C}}$$

The rate of reaction is given by

$$\frac{dx}{dt} = k_1 (a - x) \{b - 2x\}^2 - k_2 (2x)^2.$$

If $k_1 / k_2 = K$ and $x = x_e$ at equilibrium, we have

$$\frac{dx}{dt} = 4k_1 \left\{ (a - x_e)(b - 2x_e)^2 \frac{x_e^2}{K} \right\}$$

Problem 1. ***Consider the opposing second order reaction :***

$$A_2 + B_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2AB \qquad \text{...(i)}$$

Derive an expression for K in terms of k_1 and k_2.

Solution : For component A at equilibrium,

$$\frac{-d\,C_{A_2}}{d\,t} = k_1\,C_{A_2} \,.\, C_{B_2} - k_2\,C_{AB}^2 = 0$$

From law of mass action : $K = C^2{}_{AB} / C_A \,.\, C_B$

$\therefore$ From (i), we have $K = \dfrac{k_1}{k_2}$

[III] Consecutive, Simultaneous or Parallel Reactions

Chemical reactions which proceed from reactants to products through one or more intermediate stages are called ***consecutive reactions.*** The simplest case arises when both the consecutive reactions are of the same order, *viz.,*

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Suppose we start with a mole of A. Let after a time t, x mole of A is left behind, giving y mole of B and z mole of C. Therefore, x, y and z are connected as,

$$x + y + z = a \qquad \text{...(12)}$$

The rate of disappearance of A, *i.e.*, $(-\,dx/dt)$ is given by

$$\frac{-\,d\,x}{d\,t} = k_1\,x \qquad \text{...(13)}$$

where k_1 = rate constant for transformation of A to B.

The rate of formation of C, *i.e.*, (dz/dt) is given by

$$\frac{+\,d\,z}{d\,t} = k_2\,y \qquad \text{...(14)}$$

where k_2 = rate constant for the formation of C from B.

The rate at which B accummulates, *i.e.*, (dy/dt) in the system is thus the difference between the rate of formation of B from A and the rate of transformation of B into C. Therefore,

$$\frac{dy}{dt} = -\frac{dx}{dt} - \left(+\frac{dz}{dt}\right)$$

$$= k_1 x - k_2 y \qquad \text{...(15)}$$

On integrating equation (13), and finding the proper value of integration constant, as usual, we have

$$-\int \frac{dx}{x} = \int k_1\,dt$$

Therefore, $-\log x = k_1 t - \log a$

$$\frac{x}{a} = e^{-k_1 t}$$

or $$x = ae^{-k_1 t}$$

This shows that [A] decreases exponentially with time as in first order reactions [Fig. (7)].

To get the value of [B], *i.e.*, y, substitute the value of x in equation (15). So,

$$\frac{dy}{dt} = k_1 ae^{-k_1 t} - k_2 y$$

This is a linear differential equation of the first order, whose solution is

$$y = e^{-k_2 t}\left[\frac{k_1 a \, . \, e^{(k_1 - k_2)t}}{(k_2 - k_1)} + c\right]$$

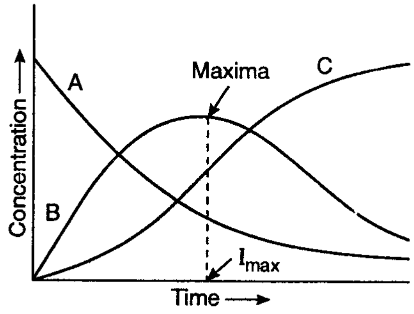


Fig. 7.

When $t = 0, y = 0$. So, $c = -k_1 a/(k_2 - k_1)$

$$\therefore \quad y = e^{-k_2 t}\left[\frac{k_1 ae^{(k_2 - k_1)t}}{(k_2 - k_1)} - \frac{k_1 a}{k_2 - k_1}\right]$$

or $$y = \frac{ak_1}{(k_2 - k_1)}(e^{-k_1 t} - e^{-k_2 t}). \qquad ...(16)$$

Substituting the values of x and y in equation (12), we get

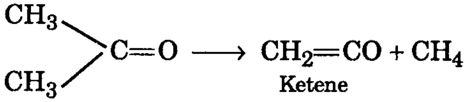
$$z = a - x - y$$

or $$z = a - ae^{-k_1 t} - \frac{ak_1}{(k_2 - k_1)}[e^{-k_1 t} - e^{-k_2 t}]$$

or $$z = \left(1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{(k_2 - k_1)}\right) \qquad ...(17)$$

Some examples of consecutive reactions are

(a) Thermal decomposition of acetone



$$CH_3COCH_3 \longrightarrow \underset{\text{Ketene}}{CH_2{=}CO} + CH_4$$

$$CH_2{=}\ CO \longrightarrow \frac{1}{2}C_2H_4 + CO$$

(b) Decomposition of dimethyl ether

$$(CH_3)_2O \xrightarrow{k_1} CH_4 + HCHO$$

$$HCHO \xrightarrow{k_2} H_2 + CO$$

The simplest case of consecutive reactions of the first order is that involving radioactive series. Suppose an element A undergoes radioactive disintegration, emitting α or β particles, to give element B, which in turn gives element C, as follows :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

where k_1, k_2 and k_3 are the velocity constants for the respective consecutive reactions. The constant k of a reaction of first order is known as **decay constant,** which is the number of atoms disintegrating per second referred to a system which has one atom present. We can write the following expressions (18), (19) and (20) for the decay of elements A, B and C, respectively.

$$-\frac{da}{dt} = k_1 a \qquad \text{...(18)}$$

$$-\frac{db}{dt} = k_2 b - k_1 a \qquad \text{...(19)}$$

$$-\frac{dc}{dt} = k_3 c - k_2 b$$

where a, b and c are the concentrations of A, B and C at time t.

On integrating equation (18), we get

$$a = A_0\, e^{-kt}$$

From equation (19), we get $-\dfrac{db}{dt} = k_2 b - k_1 A_0\, e^{-k_1 t}$

On integrating it, we obtain $b = A_0 - \dfrac{k_1}{(k_2 - k_1)}\,(e^{-k_1 t} - e^{-k_2 t})$

Substituting the value of b in equation (20), we get

$$-\frac{dc}{dt} = k_3 c - A_0 \frac{k_1}{k_2 - k_1}\,(e^{-k_1 t} - e^{-k_2 t})$$

The last equation on integration gives

$$c = A_0\,(\alpha e^{-k_1 t} + \beta e^{-k_2 t} + \gamma e^{-k_3 t})$$

where

$$\alpha = \frac{k_1 k_2}{(k_2 - k_1)\,(k_3 - k_1)}$$

$$\beta = \frac{k_1 k_2}{(k_1 - k_2)\,(k_3 - k_2)}$$

$$\gamma = \frac{k_1 k_2}{(k_1 - k_3)\,(k_2 - k_3)}$$

Problem 1. ***For a series of competing reactions :***

$$\mathbf{H + HO_2 \xrightarrow{k_1} H_2 + O_2;\ H + OH_2 \xrightarrow{k_2} H_2O + O \qquad H + HO_2 \xrightarrow{k_3} 2OH;}$$

Westenberg and de Hass reported that $k_1/k_2/k_3 = 0.62/0.27/0.11$. ***Find the ratio of products at time*** t.

Solution : The rate equation for the reactions is

$$\text{Rate} = k_1\, C_H\, C_{HO_2} + k_2\, C_H{\cdot}C_{HO_2} + k_3\, C_H C_{HO_2} = k\, C_H{\cdot}C_{HO_2}$$

where, $k = k_1 + k_2 + k_3$. The given ratio of rate constants implies that 62% of the reactants will form the products of the first reaction, 27% will form the products of the second reaction and so on. Thus, the ratio of the products will be

$$(C_{H_2} = C_O)/C_{OH}/(C_{H_2O} = C_O) = 0.62/0.54/0.11$$

Evaluation of decay constant : The decay constant can be evaluated directly for transformations proceeding at a rate similar to that of chemical reactions at ordinary temperatures. For very slow or very fast reactions, two methods are used. One is based on the idea of a stationary state and the other on the range of particles emitted during disintegration. Consider the reaction,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

If all the atoms of A, B and C are retained in the system for a long time, atoms of B reach a stationary state or concentration, *i.e.*, one which does not depend on time except in so far as the concentrations of A and C depend on time. For the stationary state,

$$\frac{-db}{dt} = k_2 b - k_1 a = 0$$

$$\frac{k_1}{k_2} = \frac{b}{a}$$

The stationary concentrations of A and B are thus inversely proportional to their decay constants.

The second indirect method is based on the Geiger-Nuttall rule connecting the value of k and the range R_0 over which it can propel a particle under standard conditions, *i.e.*,

$$k = A . R_0^B$$

where $B = 53.9$ and $A = 2 \times 10^{-38}$

$\therefore$ $\log k = 37.7 + 53.9 \log R_0$

Thus, the value of k can be evaluated.

In uranium and radium bearing ores, when the stationary state has reached, the approximate value of [Ra]/[U] is 3.4×10^{-7}. The decay constant of Ra has been determined by directly counting the number of α-particles emitted, viz., $k_{Ra} = 1.38 \times 10^{-11}$ sec^{-1}. Therefore,

$$\frac{k_U}{k_{Ra}} = \frac{k_U}{1.38 \times 10^{-11}} = 3.4 \times 10^{-7}$$

$$k_U = 4.70 \times 10^{-18} \text{ sec}^{-1}$$

Problem 2. ***The acid catalysed conversion of γ-hydroxy butyric acid into its lactone was studied in 0.2 N HCl solution at 25°C. The initial concentration of the hydroxy acid was 18.23 (measured in arbitrary units). The concentration of lactone (expressed in the same units) is shown as a function of time in the following table :***

Time (min.)	**0**	**21**	**36**	**50**	**65**	**80**	**100**	**∞**
Lactone conc.	**0**	**2.41**	**0.73**	**4.96**	**6.10**	**7.08**	**8.11**	**13.28**

Calculate the equilibrium constant and first order velocity coefficient for the forward and reverse processes.

Solution. The reaction scheme may be represented as

$$\text{Acid} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Lactone}$$

where k_1 and k_2 are the first order velocity coefficient for the forward and backward process, respectively. Let

	$\text{Acid} \underset{k_2}{\overset{k_1}{\rightleftharpoons}}$	Lactone
Initial conc.	a	0
Conc. at time t	$(a - x)$	x
Equilibrium conc.	$(a - x_e)$	x_e

Then, $$t = \frac{2.303}{(k_1 + k_2)} \log\left(\frac{x_e}{x_e - x}\right)$$

or
$$t = \frac{2.303}{(k_1 + k_2)} \log x_e - \frac{2.303}{(k_1 + k_2)} \log (x_e - x)$$

Thus, a graph of t versus $\log (x_e - x)$ should give a straight line, whose slope is given by

$$\text{Slope} = \frac{-2.303}{(k_1 + k_2)}$$

Figure (8) shows such a plot made from the data as given in the following table :

$$x_e - x = (\infty \text{ reading} - \text{reading at time } t)$$

Time (min.)	0	21	36	50	65	80	100
$(x_e - x)$	13.28	3.28 – 2.41= 10.87	9.55	8.32	7.18	6.20	13.28 – 8.11 = 5.17
$\log (x_e - x)$	1.123	1.036	0.980	0.920	0.856	0.792	0.714

$$\text{Slope} = -\frac{2.303}{(k_1 + k_2)} = -243$$

$\therefore$
$$k_1 + k_2 = 9.48 \times 10^{-3} \text{ min}^{-1}$$

Now,
$$\frac{x_e}{a} = \frac{K}{1+K}$$

$\therefore$
$$K = \frac{x_e}{(a - x)}$$

For the given data, $x_e = 13.28$ and $a = 18.23$

$\therefore$
$$K = \frac{13.28}{18.23 - 13.28} = \mathbf{2.68}$$

Now
$$K = \frac{k_1}{k_2} = 2.68$$

$\therefore$
$$k_1 = 2.68\, k_2$$

Now,
$$k_1 + k_2 = 9.48 \times 10^{-3}$$
$$2.68\, k_2 + k_2 = 9.48 \times 10^{-3}$$
$$3.68\, k_2 = 9.48 \times 10^{-3}$$

$\therefore$
$$k_2 = \frac{9.48 \times 10^{-3}}{3.68}$$
$$k_2 = \mathbf{2.58 \times 10^{-3}\ min^{-1}}$$

Hence
$$k_1 = K \,.\, k_2$$
$$= 2.68 \times 2.58 \times 10^{-3} = 6.90 \times 10^{-3} \text{ min}^{-1}$$

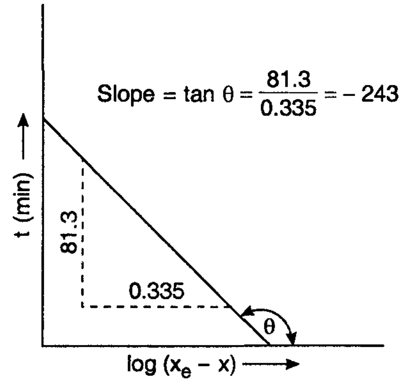


Fig. 8.

Problem 3. ***For the given reaction*** **A $\underset{k_f}{\overset{k_f}{\rightleftharpoons}}$ B**

Calculate **k_f, k_r.** ***Given that*** **$[A]_0 = 0.15$ M, $[A]_e = 0.086$ M, $[A]_{10} = 0.142$** ***M and*** **$[A]_{100} = 0.102$ M.**

Solution.
$$A \underset{k_f}{\overset{k_f}{\rightleftharpoons}} B$$

	A	B
Initial conc.	a	0
Conc. at time t	$(a - x)$	x
Equilibrium conc.	$(a - x_e)$	x_e

According to the problem,

$$[A]_0 = a = 0.15 \text{ M}$$

$$[A]_e = a - x_e = 0.086 \text{ M}$$

$$x_e = a - 0.086$$

or $$x_e = 0.15 - 0.086 = 0.064 \text{ M}$$

At time 10 sec : $$[A]_{10} = a - x = 0.142 \text{ M}$$

∴ $$x = a - 0.142$$

or $$x = 0.150 - 0.142 = 0.008 \text{ M}$$

We know that

$$k_f = \frac{2.303\, x_e}{at} \log\left(\frac{x_e}{x_e - x}\right)$$

On substitution,

$$k_f = \frac{2.303 \times 0.064}{0.15 \times 10} \log\left(\frac{0.064}{0.064 - 0.008}\right)$$

$$= 5.69 \times 10^{-3} \text{ sec}^{-1}$$

At time 100 sec : $$[A]_{100} = 0.102 \text{ M} = a - x$$

∴ $$x = a - 0.102$$

or $$x = 0.150 - 0.102 = 0.048 \text{ M}$$

Now $$k_f = \frac{2.303\, x_e}{a\,.\,t} \log\left(\frac{x_e}{x_e - x}\right)$$

$$= \frac{2.303 \times 0.064}{0.15 \times 100} \log\left(\frac{0.064}{0.064 - 0.048}\right)$$

$$\mathbf{k_f = 5.91 \times 10^{-3} \text{ sec}^{-1}}$$

Hence, average value of $$k_f = \frac{5.69 \times 10^{-3} + 5.91 \times 10^{-3}}{2}$$

$$= \mathbf{5.8 \times 10^{-3} \text{ sec}^{-1}}$$

Now $$K = \frac{x_e}{a - x_e}$$

$$= \frac{0.064}{0.086} = 0.744$$

But $$K = \frac{k_f}{k_r}$$

∴ $$k_r = \frac{k_f}{K}$$

$$= \frac{5.8 \times 10^{-3}}{0.744}$$

$$= \mathbf{7.79 \times 10^{-3} \text{ sec}^{-1}}$$

Problem 4. ***Consider the following consecutive reaction***

$$\mathbf{R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3}$$

***(a) If the initial concentration* R_1 *is 100 M and* $k_1 : k_2 = 1.0 : 0.15$*, calculate the concentrations of each species after 10 seconds. Given* $k_1 = 4.0 \times 10^{-2}$ min^{-1}.**

***(b) Calculate* $[R_2]_{max}$ *and* t_{max}.**

Solution. $k_1 = 4.0 \times 10^{-2}\ \text{min}^{-1}$

But $\dfrac{k_1}{k_2} = \dfrac{1.0}{0.15}$

$\therefore$
$$k_2 = 0.15 \times 4.0 \times 10^{-2}$$
$$= 0.60 \times 10^{-2}\ \text{min}^{-1}$$

Now,
$$\begin{array}{lccc} & R_1 \xrightarrow{k_1} & R_2 \xrightarrow{k_2} & R_3 \\ \text{Initial conc.} & a & 0 & 0 \\ \text{Conc. after time } t & x & y & z \end{array}$$

$\therefore$ $[R_1]_t = x$; $[R_2]_t = y$ and $[R_3]_t = z$

We know that
$$x = a \,.\, e^{k_1 t}$$
$$a = 100\ \text{M}, t = 10\ \text{sec}, k_1 = 4.0 \times 10^{-2}$$

On substitution,
$$x = 100 \,.\, e^{-4 \times 10^{-2} \times 10}$$
$$x = 100 \,.\, e^{-0.4}$$

Now $\log_e e^{-0.4} = -0.4$

or $2.303 \log_{10} e^{-0.4} = -0.4$
$$\log e^{-0.4} = \frac{-0.4}{2.303}$$
$$= -0.1736 = \bar{1}.8264$$

Taking antilog,
$$e^{-0.4} = \text{antilog } \bar{1}.8264$$
$$= 0.6707$$

$\therefore$ $[R_1]_{10} = x = 100 \times 0.6707 = \mathbf{67.07\ M}$

Now
$$[R_2]_{10} = y = \frac{k_1 a}{(k_2 - k_1)}\,[e^{-k_t t} - e^{-k_2 t}]$$
$$= \frac{100 \times 4.0 \times 10^{-2}}{(0.6 \times 10^{-2}) - (4.0 \times 10^{-2})}\,[e^{-4 \times 10^{-2}} \times 10 - e^{-0.6 \times 10^{-2} \times 10}]$$
$$= -\frac{4}{3.4 \times 10^{-2}}\,[e^{-0.4} - e^{-0.06}]$$
$$[R_2]_{10} = y = \mathbf{31.76\ M}$$

Now $x + y + z = a$

$\therefore$
$$z = a - (x + y)$$
$$= 100 - (67.07 + 31.76)$$
$$[R_3]_{10} = z = \mathbf{1.17\ M}$$

(b)
$$[R_2]_{max} = [R_1]_0 \left(\frac{k_2}{k_1}\right)^{k_2/(k_1 - k_2)}$$
$$= 100 \left(\frac{0.15 \times 10^{-2}}{1.0 \times 10^{-2}}\right)^{0.15 \times 10^{-2}/(1 - 0.15) \times 10^{-2}}$$
$$= 100 \left(\frac{0.15}{1.0}\right)^{(0.15/0.85)}$$

$$[R_2]_{max} = \mathbf{71.55\ M}$$

$$t_{max} = \frac{2.303}{(k_1 - k_2)} \log (k_1/k_2)$$

$$= \frac{2.303}{(1.0 - 0.15) \times 10^{-2}} \log^{(1 \times 10^{-2}/0.15 \times 10^{-2})}$$

$$= \frac{2.303}{0.85 \times 10^{-2}} \log^{(110.15)}$$

$$t_{max} = \mathbf{55.80\ minutes}$$

7·16. ARRHENIUS EQUATION

van't Hoff showed that the value of equilibrium constant changes with temperature. On this basis, he suggested that the logarithm of the specific reaction rate must be a linear function of the reciprocal of absolute temperature. Arrhenius extended this suggestion and gave his own hypothesis. According to it,

(i) All molecules of a system cannot take part in a chemical reaction.

(ii) It is only a certain number of molecules which react. These reacting molecules are known as ***active molecules.*** These molecules have sufficient energy.

(iii) The molecules which do not take part in the chemical reaction are known as ***passive molecules.*** These molecules have poor energy content.

(iv) An equilibrium exists between active and passive molecules, *i.e.*,

$$\text{M (active)} \rightleftharpoons \text{M (passive)}$$

(v) When temperature is raised, the above equilibruim shifts to the left. This increases the number of active molecules which are ready to take part in a reaction. Thus, the increase in reaction rate with increase in temperature is due to an increase in the number of active molecules than due to the number of collisions.

So, the basic concept of Arrhenius theory is that ***the passive or non-active molecules become active due to the absorption of heat energy.***

[I] Derivation of Arrhenius Equation

Consider the following reversible reaction,

$$A + B \rightleftharpoons C + D$$

Rate of forward reaction, $r_f = k_1 [A] [B]$

Rate of backward reacion, $r_b = k_2 [C] [D]$

At equilibrium, $r_f = r_b$

$\therefore$ $k_1 [A] [B] = k_2 [C] [D]$

$$K_C = \frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]}$$

From thermodynamics, van't Hoff reaction isochore is, ...(1)

$$\frac{d \ln K_c}{dT} = \frac{\Delta E}{RT^2}$$

where ΔE is the heat of reaction of constant volume, K_c is the equilibrium constant. The value of $K_c = k_1/k_2$, where k_1 and k_2 are the rate constants of the forward and the backward reactions, respectively. Equation (1) becomes

$$\frac{d\ln k_1 - d\ln k_2}{dT} = \frac{\Delta E}{RT^2}$$

or
$$\frac{d\ln k_1}{dT} - \frac{d\log k_2}{dT} = \frac{\Delta E}{RT^2}$$

The heat of reaction ΔE may be written as $E_1 - E_2$ and then

$$\frac{d\ln k_1}{dT} - \frac{d\ln k_2}{dT} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2}$$

If E_1 and E_2 are assumed to be characteristic of the forward and backward reactions only, then

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} + I$$

$$\frac{d\ln k_2}{dT} = \frac{E_2}{RT^2} + I$$

It has been found that I is independent of temperature and is equal to zero. So, we can write

$$\frac{d\ln k_1}{dT} = \frac{E_1}{RT^2} \qquad ...(2)$$

and
$$\frac{d\ln k_2}{dT} = \frac{E_2}{RT^2} \qquad ...(3)$$

Equations (2) and (3) were proposed by Arrhenius and are known as ***differential forms of Arrhenius equation.*** The term E is called the energy of activation, which may be defined as the ***energy in excess to the average energy of the molecules at a given temperature which a molecule must have to enter into a chemical reaction.***

Integrating equation (2), *i.e.*,

$$\int d\ln k_1 = \frac{E_1}{R}\int \frac{dT}{T^2} + \text{constant (A)}$$

$$\ln k_1 = -\frac{E_1}{RT} + \text{constant } (A)$$

or
$$k_1 = Ae^{-E_1/RT}$$

Integrating equation (3), we get

$$\ln k_2 = -\frac{E_2}{R\,T} + \text{constant } (A)$$

$$k_2 = Ae^{-E_2/RT}.$$

In general,
$$k = A\,e^{-E/RT} \qquad ...(4)$$

In equation (4), A is constant. The factor $e^{-E/RT}$ is responsible for the marked influence of temperature on the reaction rate. The factor A is known as ***frequency factor*** of the reaction or ***collision number***. It is also called ***pre-exponential factor.***

[II] Determination of Activation Energy

The frequency factor (A) and energy of activation (E) can be determined by two methods.

(1) First method. This is a graphical method. The quantities A and E are characteristics of the given reaction, *i.e.*, they have fixed values for a given reaction. According to Arrhenius equation,

$$k = Ae^{-E/RT}$$

Taking logarithm of both sides, we get

$$\ln k = \ln A - \frac{E}{RT}$$

or

$$2.303 \log k = 2.303 \log A - \frac{E}{RT}$$

or

$$\log k = \log A - \frac{E}{2.303\, RT} \quad \dots (5)$$

The above equation represents a straight line, *i.e.*, a plot of log k against $1/T$ will give a straight line as shown in figure (9).

The tangent of the angle of inclination, *i.e.*, slope of the straight line with $1/T$ axis is given by,

$$\text{Slope} = \tan\theta = -\frac{E}{2.303R} \quad \dots (6)$$

The line AB is extrapolated to cut the log k axis at point C. The intercept (OC) of this line is equal to log A, *i.e.*,

$$\text{Intercept} = \log A \quad \dots (7)$$

Thus, knowing the slope and intercept from equations (6) and (7), we can calculate the values of E and A, respectively.

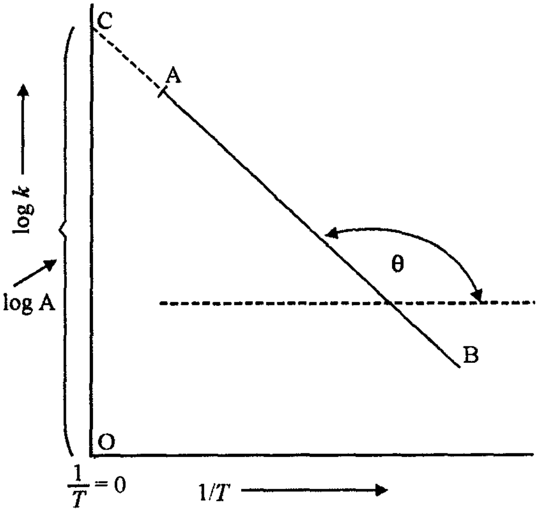


Fig. 9. Logarithm of rate constant (log *k*) of reaction versus inverse temperature (1/*T*).

(2) Second method. From Arrhenius equation, we can get the following equation

$$\log k = \log A - \frac{E}{2.303RT} \quad \dots (8)$$

We know that k has different values at different temperatures for a given reaction. Since E and A are the characteristics of the given reaction, they do not depend on the temperatures for a given reaction. Thus, from equation (8),

$$\text{At temperature } T_1, \log k_1 = \log A - \frac{E}{2.303\, RT_1} \quad \dots (9)$$

$$\text{At temperature } T_2, \log k_2 = \log A - \frac{E}{2.303\, RT_2} \quad \dots (10)$$

Subtracting equation (9) from equation (10), we get

$$\log k_2 - \log k_1 = -\frac{E}{2.303\,RT_2} + \frac{E}{2.303\,RT_1}$$

or $$\log (k_2/k_1) = \frac{E}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or $$\log (k_2/k_1) = \frac{E}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \quad \ldots (11)$$

So, by measuring the velocity constants k_1 and k_2 at two temperatures, T_1 and T_2, respectively we can calculate the value of E from equation (11). When the value of E is known we can calculate the value of A by putting the value of E in equation, $k = Ae^{-E/RT}$.

The Arrhenius equation holds equally good for homogeneous and heterogeneous reactions. Heterogeneous and catalytic reactions also give straight lines over a very wide range of temperatures.

If there is a marked deviation from a straight line on plotting log k and $1/T$, then it gives an indication that the observed reaction is a composite one made up of two or more concurrent reactions influenced by one of the reactions and it may predominate so that the slope of the curve corresponds to the value of E proper to this reaction.

For many reactions taking place at ordinary temperatures, the energy of activation is of the order of 20,000 cal/mole. Under such circumstances, the temperature coefficient (t_c) is found to satisfy van't Hoff rule. At 300 K, the value of t_c is given by,

$$\log_e t_c = \log_e \frac{k_{T+10}}{k_T} = \frac{d \log k}{d\,T} \times 10 = \frac{E}{R\,T^2} \times 10$$

$$\therefore \quad \log_e \frac{k_{T+10}}{k_T} = \frac{20{,}000}{2 \times 300^2} \times 10 = 1$$

$$\therefore \quad \frac{k_{T+10}}{k_T} \approx e \approx 2.7 \quad \ldots (11)$$

[III] Activation Energy and Chemical Reactions

We know that for a chemical reaction to occur, collisions between reactant molecules must occur. It has been postulated that only those collisions between reactant molecules which are associated with a certain minimum amount of energy can cause a chemical reaction. *The minimum amount of energy which must be associated with molecules so that mutual collisions may result in chemical reaction is termed as* ***threshold energy.*** Molecules possessing energy less than threshold energy will not react on collisions. Molecules possessing energy equal to or in excess of threshold energy constitute only a small fraction of the total number of molecules. This explains why a small fraction of the total number of collisions result in chemical reactions. *The number of molecules possessing energy equal to or in excess of threshold energy increase appreciably even with a small rise in temperature.* So, the rate of reaction increases considerably even with a small increase of temperature.

As already explained, there is a certain minimum energy (or threshold energy) which the colliding molecules must acquire before they are in a position to react. Most of the molecules have much less kinetic energy than the threshold energy. *The excess energy that the reactant molecules having energy less than the threshold energy must acquire in order to react to give the final products* is known as ***activation energy.*** Therefore,

Activation energy = Threshold energy – Energy possessed by the molecules initially.

In other words, passive or non-active molecules, *i.e.*, molecules possessing energy less than threshold energy, can be activated by absorption of excess energy known as activation energy. As already stated, the reactant molecules have to aquire a minimum amount of energy before they can yield products on mutual collisions, *i.e.*, there is an ***energy barrier*** placed between reactants and products. [Fig. (10a)]. This barrier has to be crossed before the reactants can yield products. It determines the magnitude of threshold energy which the reactant molecules must acquire before they can react to give products.

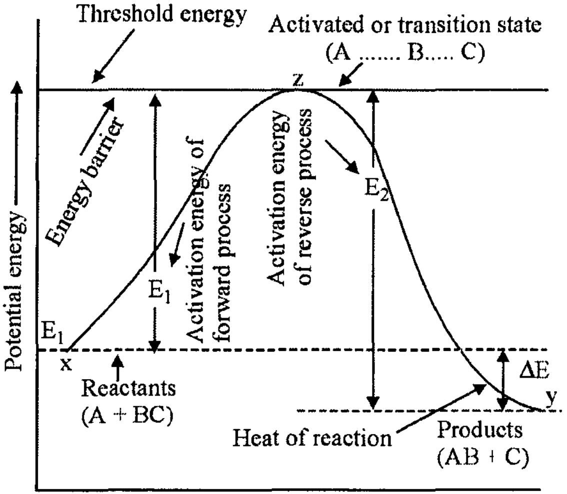


Fig. 10 (a). Exothermic reaction.

Further, different reactions require different amounts of activation energy. The concept of activation energy gives us an idea whether a given reaction is slow or fast at a given temperature. A reaction which has lower activation energy will proceed at a faster rate at a given temperature or vice versa. *The differences in activation energy are mainly responsible for observed difference in rates of reactions.*

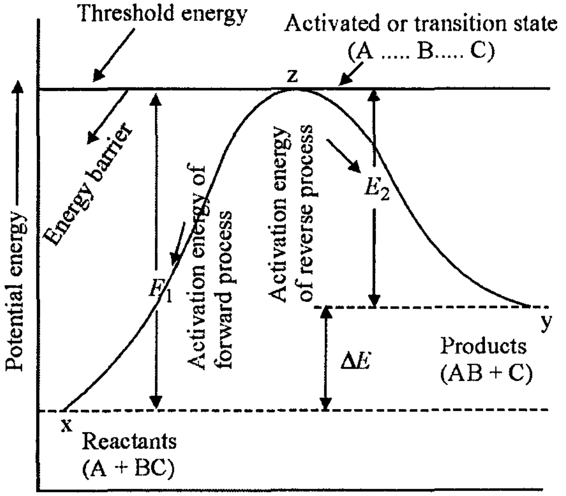


Fig. 10(b). Endothermic reaction.

The concept of activation energy as applied to chemical reactions can be explained by plotting energy against the progress of the reaction ($A + BC \rightleftharpoons AB + C$) as shown in figure (10a). The point x represents the initial energy (E_1) of the reactants, (A + BC) and represents the energy of the products (AB + C), E_2. At the beginning of rising portion of the curve the molecules come very close to each other, but they cannot react as they possess energy less than the threshold energy. If, however, sufficient energy is given to them, they can go up and reach the summit (or cliff) z of the energy barrier. The molecules are then said to be in an activated state and the configuration A ... B ... C is attained. This configuration is known as *activated complex or transition state or energy cliff state* which has the maximum potential energy.

$$\underset{\substack{\text{Reactants}\\\text{(Initial state)}}}{A + BC} \rightleftharpoons \underset{\substack{\text{Activated complex or}\\\text{transition state (Temporary)}}}{A \ldots\ldots B \ldots\ldots C} \longrightarrow \underset{\substack{\text{Products}\\\text{(Final state)}}}{AB + C}$$

In transition state, the molecules are under conditions of **acute strain**. The bonds between atoms of the reacting molecules become very feeble. The condition now is such that the probability of formation of new bonds between atoms of the moleules of the reactant is fairly strong and the transition state decomposes to give the products of the reaction (AB and C) or vice versa.

In the above case, the reactants are shown to possess a higher total energy than the products. So, according to the law of conservation of energy, there will be a release of energy, *i.e.*, heat will be evolved. The reaction is **exothermic** and the amount of heat evolved gives the **heat of reaction**. This release of energy is shown by ΔE in figure (10a). Evidently $\Delta E = E_1 - E_2$, where E_1 is the normal energy of the reactants and E_2 of the products. In this case, ΔE is negative as energy is released and not absorbed. An exothermic reaction has thus a lower activation energy or a faster rate of reaction.

Now, consider the reaction ($A + BC \rightleftharpoons AB + C$). Since the energy ($E_1$) of reactants (A + BC) is less than the energy (E_2) of the products (AB + C), as shown in figure (10b), energy will be absorbed and not released, *i.e.*, the reaction will be **endothermic**. An endothermic reaction has always a greater activation energy and hence has a slower rate of reaction than the opposing reaction.

[IV] Conclusions Drawn From Energy Profile Diagram

From figure (10a or 10b), we can draw the following conclusions:

(1) **Reaction coordinate**. The reaction coordinate is a measure of the approach of the reactant molecules towards the change. As the reactant molecules come closer, their structural orientations, internal vibrations, relative internuclear distances etc. change and even they make a transiet association. So, the reaction coordinate is a measure of these physical variations which involve potential energy changes of the system. It is not possible to get any quantitative value for the reaction coordinate but it simply gives a qualitative description of the conversion of reactants into products.

(2) In the energy profile diagram, we have

E_1 = Activation energy of reactants

E_2 = Activation energy of products

H_1 and H_2 = Enthalpies of reactants and products, respectively.

Energy profile diagram,** i.e., **potential energy changes during progress of exothermic and endothermic reactions.

$E_{(A+BC)}$ and $E_{(AB+C)}$ = Potential energies of reactants and products, respectively, which may be considered as H_1 and H_2, respectively.

(3) The difference in the level between the valley of reactants and valley of products is equal to the heat of reaction (ΔH). So,

(a) For endothermic reaction : $\Delta H = E_2 - E_1 = H_2 - H_1$ = positive, *i.e.*, energy equal to ΔH is absorbed during the chemical reaction.

(b) For exothermic reaction : $\Delta H = E_2 - E_1 = H_2 - H_1$ = negative, *i.e.*, energy equal to ΔH is evolved during the chemical reaction.

When $E_2 < E_1$, the reaction will be endothermic

When $E_2 > E_1$, the reaction will be exothermic.

(4) The difference in level between the reactant valley and the top of the hill (activated complex) is equal to energy of activation

∴ Energy of activation of forward reaction, *i.e.*, energy of activation of reactants,

$$E_1 = E_{(A\,.....\,B\,.....\,C)} - E_{(A+BC)}$$

Energy of activation of reverse reaction, *i.e.*, energy of activation of products,

$$E_2 = E_{(A\,.....\,B\,.....\,C)} - E_{(AB+C)}$$

(5) The height of the hill, *i.e.*, energy of activation determines the reaction rate. Lower the height of the hill or lower the value of energy of activation faster is the reaction. As the height of the hill, *i.e.*, energy of activation increases, the reaction rate goes on decreasing. Therefore, the substances which lower the energy of activation will increase the reaction rate. For example, addition of catalyst lowers the energy of activation of the reaction, the presence of catalyst makes the reaction faster. A catalyst gives a new reaction path with a lower energy of activation [Fig. (11)].

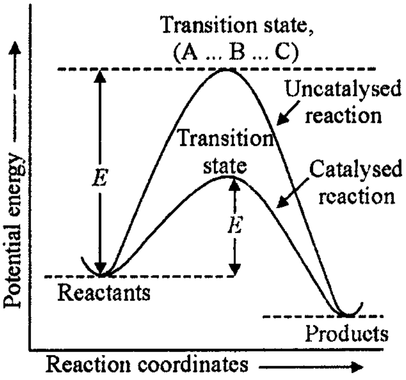


Fig. 11.

(6) In an endothermic reaction, the energy of activation must be at least as large as ΔH.

(7) The wider the hump in energy profile diagram for a given height the easier it is for the reactant molecules to form the transition state since there is now a wider latitude in nuclei positions for the activated complex.

Problem 1. ***For a first order reaction, the rate constant is found to be*** $7{\cdot}0 \times 10^{-7}$ ***at*** 7°C ***and*** 9×10^{-4} ***at*** 57°C. ***Calculate the energy of activation and its specific reaction rate at*** 127°C.

Solution : We know that, $\log \dfrac{k_2}{k_1} = \dfrac{E}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

where, E = activation energy.

$$T_1 = 273 + 7 = 280 \text{ K}, k_1 = 7 \times 10^{-7}, T_2 = 273 + 57 = 330 \text{ K}, k_2 = 9 \times 10^{-4},$$

So, from equation (11), we get

$$\log 9\times10^{-4}-\log 7\times10^{-7}=\frac{E}{2.303\times1.987}\left[\frac{1}{280}-\frac{1}{330}\right]$$

$$=\frac{E}{2.303\times1.987}\left[\frac{330-280}{280\times330}\right]$$

or
$$\log 9\times10^{-4}-\log 7\times10^{-7}=\frac{E\times50}{2.303\times1.987\times280\times330}$$

or
$$4.9042-7.8451=\frac{E}{2.303\times1.987\times280\times330}$$

or
$$E=\frac{2.303\times1.987\times280\times330\times3.1091}{50}$$

$$=\mathbf{26.29\times10^{3}\ cal/mole.}$$

Speific reaction rate at 127°C, *i.e.*, 400 K is given by

$$\log k_{400}-\log k_{280}=\frac{26290}{2.303\times1.987}\left[\frac{1}{280}-\frac{1}{400}\right]$$

$$=\frac{26290}{2.303\times1.987}\left[\frac{400-280}{400\times280}\right]$$

or
$$\log k_{400}-\log 7\times10^{-7}=\frac{26290\times120}{2.303\times1.987\times400\times230}=6.153$$

or
$$\log k_{400}-\log 7\times10^{-7}+6.153=-7.8451+6.153=-1.6921$$

or
$$k_{400}=\mathbf{0.02032\ min^{-1}}.$$

Problem 2. ***Bodenstein by studying the kinetics of decomposition of gaseous hydrogen iodide gave the values of specific reaction rates to be 3.517 × 10^{-7} and 3.954 × 10^{-2} at 556 K and 781 K. Calculate the energy of activation of the reaction.***

Solution : (a) We know that :

$$\log\frac{k_2}{k_1}=\frac{E}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

or
$$\log\frac{3.954\times10^{-2}}{3.517\times10^{-7}}=\frac{E}{2.303\times1.987}\left[\frac{1}{556}-\frac{1}{781}\right]$$

$$=\frac{E}{2.303\times1.987}\left[\frac{781-556}{556\times781}\right]$$

or
$$E=\frac{\log\dfrac{3.954\times10^{2}}{3.517\times10^{-7}}\times2.303\times1.987\times556\times781}{225}=\mathbf{44610\ cal\ mole^{-1}}$$

(b) We know that, $k=Ae^{-E/RT}$

where A = frequency factor.

Hence,
$$3.517\times10^{-7}=A.e^{-44610/1.987\times556}$$

or
$$\log 3.517\times10^{-7}=\log A-\frac{44610}{1.987\times556}$$

or
$$-6.4538=\log A-\mathbf{40.290}$$

or
$$\log A=33.8372$$

or
$$\mathrm{A}=\mathbf{6.874\times10^{34}}$$

Problem 3. ***If a first order reaction has an activation energy of 104500 J mole^{-1} and pre-exponential factor A in the Arrhenius equation has a value of 5 × 10^{13} sec^{-1}. At what temperature will the reaction has a half-life of (i) 1 minute, and (ii) 30 days ?***

Solution. (i) For a first order reaction $t_{1/2} = \frac{0.693}{k}$

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

$$= \frac{0.693}{60} = 1.155 \times 10^{-2} \text{ sec}^{-1}$$

Now, $$k = A \, . \, e^{-E_a/RT}$$

On substitution,

$$1.155 \times 10^{-2} = 5 \times 10^{-13} \, . \, e^{-104500/8.314 \times T}$$

Solving for T, we get

$$T = 348 \text{ K or } \mathbf{75°C}$$

(ii) $t_{1/2} = 30$ days $= 30 \times 24 \times 60 \times 60$ seconds

$$\therefore \qquad k = \frac{0.693}{30 \times 24 \times 60 \times 60} = 2.67 \times 10^{-4} \text{ sec.}$$

Again from Arrhenius equation

$$k = A \, . \, e^{-E_a/RT}$$

On substitution,

$$2.67 \times 10^{-4} = 5 \times 10^{13} \, . \, e^{-104500/8.314 \times T}$$

Solving for T, we have

$$T = 268 \text{ K or } -\mathbf{5°C}$$

Problem 4. ***For a given reaction at temperature T, the velocity constant, k is expressed as***

$$\boldsymbol{k = A \, . \, e^{-27000\,k/T}}$$

Given, R* = 2 cal mole^{-1} K^{-1}. *Calculate the value of energy of activation. Comment on the results.

Solution. From Arrhenius equation

$$k = A \, . \, e^{-E_a/RT}$$

Given that, $$k = A \, . \, e^{-27000\,k/T}$$

On comparison, we get

$$\frac{-E_a}{RT} = \frac{-27000\,k}{T}$$

$$\therefore \qquad E_a = 27000\,R \, . \, k \qquad \left(k = \frac{R}{N}\right)$$

$$= \frac{27000\,R^2}{N}$$

$$E_a = \frac{27000 \times 4}{6 \times 10^{23}} = \mathbf{18 \times 10^{-20} \text{ cals}}$$

Since value of E_a is very very small, the reaction would be very fast.

Problem 5. ***On the top of a certain mountain the atmospheric pressure is 530 mm Hg and pure water boils at 360 K. A climber finds that it takes* 3 × 10^2 *minutes to boil an egg as against 3 mts at 370 K.***

(i) What is the relation between rate of boiling the egg and time?

(ii) What is the ratio of the rate constants k_{370}/k_{360}?

(iii) What is the activation energy for the reaction that occurs when egg is boiled, given that the pre-exponential factor, A remains constant?

Solution. (i) According to the problem

$$\text{Rate of boiling the egg} \propto \frac{1}{\text{time}} = \frac{k}{\text{time}}$$

or $$k = \text{time} \times \text{Rate of boiling}$$

(ii) Hence, at 370 K : $k_{370} = 300 \times$ Rate of boiling

at 360 K : $k_{360} = 3 \times$ Rate of boiling

$$\therefore \quad k_{370}/k_{360} = \frac{300}{3} = \mathbf{100}$$

(iii) $$\log (k_{370}/k_{360}) = \frac{E_a}{2.303 \times 8.314}\left(\frac{370-360}{370 \times 360}\right)$$

$$\log (k_{370}/k_{360}) = \log\ 100 = 2$$

$$E_a = \frac{2 \times 2.303 \times 8.314 \times 370 \times 360}{10}$$

$$= \mathbf{997680\ J\ mole^{-1}}$$

Problem 6. ***The following data were obtained for a given reaction at 300 K :***

Reaction	***Energy of activation (kJ* mole^{-1}*)***
(1) Uncatalysed	**76**
(2) Catalysed	**57**

Calculate by what factor the rate of catalysed reaction is increased?

Solution. The Arrhenius equation is

$$k = A \,.\, e^{-E_a/RT}$$

$$\therefore \quad \log k = \log A - \frac{E_a}{2.303\,RT}$$

$$\therefore \quad \log k_1 = \log A - \frac{E_{a\,(1)}}{2.303\,RT}$$

and $$\log k_2 = \log A - \frac{E_{a\,(2)}}{2.303\,RT}$$

$$\therefore \quad \log k_2 - \log k_1 = \frac{1}{2.303\,RT}\,[E_{a\,(1)} - E_{a\,(2)}]$$

or $$\log (k_2/k_1) = \frac{1}{2.303\,RT}\,[E_{a\,(1)} - E_{a\,(2)}]$$

$$= \frac{1}{2.303 \times 8.314 \times 300}\,(76000 - 57000)$$

$$\log (k_2/k_1) = \frac{19000}{2.303 \times 8.314 \times 300}$$

$$= \frac{190}{6.909 \times 8.314}$$

Taking the antilog

$$\frac{k_2}{k_1} = \mathbf{2000}$$

i.e., rate of catalysed reaction is increased by a factor 2000.

Problem 7. ***A bottle of milk stored at* 30°C *sours in 36 hours, stored in a refrigerator at* 5°C *sours after one week. Assuming the rate constant to be inversely related to the souring time, estimate the activation energy of the chemical reaction involved in the souring reaction.***

Solution. We know that

$$\log(k_2/k_1) = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_2 \, . \, T_1}\right)$$

Let souring time = t, then as per problem,

$$k \propto \frac{1}{t}$$

$$\therefore \quad \frac{k_2}{k_1} = \frac{t_1}{t_2}$$

Hence

$$\log(t_1/t_2) = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_2 \, . \, T_1}\right)$$

Now

$$T_1 = 30 + 273 = 303 \text{ K} \text{ and } t_1 = 36 \text{ hrs.}$$

$$T_2 = 5 + 273 = 278 \text{ K} \text{ and } t_2 = 7 \times 24 = 168 \text{ hrs.}$$

On substitution,

$$\log(36/168) = \frac{E_a}{2.303 \times 8.314}\left(\frac{278 - 303}{278 \times 303}\right)$$

$$\therefore \quad E_a = \mathbf{43.15 \text{ kJ mole}^{-1}}$$

7·17. THEORIES OF REACTION RATES

Attempts have been made to derive Arrhenius equation in terms of atomic and molecular motions or in terms of energies of reacting particles without any reference to any precise motion of the molecules. We shall discuss the following main theories which dominate this field of investigation.

[I] Collision Theory for Unimolecular Reactions

It seems to be difficult as to how the collision theory could possibly be used to explain the mechanism of unimolecular reactions. In unimolecular processes only one molecule takes part in the reaction, then a question arises :

How do molecules in unimolecular reactions attain their energy of activation ? Lindemann (1922) suggested its answer by pointing out that the behaviour of unimolecular reactions can be explained on the basis of bimolecular collisions provided we postulate that a time lag exists between activation and reaction during which activated molecules may either react or get deactivated to ordinary molecules. Thus, the rate of reaction will not be proportional to all the molecules activated, but only to those which remain active.

Lindemann suggested that the above reaction takes place as follows :

First stage : $$\mathrm{A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A}$$

Second stage : $$\mathrm{A^* \xrightarrow{k_3} Products}$$

The first stage involves collision of reacting molecules forming a few activated molecules represented by A^*, with a velocity constant k_1, after which time–lag occurs. During this time-lag the activated molecules lose their excess energy and revert to the original state, with a velocity constant k_2.

Alternatively, the activated molecules may decompose into products, with a velocity constant k_3.

Rate of activation $= k_1 [A]^2$

Rate of deactivation $= k_2 [A^*] [A]$

Rate of decomposition $= k_3 [A^*]$

According to the stationary or steady state principle, whenever a short-lived reaction intermediate occurs in a system, its rate of formation can be taken as equal to its rate of disappearance. Applying this principle, we have

$$k_1 [A]^2 = k_2 [A^*] [A] + k_3 [A^*]$$

$$= [A^*] \{k_2 [A] + k_3\}$$

or
$$[A^*] = \frac{k_1 [A]^2}{k_2 [A] + k_3}$$

Since the rate of reaction is proportional to the concentration of activated molecules, we can, therefore, write that

$$\text{Rate of reaction} = -\frac{d [A]}{d t} = k_3 [A^*]$$

or
$$-\frac{d [A]}{d t} = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3} \quad ...(1)$$

(i) At high pressure. At sufficiently high pressure the term $k_2 [A]$ is far greater than k_3, which can thus be neglected. Equation (1) then reduces to

$$-\frac{d [A]}{d t} = \frac{k_1 k_3}{k_2} [A] = k' [A]$$

Hence, the reaction is of the **first order,** as the rate of reaction is proportional to the concentration of only one molecule of the reactant. Thus, if concentration of A is high, the reaction should be of the first order.

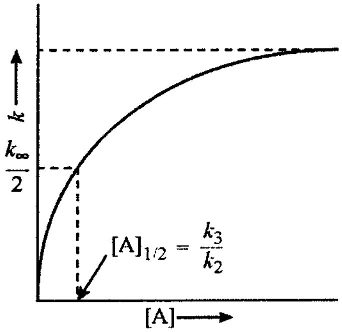


Fig. 12.

(ii) At low pressure. At low pressure, $k_3 \gg k_2 [A]$, therefore, $k_2 [A]$ can be neglected in comparison to k_3. Therefore, equation (1) reduces to

$$-\frac{d [A]}{d t} = \frac{k_1 k_3}{k_3} [A]^2 = k_1 [A]^2 \quad ...(2)$$

Hence, the reaction is of the **second order**. Thus, if the concentration of A is low, the reaction becomes of the second order.

Criticism of Lindemann's theory. According to this theory, there is a change from first order to second order kinetics as the pressure is lowered. This has been observed experimentally in a number of cases. This evidence is against the radiation theory but it is in favour of Lindemann's theory.

Although this theory gives a satisfactory qualitative intepretation of unimolecular reactions, yet it is not completely satisfactory quantitatively. Certain modifications are required. However, the two main difficulties of this theory are as follows :

(i) Suppose that a first order rate constant, *k* is defined by the equation

$$\frac{-d\,[\mathrm{A}]}{d\,t} = k\,[\mathrm{A}] \qquad \text{...(3)}$$

Equations (2) and (3) give rise to,

$$k\,[\mathrm{A}] = \frac{k_1 k_3\,[\mathrm{A}]^2}{k_2[\mathrm{A}] + k_3} = \frac{k_\infty}{1 + \dfrac{k_3}{k_2\,[\mathrm{A}]}} \qquad \text{...(4)}$$

The concentration $[\mathrm{A}]_{1/2}$ at which *k* should become equal to $k_\infty/2$ is defined by the equation

$$k_1\,[\mathrm{A}]_{1/2} = k_3 \qquad \text{...(5)}$$

So, when $k = k_\infty/2$, then

$$k_1\,[\mathrm{A}]_{1/2} = \frac{k_1 k_3}{k_2} = k_\infty$$

$$[\mathrm{A}]_{1/2} = \frac{k_\infty}{k_1} \qquad \text{... (6)}$$

The value of k_∞, the first order rate constant at high pressure can be obtained experimentally and the value of k_1 can be obtained from $Ze^{-E^*/RT}$, where E^* is the energy of activation. For several reasons, this method gave rise to the result that the first order rate constant should fall at a much higher pressure than was actually observed. There can be no doubt about the value of k_∞ so the error must be in the estimation of k_1. So, it became necessary for the collision theory to be modified in such a way as to give larger values of k_1. This difficulty was overcome by Hinshelwood.

(ii) The second difficulty becomes apparent when the experimental results are plotted. Equation (4) may be written as,

$$\frac{1}{k} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1\,[\mathrm{A}]} \qquad \text{...(7)}$$

According to equation (7), a plot of $1/k$ against $1/[\mathrm{A}]$ should give a straight line. However, deviations from linearity are observed as shown in figure (13). The deviations are explained according to the theories of Kassel, Rice and Ramsperger and the theory due to Slater.

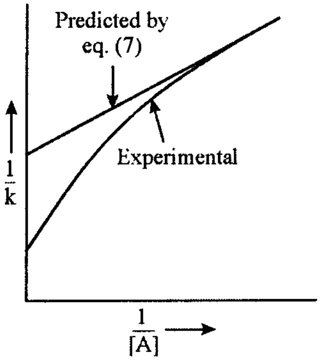


Fig. 13.

[II] Collision Theory of Bimolecular Reactions

If every collision between reacting gases were to result in chemical combination, the velocity of the reaction would be far greater than the one actually observed by experiments. Therefore, this theory received a serious setback. But the concepts of activated molecules and activation energy given by Arrhenius led to the revival of this theory in a modified form.

The postulates of the collision theory are :

(1) A reaction occurs on the collision of two molecules only if they possess a certain minimum amount of energy in excess to the normal energy of the molecules.

(2) The collisions between the molecules other than activated molecules do not lead to chemical reaction at all.

(3) The minimum energy in excess to their normal energy which the molecules must possess before chemical reaction on collision is known as and equal to the activation energy.

The probability that a molecule will possess energy in excess of an amount E per mole at a temperature T is given by the Boltzmann factor, $e^{-E/RT}$. If the energy is restricted to two components for a single molecule or two components for each of the two molecules making a total of two square terms, then the fraction of molecules which have energy in excess of E is actually equal to $e^{-E/RT}$.

For a chemical reaction to occur when two molecules collide, it is supposed that molecules must have energy greater than E_1 and the other than E_2, where $E_1 + E_2 = E =$ energy of activation. The probability of collisions is then given by

$$-e^{(E_1+E_2)/RT} = -e^{-E/RT}$$

For simplicity, this is the condition that a pair of molecules must have the energy necessary for the reaction.

Consider a bimolecular gaseous reaction, *e.g.*,

$$2\text{HI}\,(g) \rightleftharpoons \text{H}_2\,(g) + \text{I}_2\,(g)$$

The reaction for the present purpose can be considered to take place in the forward direction—a correct assumption only in the initial stages of the reaction. Evidently, two molecules of HI must collide with each other, before the bonds existing between H and I can break to form new bonds between H and H; I and I. This gives rise to one molecule each of H_2 and I_2.

If z' is the number of molecules per ml of the gas taking part in binary collisions per second and E be the energy of activation, then the reaction velocity is given by

$$\frac{dx}{dt} = z'\,e^{-E_1/RT} \qquad \ldots(8)$$

If n number of molecules of the same kind are involved in the bimolecular reaction, then

$$\frac{dx}{dt} = kn^2$$

Hence $$z'\,e^{-E/RT} = kn^2$$

or $$k = \frac{z'}{n^2}\,e^{-E_1/RT} \qquad \ldots(9)$$

Now z' is twice the number of molecular collisions per ml per second, as two molecules take part in every collision. Hence,

$$z' = 4\,n^2\,\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2}$$

where, σ is the molecular collision diameter and M is the molecular weight.

Therefore, equation (9) reduces to

$$k = \frac{4n^2\sigma^2}{M}\left(\frac{\pi RT}{M}\right)^{1/2} e^{-E_1/RT}$$

$$= 4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2} e^{-E_1/RT} \qquad ...(10)$$

$$= Ze^{-E_1/RT}$$

where $Z = 4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2}$ and is known as **collision number**. It is defined as, ***'number of collisions per second when there is only one mole of reactant per unit volume'.***

On taking logarithm of equation (10), we get

$$\log k = \log\left[4\sigma^2\left(\frac{\pi RT}{M}\right)^{1/2}\right] - \frac{E}{RT}$$

Differentiating the above expression with respect to temperature, we get

$$\frac{d \log k}{dT} = \frac{1}{2T} + \frac{E}{RT^2} \qquad ...(11)$$

Neglecting $\frac{1}{2T}$ (as in most cases $2T$ is small as compared to E/RT^2), equation (11) reduces to

$$\frac{d \log k}{dT} = \frac{E}{RT^2} \qquad ...(12)$$

This equation is identical with Arrhenius equation. If the value of σ (collision diameter) is known, the collision number (Z) can be calculated. It is thus possible to compare it with the experimental value of the frequency factor.

If the bimolecular reaction involves two molecules of different species, then the collision number (Z) is given by

$$Z = \sigma^2\left[8\pi RT\left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2}\right]$$

where M_1 and M_2 are the respective molecular weights of different species.

The equations developed are applicable to simple homogeneous reactions but will not apply to heterogeneous reactions or chain reactions. A plot between log k and $1/T$ will not be exactly linear, but less deviations are observed on plotting $\log k/T^{1/2}$ against $1/T$.

Table-3

Reactions	*E* (calculated) in calories	*E* (experimental) in calories
1. $2N_2O \rightarrow 2N_2 + O_2$	56,000	58,000
2. $2HI \rightarrow H_2 + I_2$	44,000	44,000
3. $H_2 + I_2 \rightarrow 2HI$	40,000	39,500

The success of the collision theory can be judged from the above table in which the activation energies calculated according to equation (11) [cf § 7.16] as well as those based upon experimental data have been compared. It will thus be seen that there is a very good agreement between the calculated and experimental values.

Failures of Collision Theory. However, there are certain reactions where the experimental and calculated values differ, *e.g.*, the reaction between vapours of ethanol and acetic anhydride, combination of two molecules of ethylene etc.

In the bimolecular polymerisation of ethylene, the reaction occurs only once in about 2000 collisions between activated molecules. In the polymerisation of 1 : 3 butadiene the reaction occurs only once in about 10,000 collisions between activated molecules.

A sufficient number of slow reactions are known which show that the phenomenon is limited to few instances and the equation $k = Ze^{-E/RT}$ reduces to,

$$k = PZe^{-E/RT}$$

where P = *probability factor or steric factor*, which makes allowances for effects causing deviations from the ideal behaviour. The value of P varies from unity to 10^{-8} depending upon the nature of the reaction.

Anomalies were also found to exist in liquid systems. These were assumed to be due to solvent effects, but in some cases these were found to be present in gaseous systems also. Several weaknesses of collision theory have been found in recent years.

(1) Firstly, attempts to correlate the value of P-probability factor-with the structure and properties of reacting molecules have not been successful.

(2) Secondly, on this basis it is not possible to advance an explanation for abnormally high rates.

(3) Thirdly, a logical weakness is observed when reversible reactions are considered.

Consider the following reaction :

$$\mathrm{X + Y} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{XY}$$

For the forward reaction : $k_1 = P_1Z_1\, e^{-E_1/RT}$

For the backward reaction : $k_2 = P_2Z_2\, e^{-E_2/RT}$

Since, $K = k_1 / k_2$, we have,

$$K = \frac{P_1Z_1\, e^{-E_1/RT}}{P_2Z_2\, e^{-E_2/RT}}, \text{ i.e., } K = \frac{P_1Z_1}{P_2Z_2} \cdot e^{(E_1 - E_2)/RT}$$

According to thermodynamics, we have

$$K = e^{-\Delta G/RT} = e^{-\Delta S/RT} \cdot e^{-\Delta H/RT}$$

where, ΔG = increase in free energy, ΔS = increase in entropy,
ΔH = increase in heat content.

Comparing these expressions for K it is clear that $e^{-(E_1 - E_2)/RT}$ and $e^{-\Delta H/RT}$ correspond with one another. If the molecules of the reactants and products are of comparable dimensions, $Z_1 = Z_2$, so that entropy term $e^{-\Delta S/RT}$ must be equal to P_1/P_2. It is, therefore, not sufficient to correlate the probability of certain reacting groups being together in collision. They should be interpreted in terms of entropy factor.

[III] Theory of Absolute Reaction Rates

Eyring and Polanyi (1935) attempted to give an alternative approach to reaction kinetics. The theory given by them is known as absolute reaction rate or activated complex theory. According to this theory, the reactant molecules before reacting, form an activated complex in equilibrium with the reactants. The activated complex has the property of an ordinary molecule but its existence is only transient. It then decomposes to give the products. The reaction velocity is given by the decomposition of this activated complex.

If two reactants A and B react to give products, then according to this theory the following steps take place :

$$\underset{\text{Reactants}}{A + B} \rightleftharpoons \underset{\substack{\text{Activated}\\\text{complex}}}{[AB]} \rightarrow \text{Products}$$

After a long period, Erying, Polyani and Evans gave a theory which deals with the fundamental properties such as dimensions, vibrational frequency, mass, etc. of the reactants. The theory is known as **'absolute theory of reaction rates'.** According to this theory, ***before the molecules can react, they must collide to form an activated complex which in turn decomposes to give the products.***

We can also calculate the frequency with which it occurs. Consider a reaction,

$$A + B \rightleftharpoons [AB^*] \rightarrow \text{Products}$$

where [AB*] is the activated complex. Its concentration can be calculated from the concentrations of reactants A and B by means of statistical mechanics. From the first equilibrium, we have

$$k_0 = \frac{[AB^*]}{[A]\,[B]}$$

where k_0 = equilibrium constant, which is given by

$$k_0 = \frac{f_0}{f_A f_B} e^{-E_0/RT}$$

where f_A, f_B and f_0 are the partition functions of reactants A, B and activated complex, respectively, E_0 is the difference between zero point energy per mole of the activated complex and that of the reactants. Since it is the energy which the reactants must acquire at 0K before they can react, E_0 is thus also the energy of activation at this temperature. So,

$$\frac{[AB^*]}{[A]\,[B]} = \frac{f_0}{f_A f_B} \cdot e^{-E_0/RT}$$

The partition functions can be factorised into corresponding terms of translational, rotational, vibrational and electronic energy.

If a reactant A consists of n_A atoms, there will be $3n_A$ such partition functions of which three are for translational motion, three are for rotational motion (or two if molecule is linear) and hence $3n_A - 6$ for vibrational motion or $3n_A - 5$ for linear molecule. For the activated complex which consists of n_A and n_B atoms we have $3\,(n_A + n_B) - 6$ vibrational terms, if molecule is non-linear and $3\,(n_A + n_B) - 5$ if molecule is linear. One of these vibrational terms is of different character from the rest, since it corresponds to every loose vibration which allows the activated complex to dissociate into products. For this one degree of freedom we may employ instead of ordinary factor, the equation

$$f_v = \underset{v \to 0}{\text{Lt}}\ (1 - e^{-hv/KT})^{-1}$$

$$= \frac{1}{1 - \left(1 - \frac{hv}{KT}\right)} = \frac{KT}{hv}$$

Therefore, $$k_0 = \frac{[AB^*]}{[A]\,[B]} = \frac{f_0}{f_A \cdot f_B} \cdot \frac{KT}{hv}\, e^{-E_0/RT}$$

where f_0 is the partition function which refers to $3(n_A + n_B) - 7$ degrees of vibrational freedom. From the last expression,

$$v\,[AB^*] = [A]\,[B]\,.\,\frac{KT}{h} \cdot \frac{f_0}{f_A \cdot f_B} \cdot e^{-E_0/RT}$$

where v = frequency of vibration of activated complex in the degree of freedom corresponding to its decomposition.

Therefore, $v\,[AB^*]$ = Rate of reaction (r)

$$= [A]\,[B] \cdot \frac{KT}{hv} \cdot \frac{f_0}{f_A \cdot f_B} \cdot e^{-E_0/RT}$$

Rate of reaction, $r \propto [A]\,[B] = k_1\,[A]\,[B]$

$$k_1 = \frac{r}{[A]\,[B]}$$

$$= \frac{KT}{h} \cdot \frac{f_0}{f_A \cdot f_B} \cdot e^{-E_0/RT}$$

k_1 = specific rate constant.

The factor KT/h has the dimensions of frequency and its value is 61×10^{-12} sec^{-1} at 300K. This expression holds good when the activated complex is made up of only one molecule of A and B. In general, if the activated complex is composed of A_x and B_y number of atoms, the rate will be proportional to $[A]^x\,[B]^y$. The structure of the activated complex is determined by methods of quantum mechanics.

The activated complex formed between atoms is a diatomic molecule AB which has 3 degrees of translational freedom, 2 of rotational and 1 of vibrational freedom. As the activated complex decomposes, the vibrational freedom will correspond to its decomposition and, therefore, can be neglected. Now translational partition function due to translational degree of freedom is given by

$$f_t = \frac{[2\pi\,(m_A + m_B)\,KT]^{3/2}}{h^3}$$

Due to rotation the rotational partition function is given by

$$f_r = \frac{8\,\pi^2\,I\,KT}{h^2}$$

where, I = moment of inertia. We know that,

$$f_0 = f_t \cdot f_r$$

$$= \frac{[2\pi(m_A + m_B)KT]^{3/2}}{h^3} \cdot \frac{8\pi^2 I . KT}{h^2}$$

and $$I = \sigma_{AB}^2 \left(\frac{m_A + m_B}{m_A\, m_B} \right)$$

In case of atoms, the partition functions of A and B are given by

$$f_A = \frac{(2\pi m_A KT)^{3/2}}{h^3} \text{ and } f_B = \frac{(2\pi m_B KT)^{3/2}}{h^3}$$

$$\therefore \quad k_1 = \frac{KT}{h} \cdot \frac{f_0}{f_A f_B} e^{-E_0/RT}$$

$$= \sigma_{AB}^2 \left\{ 8\pi KT \left(\frac{m_A + m_B}{m_A\, m_B} \right) \right\}^{1/2} . e^{-E_0/RT}$$

An identical equation is given by collision theory according to which

$$k_1 = A\, e^{-E_0/RT}$$

Comparing the last two equations, we have

$$A = \sigma_{AB}^2 \left\{ 8\pi KT \left(\frac{m_A + m_B}{m_A\, m_B} \right) \right\}^{1/2}$$

If both the numerator and denominator are multiplied by Avogadro's number then

$$A = \sigma_{AB}^2 \left\{ 8\pi RT \left(\frac{M_A + M_B}{M_A\, M_B} \right) \right\}^{1/2}$$

where M_A and M_B are the respective molecular weights.

So, it is seen that the above expression is identical with the collision number given for bimolecular reactions. It, therefore, follows that statistical mechanics and collision theory lead to the same results provided the reactants are atoms. The treatment can be extended to molecules also, but an agreement between the theories is not found.

The hydrolysis of tertiary butyl chloride is a first order reaction. The mechanism suggested is :

(i) $$(CH_3)_3\, C - Cl \xrightarrow{\text{Slow}} \underset{\text{Activated complex - I}}{(CH_3)_3\, C^+ \ldots Cl^-} \rightarrow (CH_3)_3\, Cl^+ + Cl^-$$

(ii) $$(CH_3)_3\, C^+ + OH^- \xrightarrow{\text{Fast}} \underset{\text{Activated complex - II}}{(CH_3)_3\, C^+ \ldots OH^-} \rightarrow (CH_3)_3\, C - OH$$

The overall kinetics of the reaction is determined by the slow step, so when we are measuring the rate of reaction we are in fact mesuring the rate of the first stage reaction. Since only one molecule of the reactant is involved in the formation of the activated complex, the reaction is unimolecular. Ingold gave the notation for this type of mechanism as $S_N{}^1$.

[IV] Transition State Theory

According to transition state theory, the rate of a reaction is the number of activated complexes passing per second over the top of potential energy barrier.

This rate is equal to the concentration of activated complex times the average velocity with which a complex moves across to the product side. The activated complex is not in a state of stable equilibrium, since it lies at a maximum potential energy.

(1) Postulates of transition state theory. The postulates of this theory are as follows :

(i) As the reacting molecules approach each other, there is a continuous series of changes in bond distance. These changes are accompanied by energy changes.

(ii) The reactant molecules are changed into an energy rich intermediate called *activated complex or transition state* [Fig. (14)].

(iii) The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy. If it is a unimolecular reaction, the reactant molecule may produce the activated complex by rearrangement of atoms and redistribution of energy.

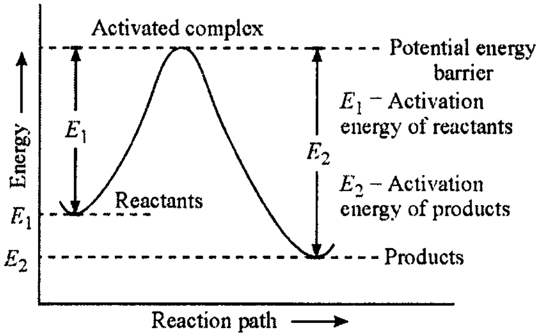


Fig. 14.

(iv) The activated complex, though unstable, has a transient existence. It is treated formally as a definite molecule with an independent entity. The activated complex remains in equilibrium with the reactants and its potential energy is maximum. Finally, the activated complex decomposes into products.

(v) The activation energy of reaction in the light of this theory, is the additional energy which the reacting molecules must acquire to form the activated complex.

(2) Thermodynamic or mathematical treatment of transition state theory. Consider a bimolecular reaction between reactants A and B. According to transition state theory.

$$\underset{\text{Reactants}}{A + B} \rightleftharpoons \underset{\substack{\text{Activated}\\ \text{complex}}}{[X^*]} \longrightarrow \text{Products}$$

The equilibrium constant (K^*) for the formation of activated complex is

$$K^* = \frac{[X^*]}{[A]\,[B]} \quad \text{or} \quad [X^*] = K^*\,[A]\,[B] \qquad \ldots(13)$$

According to transition state theory, the rate of reaction is the number of activated complexes which pass over the potential barrier per unit time. This, in turn, is equal to the concentration of activated complex multiplied by the frequency at which the complex would decompose into products. Mathematically,

$$\frac{dx}{dt} = [X^*] \times \text{Rate (or frequency) of dissociation of activated complex} \quad \ldots(14)$$

From equations (13) and (14), we get

$$\frac{dx}{dt} = K^*[A]\,[B] \times \text{Rate (or frequency) of dissociation of activated complex.}$$

The activated complex would decompose only if enough vibrational energy is supplied to the system, so that the atoms vibrate with certain critical frequency, leading to bond breaking. Therefore,

Frequency of dissociation of activated complex $= E_{\text{vib}}/h$ ...(15)

where $E_{\text{vib}} =$ average vibrational energy at temperature T and $h =$ Planck's constant.

But $$E_{\text{vib}} = kT = \frac{RT}{N} \qquad (\because k = R/N) \qquad \text{...(16)}$$

From equations (15) and (16), frequency of dissociation of activated complex $= RT/Nh$.

$$\therefore \qquad \frac{dx}{dt} = K^* \,[\text{A}]\,[\text{B}]\,.\,\frac{RT}{Nh} \qquad \text{...(17)}$$

For conversion of reactants into products,

$$\frac{dx}{dt} = k\,[\text{A}]\,[\text{B}] \qquad \text{...(18)}$$

From equations (17) and (18),

$$k\,[\text{A}]\,[\text{B}] = K^*\,[\text{A}]\,[\text{B}]\,.\,\frac{RT}{Nh}$$

or $$k = K^*\,.\,\frac{RT}{Nh} \qquad \text{...(19)}$$

Equation (19) is the ***mathematical statement of transition state theory.***

According to thermodynamics, K^* can be correlated with ΔG^* through the following relation,

$$\Delta G^* = -RT \ln K^*$$

where $\Delta G^* =$ [Free energy of activated complex) – (Free energy of reactants)]. It is known as standard free energy change. We know that

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$\therefore \qquad -RT \ln K^* = \Delta H^* - T\Delta S^*$$

or $$\ln K^* = \frac{-(\Delta H^* - T\Delta S^*)}{RT}$$

or $$K^* = e^{-(\Delta H^* - T\Delta S^*)/RT} \qquad \text{...(20)}$$

From equations (19) and (20) we get,

$$k = \frac{RT}{Nh}\,.\,e^{-(\Delta H^* - T\Delta S^*)/RT}$$

$$k = \frac{RT}{Nh}\,.\,e^{-\Delta H^*/RT}\,.\,e^{\Delta S^*/R} \qquad \text{...(21)}$$

where, ΔH^* = standard enthalpy change, *i.e.*, standard heat of activation

ΔS^* = standard entropy change, *i.e.*, standard entropy of activation.

Equation (21) can be applied not only to bimolecular processes, but also to unimolecular and trimolecular processes. Morever, it can be applied to reactions in solutions also. Equation (21) has the following advantages :

(1) It is not restricted to bimolecular processes, but it is equally applicable to unimolecular and trimolecular processes.

(2) It can be applied to reactions in solution.

Equation (21) can also be expressed in a different form involving experimental energy of activation E_a instead of the heat of activation ΔH^*. The change of equilibrium constant K^* with temperature is given by,

$$\frac{d \ln K^*}{dT} = \frac{\Delta E^*}{RT^2} \qquad \text{...(22)}$$

where ΔE^* = increase in the energy of activation when the reactants go from the initial to the activated state.

According to equation (19),

$$k = K^* \cdot \frac{RT}{Nh}$$

$$\therefore \qquad \ln k = \ln K^* + \ln T + \ln\left(\frac{R}{Nh}\right)$$

Differentiating it with respect to temperature, T, we get

$$\frac{d \ln k}{dT} = \frac{d \ln K^*}{dT} + \frac{1}{T} = 0 \qquad \text{... (23)}$$

Combining equations (22) and (23),

$$\frac{d \ln k}{dT} = \frac{\Delta E^*}{RT^2} + \frac{1}{T}$$

$$\text{or} \qquad \frac{d \ln k}{dT} = \frac{\Delta E^* + RT}{RT^2} \qquad \text{...(24)}$$

According to Arrhenius equation,

$$k = A \cdot e^{-E_a/RT}$$

$$\therefore \qquad \ln k = \ln A - \frac{E_a}{RT}$$

Differentiating it with respect to temperature,

$$\frac{d \ln k}{dT} = 0 + \frac{E}{RT^2} \qquad \text{...(25)}$$

From equations (24) and (25),

$$\frac{E_a}{RT^2} = \frac{\Delta E^* + RT}{RT^2}$$

$$\text{or} \qquad E_a = \Delta E^* + RT \qquad \text{...(26)}$$

$$\text{Now,} \qquad H^* = E^* + PV^*$$

For a change at constant P,

$$\Delta H^* = \Delta E^* + P\Delta V^*$$

$$\text{or} \qquad \Delta E^* = \Delta H^* - P\Delta V^* \qquad \text{...(27)}$$

Combining equations (26) and (27),

$$E_a^* = \Delta H^* + RT - P\Delta V^* \qquad \text{...(28)}$$

$$\text{For an ideal gas,} \qquad PV = nRT$$

$$\therefore \qquad P\Delta V^* = \Delta n^* \cdot RT \qquad \text{...(29)}$$

Combining equations (28) and (29),

$$E_a = \Delta H^* + RT - \Delta n^* RT \qquad \text{...(30)}$$

where, Δn^* = change in the number of moles in passing from initial to activated state and ΔV^* = change in volume when the reactants pass from initial to activated state.

Case [I]. For a *unimolecular reaction*, there is no change in the number of molecules (or moles) as the activated complex is formed. So,

$$\Delta n^* = 0 \quad \text{and} \quad \Delta V^* = 0$$

Thus, from equation (30),

$$E_a = \Delta H^* + RT \qquad ...(31)$$

According to equation (21),

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R'} \qquad ...(32)$$

Substituting the value of ΔH^* from equation (31), we get,

$$k = \frac{RT}{Nh} e^{-(E_a - RT)/RT} \cdot e^{\Delta S^*/R}$$

or

$$k = \frac{RT}{Nh} e^1 \cdot e^{-E_a/RT} \cdot e^{\Delta S^*/R} \qquad ...(33)$$

Case [II]. For a *bimolecular reaction*, $\Delta n^* = 1$, so from equation (30),

$$E_a = \Delta H^* + 2RT$$

Therefore, rate equation (32), becomes,

$$k = \frac{RT}{Nh} \cdot e^{-(E_a - 2RT)/RT} \cdot e^{\Delta S^*/RT} \qquad ...(34)$$

or

$$k = \frac{RT}{Nh} \cdot e^2 \cdot e^{-E_a/RT} \cdot e^{\Delta S^*/R} \qquad ...(35)$$

It has been found that the difference between ΔH^* and E_a is small and in fact, for reactions in solution and for unimolecular reactions, $\Delta H = E_a$. In cases involving gases, an additional term $\Delta n^* RT$ has been added. So, without much error, we may write

$$k = \frac{RT}{Nh} \cdot e^{-E_a/RT} \cdot e^{\Delta S^*/R} \qquad ...(36)$$

Equation (36) is similar to Arrhenius equation except that ΔH^* appears instead of E_a. The comparison of equation (36) with Arrhenius equation, $k = A\, e^{-E_a/RT}$ shows that the frequency factor A is related to the entropy of activation (ΔS^*) as

$$A = \frac{RT}{Nh} \cdot e^{\Delta S^*/R} \qquad ...(37)$$

(3) Discussions of equation (37)

(1) An exact calculation of A needs the evaluation of ΔS^*. The value of ΔS^* may be negative or positive.

(2) A negative value of ΔS^* means that the activated complex is more ordered than the reactants. A more negative value of ΔS^* shows that the factor A will have a smaller value, which means that the reaction will be slower.

(3) A positive value of ΔS^* means that the entropy of complex is greater than the entropy of the reactants. A loosely bound complex has a higher entropy than a tightly bound one. There is a decrease in entropy in passing through the activated complex.

(4) Comparison of transition state theory with collision theory

(i) From transition state theory,

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \qquad \ldots (38)$$

From collision theory, $k = PZe^{-E/RT}$ ... (39)

where P = probability factor or steric factor

Z = collision number or collision frequency.

Comparing equations (38) and (39), we have

$$PZe^{-E/RT} = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R}$$

or

$$PZe^{-\Delta H^*/RT} = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \cdot e^{\Delta S^*/R} \qquad (\because E = \Delta H^*)$$

or

$$PZ = \frac{RT}{Nh} \cdot e^{\Delta S^*/R}$$

or

$$P = \frac{RT}{ZNh} \cdot e^{\Delta S^*/R}$$

The steric factor P is thus related to entropy of activation.

(ii) In collision theory, no account is taken of the internal motions of the reactant molecules, whereas in transition state theory, account is taken of the internal degrees of freedom of reactant molecules and the changes these undergo on reaction.

(iii) The concept of entropy of activation in transition state theory is very useful for qualitative purposes. Thus, for bimolecular processes, this is an advantage over the collision theory.

Problem 1. ***For the hydrolysis of sulphamic acid, the velocity constant is*** **1.16×10^{-3} mole^{-1} dm^3 sec^{-1}** ***at 363 K, while*** **$E_a = 127490$** ***J mole^{-1}. From these data find ΔG^*, ΔH^*, and ΔS^* of the reaction at 363 K.***

Solution. W know that

$$k = \frac{RT}{Nh} K^*$$

$\therefore$

$$K^* = \frac{k \,.\, N \,.\, h}{RT}$$

$$= \frac{(1.16 \times 10^{-3}) \times (6.023 \times 10^{23}) \times (6.626 \times 10^{-34})}{(8.314) \times (363)}$$

$$K^* = \mathbf{1.534 \times 10^{-16}\ mole^{-1}\ dm^3}$$

Now

$$\Delta G^* = -RT \ln K^*$$

$$= -2.303\, RT \log K^*$$

$$\Delta G^* = -2.303 \times 8.314 \times 363 \times \log (1.534 \times 10^{-16})$$

$$= \mathbf{109900\ J\ mole^{-1}}$$

Since we know

$$E_a = \Delta H^* + RT$$

$\therefore$

$$\Delta H^* = E_a - RT$$

$$= (127490) - (8.314) \times (363)$$

$$= \mathbf{124473\ J\ mole^{-1}}$$

Again,

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$\therefore \quad \Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$

$$= \frac{124473 - 109900}{363}$$

$$= \mathbf{40.14\ J\ mole^{-1}\ K^{-1}}$$

Problem 2. ***Calculate ΔH^*, ΔG^** and *ΔS^* for the second order reaction***

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

***at 500 K. Given $A = 2.0 \times 10^9\ sec^{-1}$ and the energy of activation* = 111 kJ mole^{-1}.**

Solution. For a bimolecular reaction,

$$E_a = \Delta H^* + 2RT$$

$$\therefore \quad \Delta H^* = E_a - 2RT$$

$$= 111 - 2 \times 8.314 \times 500$$

$$= 102700\ \text{J mole}^{-1}$$

$$\Delta H^* = \mathbf{102.7\ kJ\ mole^{-1}}$$

Now

$$A = \frac{RT}{Nh} \,.\, e^{\Delta S^*/R}$$

$$\therefore \quad e^{\Delta S^*/R} = \frac{ANh}{RT}$$

$$\therefore \quad \frac{\Delta S^*}{R} = \ln\left(\frac{ANh}{RT}\right)$$

$$\Delta S^* = 2.303\, R \log\left(\frac{Ah}{kT}\right) \qquad \left(\because k = \frac{R}{N}\right)$$

$$= 2.303 \times 8.314 \times \log\left(\frac{2 \times 10^9 \times 6.626 \times 10^{-34}}{1.38 \times 10^{-23} \times 500}\right)$$

$$\Delta S^* = \mathbf{-\,71.17\ J\ mole^{-1}\ K^{-1}}$$

Since

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

$$= 102700 - 500 \times (-\,71.17)$$

$$\Delta G^* = \mathbf{138300\ JK\ mole^{-1}}$$

Problem 3. ***For the unimolecular reaction***

Cyclopropane ⟶ Propylene

the value of log A for high pressure limit is 15.17. Calculate,

(i) ΔS^* for the reaction at 298 K

(ii) Contribution of ΔS_{trans} at 298 K

(iii) Sum of the contributions of ΔS^*_{vib}, ΔS^*_{rot}* and *$\Delta S^*_{electronic}$.

Solution. For unimolecular reaction

$$\Delta n^* = 0$$

Hence

$$k = \frac{RT}{Nh} \,.\, e \,.\, e^{-E_a/RT} \,.\, e^{\Delta S^*/R}$$

or

$$k = A \,.\, e^{-E_a/RT}$$

where $$A = \frac{RT}{Nh} \cdot e \cdot e^{\Delta S^*/R}$$

or $$A = \frac{kT}{h} \cdot e \cdot e^{\Delta S^*/R}$$

$$\therefore \quad \ln A = \ln \frac{kT}{h} + \ln e + \frac{\Delta S^*}{R}$$

$$\ln A = \ln \frac{kT}{h} + 1 + \frac{\Delta S^*}{R}$$

$$\log A = \log \frac{kT}{h} + \frac{1}{2.303} + \frac{\Delta S^*}{R \times 2.303}$$

$$\therefore \quad \Delta S^* = 2.303R \left[\log A - \log \frac{kT}{h} - \frac{1}{2.303} \right]$$

On substitution, $$\Delta S^* = 2.303 \times 8.314 \left[15.17 - \log \left(\frac{1.38 \times 10^{-23} \times 298}{6.62 \times 10^{-34}} \right) - \frac{1}{2.303} \right]$$

or $$\Delta S^* = \mathbf{37.130\ JK^{-1}\ mole^{-1}}$$

Since in the above reaction, reactant and product have the same mass, hence

$$\Delta S^*_{\text{trans}} = 0$$

Therefore, the whole contribution is due to internal degrees of freedom, that is,

$$\Delta S^* = \Delta S^*_{\text{rot}} + \Delta S^*_{\text{vib}} + \Delta S^*_{\text{electronic}} = \mathbf{37.130\ JK^{-1}\ mole^{-1}}$$

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. The determination of the order of a reaction is a complicated process. Mention the complicating factors that one comes across in determining the order of a reaction.
2. Explain why the hydrolysis of an ester in the presence of a dilute acid follows first order kinetics, while that in the presence of dilute alkali follows a second order kinetics.
3. Iodine is liberated when an iodide is reacted with a nitrite solution according to the equation :

   $$2NO_3^- + 4H^+ + 2I^- \longrightarrow I_2 + 2NO + 2N_2O$$

   The experimental rate law for the reaction has been found to be

   $$R = k\,[NO_2^-]\,[I^-]\,[H^+]^2$$

   How would the reaction rate change with the following changes in concentration of various reactants :

   (i) $[NO_2^-]$ is doubled keeping the concentration of the other two reactants constant.

   (ii) $[H^+]$ is doubled keeping the concentration of the other two reactants constant.

   (iii) $[H^+]$ is halved keeping the other two concentrations unaltered.

   (iv) Concentrations of all the three reactants are doubled?
4. What is meant by a reaction being of first, second or zero order ? What are pseduo-unimolecular reactions ?
5. Discuss in details the factors which influence the rate of reactions. Illustrate your answer by giving suitable examples.
6. Bring out clearly the main features of the collision theory of reaction rates. What do you mean by effective collisions ?

7. Discuss in detail the importance of the study of chemical kinetics in understanding the mechanisms of reactions. Illustrate your answer by giving suitable examples.

8. What is meant by the term temperature coefficient of a reaction ? How would you explain on the basis of collision theory, the effect of temperatures on rate of reactions ?

9. Write a short note on energy distribution in molecules. What is the importance of energy distribution curves ?

10. What is meant by activation energy ? Invoking the concept of activation energy, explain why reactions having the same concentration of reactants, differ so much in their rates ?

11. Derive the integrated equation for a second order reaction.

12. Derive the equation

$$k = \frac{2{\cdot}303}{t} \log_{10} \frac{a}{a-x}$$

for a unimolecular reaction where a is the initial concentration (mol L^{-1}) and x is the number of moles decomposed in time t.

13. Derive an expression for the number of bimolecular collisions of a gas.

14. Describe the experimental determination of the rate constant of an acid catalysed hydrolysis of methyl acetate.

15. What is a second order reaction ? Deduce an equation giving the velocity constant of a second order reaction. What are the characteristics of a second order reaction.

16. Show that (i) for a first order reaction A $\longrightarrow$ Products, $t_{1/2} = 0{\cdot}693\ /\ k$ (ii) for a second order reaction 2A $\longrightarrow$ Products, $t_{1/2} = (1/k_2)\,a$ (iii) for a third order reaction 3A $\longrightarrow$ Products, $t_{1/2} = 3\ (2ka^2)$.

17. Enumerate the methods employed in determining the order of a reaction. Discuss one method in detail.

18. What do you undestand by the order of a reaction ? How would you study (a) the rate of hydrolysis of an ester (b) the rate of inversion of cane-sugar ?

19. Describe what is meant by order of a chemical reaction and velocity constant of the reaction. Describe suitable methods by which the order of a reaction can be determined.

20. Explain the terms : energy of activation and energy barrier. Illustrate your answer by giving some suitable analogies. Explain why the reaction

$$NO(g) + 1/2\ O_2\ (g) \longrightarrow NO_2\ (g)$$

is fast, while the reaction

$$CO\ (g) + 1/2\ O_2\ (g) \longrightarrow CO_2\ (g)$$

is slow at ordinary temperatures ?

21. Why does a catalyst speed up a reaction ? Comment on the statement "A catalyst only hastens the approach of equilibrium in a reversible reaction but does not alter the position of equilibrium."

22. What is meant by order of a reaction ? Derive the equation for first-order reactions. What are the characteristics of these reactions ?

23. (a) What are pseudo-unimolecular reactions ? Give examples. How would study the kinetics of the reaction :

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+\ \text{ions}} CH_3COOH + C_2H_5OH?$$

24. Describe the methods of determining the order of a reaction.

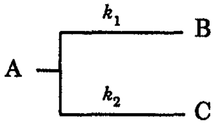
25. What is meant by the term order of a reaction ? Give an outline of one method used for determining the order of a reaction.

26. Give an account of the theory of absolute reaction rates.

27. Explain with an example Ostwald's isolation method in chemical kinetics.

28. Write the Arrhenius rate equation. How are the parameters in the equation determined experimentally ?

29. Discuss the kinetics of the first-order parallel reaction :



$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$$

Explain clearly how the values of k_1 and k_2 can be determined, separately. Show that the reaction as a whole is first-order.

30. What are the equations for the velocity constants of unimolecular and bimolecular reactions ? How will you show experimentally that hydrolysis of ethyl acetate by alkali when the latter is not used in great excess, is a bimolecular reaction ?

31. What is the difference between molecularity and order of a reaction ? Comment on the statement : "The molecularity of the slowest step in a chemical reaction gives the order of the overall reaction".

32. What are consecutive reactions ? Discuss the kinetics of the first-order consecutive reactions :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C.$$

Depict graphically the variation of concentrations of A, B and C with time.

33. Describe in detail the collision theory for unimolecular reactions.

34. What is meant by a reaction being first, second or zero order ? What are pseudo-unimolecular reactions ?

35. The reaction $S_2O_8^{2-} + 3I^- \longrightarrow 2SO_4^{2-} + I_3^-$ is of first order with respect to the persulphate and the iodide ions. The initial concentrations of the persulphate ion and the iodide ion are a and b mole per litre, respectively. If at time t , x mole of iodide ion have reacted, what will be the differential rate equation in terms of x and t. What will be initial rate of reaction ?

36. Discuss carefully the kinetics of the first-order reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$. Illustrate how the values of k_1 and k_2 are determined in reversible reactions?

37. Give a detailed account of the collision theory of reaction rates. How would you apply this theory to :

(i) bimolecular reactions (ii) monomolecular reactions ?

38. Discuss in detail the transition state theory of reaction rates. In what way is this theory superior to the collision rate theory ?

[II] Short Answer and Very Short Answer Type Questions

1. What do you understand by energy of activation ?

2. Explain why the rate of reaction cannot be measured by dividing the total amount of a substance reacted by the total time taken.

3. What is meant by temperature coefficient of a reaction ?

4. Predict order of the reaction in the following cases :

(a) $t_{0\cdot5} \propto \frac{1}{a}$; (b) $t_{0\cdot5} \propto \frac{1}{a^2}$

5. What is the shape of the graph drawn between :

(a) k and T; (b) $\log k$ and $\frac{1}{T}$?

6. Define molecularity of a reaction.
7. State the units of the rate constant for a zero order reaction of the type: A $\longrightarrow$ Products.
8. Give the relationship between $t_{1/2}$ and initial concentration of a second order reaction involving only one reactant.
9. Write as many expressions for rate of reaction in the following reaction as you can.

$$A + 2B \longrightarrow C + D$$

10. For the reaction

$$A + 2B + C \longrightarrow D + 2E$$

the rate of formation of D is found to be :

(i) doubled when [A] is doubled keeping [B] and [C] constant.

(ii) doubled when [C] is doubled keeping [A] and [B] constant.

(iii) remains unaltered when [B] is doubled keeping [A] and [C] constant.

Write rate equation for the reaction.

11. What is the interpretation of *A* in Arrhenius equation ?
12. Explain the meaning of any one of the following :

(a) Steady state approximation. (b) Transition state.

(c) Entropy of transition. (d) Probability factor.

13. The rate law decomposition of O_3 is believed to be

$$\text{rate} = k\frac{[O_3]^2}{[O_2]}$$

Which of the following mechanisms is consistent with this rate law ?

(a) $2O_3 = 3O_2$ (b) (i) $O_3 = O_2 + O$ (fast) (ii) $O + O_2 \rightarrow 2O_2$ (slow)

14. What is the order of the reaction when its velocity constant has the following units :

(a) $M^{-1}\,s^{-1}$; (b) $mol^{-2}/2\,s^{-1}$ (c) s^{-1} (d) $M^{-2}\,s^{-1}$; (e) $mol^{-1}\,s^{-1}$

15. Write Arrhenius equation.
16. Draw a potential energy diagram for an endothermic reaction.

(a) in the absence of a catalyst, and (b) in the presence of a catalyst.

17. Illustrate pseudo-unimolecular reactions giving two examples.
18. What is meant by the rate of a reaction ? Why do the rates of chemical reactions differ a lot from one another ?
19. Explain the term : rate of a reaction. How can it be determined ? Comment on the statement that "the concept of mechanical speed or velocity cannot be used in measuring rates of reactions".
20. Explain why the rate of a reaction cannot be measured by dividing the total amount of reactant consumed by the total time taken. Why do we represent the rate of a reaction by dc/dt ? What is implied by assigning + or − sign to dc/dt ?
21. Explain carefully the terms : order of a reaction and molecularity of a reaction.
22. Show that the time taken to complete a definite fraction of the reaction is the function of the initial concentration depending on the order of the reaction.
23. What is the difference between a steady state process and an equilibrium process ?
24. If the concentrations are measured in mole per litre, time in second, what are the units of a rate constant for :

(i) a first order reaction

(ii) a second order reaction

(iii) a third order reaction ?

25. Distinguish between the terms 'order' and 'molecularity' of a reaction. Illustrate your answer with examples as applied in chemical reactions.

26. Define specific reaction rate.

27. Show that the equation $k = A \exp (E_a / RT)$, can be cast into the form of an equation of a straight line.

28. Explain on the basis of collision theory :

(i) Why does a rise in temperature speed up a reaction ?

(ii) Why does a small rise of temperature speed up a reaction to such a large extent

29. Derive an expression for the variation of the rate constant of a reaction with temperature.?

30. Discuss the effect of a catalyst on the rate of a reaction. How can the action of a catalyst be explained ?

31. (a) Define the terms : (i) half-change time, (ii) molecularity of a reaction.

32. Describe how the activation energy of a reaction may be determined ?

[III] Numerical Problems

1. A reaction takes place like A + B $\longrightarrow$ C. With the help of the following data fill in the blanks :—

(i) The rate equation for the reaction is ......

(ii) The order of the reaction is ......

S.No.	1	2	3	4	5
C_A	1·0	2·0	3·0	1·0	1·0
C_B	1·0	1·0	1·0	2·0	3·0
Rate (moles of product per litre per minute)	0·15	0·30	0·45	0·15	0·15

[**Hint** : Rate is independent of C_B and directly proportional to C_A.]

2. From the following data show that the decomposition of H_2O_2 in aqueous solution is a first order reaction where N is the number of ml of $KMnO_4$ required to decompose a definite volume of H_2O_2.

Time (in minute)	0	10	20	30
N	25	16	10·5	7·8

3. Decomposition of diazobenzene chloride was followed at constant temperature by measuring the volume of nitrogen evolved at suitable intervals. The readings thus obtained are given below :

Time (min)	0	20	50	70	∞
Volume N_2(ml)	0	10	25	33	162

Assuming it to be a first order reaction obtain the value of specific reaction rate.

4. A first order reaction has rate constant equal to $1{\cdot}25 \times 10^{-4}$ sec^{-1} at 298K and $8{\cdot}5 \times 10^{-4}$ sec^{-1} at 318K. Calculate the activation energy of the reaction.

5. At 875K the half-life period for the thermal decomposition of acetone is 81 seconds and is independent of the initial pressure. Calculate the time required for the reaction to go to 80% completion.

6. At a given temperature the half-life periods for the decomposition of ammonia in contact with tungsten were as follows :

Pressure (in mm of Hg)	50	100	200
Relative half-life period	3·52	1·82	0·93

Find the order of the reaction.

7. The catalytic decomposition of H_2O_2 is a first order reaction. Calculate the half-life period and the velocity constant for its decomposition from the fact that the fraction decomposed at the end of 50 minutes is 0·75.
8. A second order reaction where $a = b$, is 20% completed in 500 seconds. How long will it take for the reaction to go to 60% completion?
9. At 25°C the half-life period of the decomposition of N_2O_5 is 5·7 hrs and is independent of the initial concentration of N_2O_5. Calculate the specific reaction rate and time required for 90 per cent decomposition.
10. In the reduction of nitric oxide 50% of the reaction was complete in 140 seconds when the initial pressure was 258 mm and in 224 seconds when the initial pressure was 202 mm. Find the order of the reaction.
11. In the thermal decomposition of a gaseous substance, the time required to decompose half the reactant was 105 minutes when the initial pressure was 750 mm and 950 minutes when initial pressure was 250 mm. Find the order of the reaction.
12. The conversion of *N*-chloroacetanilide (A) into p-chloroaccetanilide (B) was followed by adding KI solution and titrating the iodine liberated with standard thiosulphate solution. The KI reacts with A only.

Time in hrs.	0	1	2	3	4	6	8
Ml of 0·1 N $S_2O_3^{2-}$	49·3	35·6	25·75	18·5	14·0	7·3	4·6

Calculate the first order rate constant in sec^{-1}.

13. A certain substance A is mixed with an equal quantity of a substance B. At the end of 1 hour A is 75% reacted. How much A will be left unreacted the end of 2 hours if the reaction is (a) fist order in A and independent of B, (b) first order in A and first order in B, (c) zero order in A and independent of B.
14. Half-change time of decompositon of a compound was found to be 50 minutes. When the concentration to start with was halved, the value of $t_{0\cdot5}$ became 100 minutes. What is the order of the reaction ?
15. Calculate the fraction of the molecules of a gas at 500 K possessing kinetic energy corresponding to a minimum of (a) 3,000 cal/mole and (b) 30 cal/mole.

[Hint : Calculate E_2 / RT and then $f = \frac{N_E}{N} e^{-E_a/RT}$]

16. Applying collision theory, estimate the rate of the reaction

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

at 775 K from the following data :

[HI] = 1·0 mol $litre^{-1}$; Z = 7.1× 10^{34} molecules per litre per second and $E_a = 4{\cdot}5 \times 10^4$ cal per mole.

[**Hint** : Calculate (i) $\frac{E_a}{ER}$ (ii) $f = \frac{N_E}{N} = e^{-E_a/RT}$

(iii) rate $= Z \times f$ molecules per litre per sec.

(iv) Convert to mol lit^{-1} $hour^{-1}$]

17. The following reslts were obtained for the saponification of ethyl acetate using equal concentrations of ester and alkali :

t (minutes)	0	4	6	10	20
Volume (ml) of acid used	8.04	5.30	4.58	3.50	2.22

Show that the reaction is of second order.

18. At a certain temperature, the half-life periods for the catalytic decomposition of ammonia were as follows :

Pressure (mm. Hg)	50	100	200
Relative half-life period	3.52	1.82	0.96

Find the order of the reaction.

19. The hydrolysis of methyl bromide is a first order reaction whose progress may be followed chemically by titrating samples of the reaction mixture with silver nitrate. The volume required for 10 ml samples at 330 K in a typical experiment are :

t (min)	0	8.08	33	41.2	∞
$AgNO_3$ (ml)	0	5.9	17.3	22.1	49.5

Calculate the velocity constant for this reaction.

20. From the following data, show that the decomposition of H_2O_2 in aqueous solution is a first-order reaction :

Time (minutes)	0	15	30
N	25.4	9.83	3.81

where, N is the number of ml of $KMnO_4$ required to decompose a definite volume of hydrogen peroxide.

21. The optical rotations of sucrose in 0.5N HCl at 30°C are given below. Show that the reaction is of first oder.

Time (minutes)	0	15	30	45	60	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+16.6	+11.0

22. Hydrogen peroxide in solution decomposes to give water and oxygen gas. Describe in detail as to how you will proceed to find the order of this reaction.

From the following data on the hydrolysis of ethyl acetate in the presence of hydrochloric acid, show that it is a unimolecular reaction.

Time (minutes)	0	25	40	61	∞
N	19.24	24.20	26.20	29.50	42.1

where, N is the number of ml of NaOH required for the titration of a definite volume of the reaction mixture.

23. The mutrotation of glucose in the presence of H^+ ion as catalyst, was studied polarimetrically at 25°C. The following data were obtained :

t	0	300	1500	∞
a	33.2	31.2	25.5	18.0

The concentration of HCl in the mixture was 0.01 M. The reaction is assumed to be first order. Calculate the rate constant.

24. The following data were obtained on the isomerisation of *p*-tolyl isocyanide to *p*-tolunitrile at 190°C.

t min	9.0	14.0	19.0	25.0
% nitrile	17.5	27.0	35.0	43.0

Assuming the reaction to be of first order, calculate the rate constant and half-life period.

25. The thermal decomposition of arsine on glass surface

$$2AsH_3\,(g) \longrightarrow 2As(s) + 3H_2(g)$$

was investigated kinetically. The researchers found that below 350°C the total pressure of the system varied with time as follows :

Time (hours)	0	4.33	16.0	25.5	37.66	44.75
Pressure (cm Hg)	39.2	40.3	43.65	45.35	48.05	48.85

What is the order of the reaction with respect to arsine and what is the value of the specific rate constant ?

26. The rate of disappearance of a first-order reaction is 0.25% per minute. Calculate $t_{1/2}$.

27. Ethylene oxide decomposes in the vapour phase according to the reaction :

$$C_2H_4O \longrightarrow CH_4 + CO.$$

The following data were obtained for this reaction at 414°C :

t min	0	7	12	18
P(total), torr	119.0	130.7	138.2	146.4

Show that the reaction is first-order. Calculate the rate constant.

28. The hydrolysis of t-butyl bromide in an acetone-water mixture is a first order reaction. At 25°C, the following data were obtained as a function of time :

Time (hours)	0	5	10	15	20	25
Concentration of t-bu Br	0.1000	0.0776	0.0602	0.0467	0.0362	0.0281

Calculate the rate constant of the reaction at 25°C.

29. The gas-phase reaction : $2A(g) \longrightarrow B(g)$, was studied kinetically by measuring the total pressure of the system as a function of time.

The following data were obtained :

Time (sec)	0	100	200	300	400
Pressure (mm of Hg)	400	322	288	268	256

What is the order of the reaction and what is the specific rate constant?

30. For a second-order reaction the initial concentrations of the two reactants are 0.2 mol dm^{-3} each and the initial rate is 5.0×10^{-6} mol dm^{-3} s^{-1}. Calculate the rate constant in (i) dm^3 mol^{-1} s^{-1} and (ii) cm^3 mol^{-1} s^{-1}.

31. For a first order reaction, the initial concentration is 0.01 mol dm^{-3} and the rate constant is 2.5×10^{-5} s^{-1}. Calculate the initial rate in (i) mol dm^{-3} s^{-1} (ii) mol cm^{-3} s^{-1} (iii) in mol cm^3 min^{-1}.

32. The following data were obtained at 35°C on the decomposition of benzene diazonium chloride in aqueous solution :

$$C_6H_5N_2Cl + H_2O \longrightarrow C_6H_5OH + HCl + N_2(g)$$

by measuring the volume of N_2 gas evolved as a function of time.

t min	20	40	60	80	100	120	∞
V (N_2) ml at N.T.P.	15.0	26.9	36.0	43.4	49.5	553.7	71.2

Assuming that the reaction is first-order, calculate the rate constant.

33. The temperature-dependence of a first order reaction is given below.

Temperature (°C)	15	20	2.5	30	37
k (s^{-1})	4.18×10^{-6}	7.6×10^{-6}	1.37×10^{-5}	2.41×10^{-5}	5.15×10^{-5}

Plot log *k* vs (1/*T*) and determine the activation energy.

34. In the above problem, calculate the enthalpy of activation (ΔH^*), the Gibbs free energy of activation (ΔG^*), the entropy of activation (ΔS^*) and the frequency factor *A*.

35. For the raction the reaction ? $A + 2B \longrightarrow 2C$, the following data were obtained :

[A] (mol dm^{-3})	**[B]** (mol dm^{-3})	**Rate, r** (mol dm^{-3} s^{-1})
3.5×10^{-2}	2.3×10^{-2}	5.0×10^{-7}
7.0×10^{-2}	4.6×10^{-2}	2.0×10^{-6}
7.0×10^{-2}	9.2×10^{-2}	4.0×10^{-6}

Determine the order of reaction with respect to A and B, the overall order and the rate constant.

36. For the reaction $A + B \longrightarrow$ Products, the following data were obtained :

[A] (mol dm^{-3})	**[B]** (mol dm^{-3})	**Rate, r** (mol dm^{-3} s^{-1})
1.4×10^{-2}	2.3×10^{-2}	7.4×10^{-9}
2.8×10^{-2}	4.6×10^{-2}	5.92×10^{-8}
2.8×10^{-1}	4.6×10^{-2}	5.92×10^{-8}

Determine the order of reaction (i) with respect to A (ii) with respect to B (iii) overall order and rate constant.

37. The following data were obtained at 50°C on the saponification of ethyl acetate in aqueous solution :

$$CH_3COOC_2H_5 + OH^- \longrightarrow CH_3COO^- + C_2H_5OH$$

t, min	0	5	10	15	20	25
$[CH_3COO^-]$	0	4.9×10^{-3}	6.03×10^{-3}	6.41×10^{-3}	6.56×10^{-3}	6.62×10^{-3}

Initial concentration of $CH_3COOC_2H_5 = 6.667 \times 10^{-3}$ M; initial concentration of $OH^- = 1.333 \times 10^{-1}$ M. Show that the reaction is of second order. Calculate the rate constant.

38. The rate constant for the decomposition of nitrous oxide is $5.16 \times 104\ s^{-1}$ at 1125 K and $3.76 \times 108\ s^{-1}$ at 1085 K. Calculate the energy of activation for the reaction.

39. The rate constant of a reaction at 30°C is exactly twice that at 20°C. Calculate the energy of activation.

40. The rate constant of a reaction at 230°C is twice that at 220°C. Calculate the activation energy.

44. Two reactions at 25°C have the same value of the frequency factor A, but different values of activation energy, E_a. Calculate the ratio of the rate constants if E_a values differ by (i) 1 kcal mol^{-1} (ii) 10 kcal mol^{-1}.

[IV] Multiple Choice Questions

1. The unit of reaction rate is :

(a) mol L^{-1} (b) mol^{-1} L s^{-1}

(c) mol L^{-1} s^{-1} (d) mol L^{-1} s

2. For reaction $nA + mB \longrightarrow$Products, the molecularity is :

(a) 1 (b) 2 (c) mn (d) $m + n$

3. For a reaction $nA + mB \longrightarrow$ Products, the rate law is

$$\frac{dx}{dt} = k\,[A]\,[B]$$

The order of reaction is :

(a) 0 (b) 1 (c) 2 (d) $n+m$

4. The dimension of first order rate constant is

(a) time^{-1} (b) time (c) time × conc (d) time^{-1} × conc^{-1}

5. The dimension of second order rate constant is :

(a) time × conc (b) time^{-1} × conc^{-1}

(c) time × conc^{-1} (d) time^{-1} × conc^{-2}

6. The hydrolysis of methyl acetate by acid is of :

(a) Zero order (b) First order (c) Second order (d) Third order

7. The hydrolysis of ethyl acetate by NaOH is of :

(a) Zero order (b) First order (c) Second order (d) Third order

8. The reaction rate of a reaction $2A \longrightarrow 3B$ is given by :

(a) $-\frac{d[A]}{dt}$ (b) $-\frac{1}{2}\frac{d[A]}{dt}$ (c) $+\frac{1}{2}\frac{d[A]}{dt}$ (d) $+\frac{d[A]}{dt}$

9. For a reaction $A + B \longrightarrow$Products, the reaction rate is given by,

$$\frac{dx}{dt} = k[A]\,[B]^{\circ}$$

The order of reaction with respect to A and B are :

(a) 1, 0 (b) 1, 1 (c) 0, 1 (d) 2, 0

10. The half life period of a first order reaction is 20 min. The time required for the concentration of the reactant to change from 0.4 M to 0.1 M is :

(a) 20 min (b) 40 min (c) 60 min (d) 80 min.

11. The ratio of the time required for 75% of a first order reaction to complete to that required for 50% of the reaction is :

(a) 4 : 3 (b) 1 : 2

(c) 2 : 1 (d) 3 : 2

12. The time required to decompose half of the reaction for a n^{th} order reaction is also doubled. The order of reaction is :

(a) 0 (b) 1 (c) 2 (d) 3

13. The minimum energy required for reactant molecules to enter into chemical reaction is known as :

(a) Kinetic energy (b) Potential energy

(c) Activation energy (d) Threshold energy

14. A first order reaction is 75% completed in 32 minutes. For 50% completion, it will take:

(a) 4 min (b) 8 min (c) 16 min (d) 32 min

15. The elementary step of the reaction $2Na + Cl_2 \longrightarrow 2NaCl$ is found to follow third order reaction kinetics. The molecularity of the reaction is :

(a) 0 (b) 1 (c) 2 (d) 3

16. In a reaction $A \longrightarrow B$, the reaction rate is doubled on increasing the concentrations of reactants four times. The order of reaction is :

(a) 0.5 (b) 0 (c) 1 (d) 3

17. On plotting $\log_{10} k$ against $1/T$, the slope of the straight line is given by :

(a) $\frac{E_a}{R}$ (b) $-\frac{E_a}{R}$ (c) $\frac{E_a}{2.303\,R}$ (d) $-\frac{E_a}{2.303\,R}$

18. If the plot of $\log_{10}[A]$ against time is a straight line with a negative slope, the order of reaction is :

(a) 0 (b) 1 (c) 2 (d) 3

19. The time required to decompose half of the substance for n^{th} order reaction is given by:

(a) a^n (b) a^{n-1} (c) a^{n+1} (d) a^{n-2}

20. The rate law for the reaction $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$ is

$$\text{Rate} = k\,[NO_2Cl]$$

The rate determining step is :

(a) $NO_2Cl \longrightarrow NO_2 + Cl$ (b) $2NO_2Cl \longrightarrow 2NO_2 + 2Cl$

(c) $NO_2 + Cl_2 \longrightarrow NO_2Cl + Cl$ (d) $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$

[V] Fill in the Blanks

1. A first order reaction is 15% complete in 20 min. It will take .... min to be 60% complete.
2. The rate of reaction is nearly doubled on increasing the temperature by ....
3. Order of reaction for the hydrolysis of ethyl acetate by HCl is ....
4. For a reaction A$\longrightarrow$Products, the rate law is $\frac{dx}{dt} = k\,[A]^{1/2}$. The order of reaction is ....
5. The order of reaction of decomposition of H_2O_2 is ....
6. If the rate constant, $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$, the order of reaction is ....
7. If the rate constant has the unit sec^{-1}, the order of reaction is ....
8. The equation $k = Ae^{-E/RT}$ is known as .... equation.
9. In equation $k = Ae^{-E/RT}$, A is known as ....
10. If $E_1 > E_2$, the reaction will be ....
11. The hydrolysis of ethyl acetate in acidic medium is .... order reaction.

[VI] True or False

State whether the following statements are true (T) or false (F)?

1. The value of temperature coefficient is nearly 10.
2. Radioactive emanations are of first order.
3. The inversion of cane sugar by HCl is of second order.
4. The reaction rate is proportonal to the surface area of reactant.
5. Catalyst always increases the reaction rate.
6. The half life period of a first order reaction is $\frac{0.693}{R}$.
7. Order of reaction and molecularity are similar.
8. Order of reaction can even be 4 or more.
9. Most of the reactions are of first and second order.
10. The reaction $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ is of zero order.
11. The rate of zero order reaction depends on the concentration of the reactant.

ANSWERS

[III] Numerical Problems

1. (i) $k = \frac{2.303}{t} \log \frac{a}{a-x}$ (ii) First order w.r.t. A; zero order w.r.t. B

3. 3.28×10^{-2} min^{-1} **4.** 75.52 kJ mole^{-1} **5.** 188.1 sec.

6. Second order **7.** 25 min, 2.77×10^{-2} min^{-1} **8.** 3000 sec.

9. 0.1215 hr^{-1}, 18.93 hr **10.** Third order **11.** Third order

12. 8.903×10^{-5} sec. **13.** (a) 6.5, (b) 14.3 (c) whole of A will disappear in 80 min.

14. 2 **15.** (a) 5% (b) 9% **16.** 110 mol L^{-1} hr^{-1}

18. second **19.** 2.396×10^{-4} sec^{-1} **23.** 4.71×10^{-4} s^{-1}

24. $k = 3.8 \times 10^{-4}$ s^{-1}, $t_{1/2}$ = 1820 sec. **25.** First order, 1.52×10^{-2} hr^{-1}

26. 277 min **27.** 0.0145 min^{-1} **28.** 5.08×10^{-2} hr^{-1}

29. Second order, 1.16×10^{-4} s^{-1}

30. (i) 1.25×10^{-5} dm^{-3} mol^{-1} s^{-1} (ii) 0.125 cm^{3} mol^{-1} s^{-1}

31. (i) 2.5×10^{-6} mol dm^{-3} s^{-1} (ii) 2.5×10^{-19} mol cm^{-3} s^{-1} (iii) 1.5×10^{-6} mol cm^{-3} s^{-1}

32. 1.18×10^{-3} min^{-1}

33. 20.1 kcal mol^{-1}

34. ΔH^* = 195 kcal mol^{-1}, ΔG^* = 240 kcal mol^{-1}, ΔS^* = – 15.2 cal mol^{-1}, $A = 7.90 \times 10^{9}$ s^{-1}

35. First order, first order, second order, 6.21×10^{-4} dm^{-3} mol^{-1} s^{-1}

36. (i) second order (ii) first order, (iii) third order, (iv) 1.64×10^{-3} mol^{-2} L^{2} s^{-1}

37. 0.433 dm^{-3} mol^{-1} s^{-1} **38.** 286.06 kJ mol^{-1}

39. 12.2 kcal mol^{-1} **40.** 34.1 kcal mol^{-1} **41.** (i) 5.4 (ii) 2×10^{7}.

[IV] Multiple Choice Questions

1. (c) **2.** (d) **3.** (c) **4.** (a) **5.** (b)

6. (b) **7.** (c) **8.** (b) **9.** (a) **10.** (b)

11. (c) **12.** (a) **13.** (d) **14.** (c) **15.** (d)

16. (a) **17.** (d) **18.** (b) **19.** (b) **20.** (a).

[V] Fill in the Blanks

1. 112.8 min **2.** 10°C **3.** one **4.** 1/2 **5.** one

6. two **7.** one **8.** Arrhenius **9.** frequency factor

10. exothermic **11.** first.

[VI] True of False

1. (F) **2.** (T) **3.** (F) **4.** (T) **5.** (F)

6. (T) **7.** (F) **8.** (F) **9.** (T) **10.** (T)

11. (F).

Chapter 8

CATALYSIS

8·1. CATALYST AND CATALYSIS

Berzelius (1835) found that the speed of a number of reactions is increased due to the presence of a small quantity of a foreign substance. He also found that these substances remain chemically unchanged at the end of the reaction. He termed these substances as **catalysts** and the phenomenon itself is known as **catalysis**. A familiar example is that of the decomposition of $KClO_3$. The decomposition of $KClO_3$ is very slow even at high temperature, but a small quantity of MnO_2 increases the rate of decomposition to a very great extent and MnO_2 remains chemically unchanged at the end of the reaction.

$$2KClO_3 + \underset{\text{Catalyst}}{[MnO_2]} \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

But later on it was observed that there are certain substances which can retard the rate of a chemical reaction. Hence, Ostwald defined that,

"A catalyst is a substance which influences the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction."

8·2. TYPES OF CATALYSIS

Catalysis is mainly divided into two types, *viz.*, homogeneous catalysis and heterogeneous catalysis.

[I] Homogeneous Catalysis

When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis.

(a) Examples of homogeneous catalysis in gas phase

(i) Oxidation of sulphur dioxide (SO_2) into sulphur trioxide (SO_3) with nitric oxide (NO) as catalyst,

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Gas}}{[NO]} \longrightarrow \underset{\text{Gas}}{2SO_3} + [NO]$$

(ii) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst.

$$\underset{\text{Vapour}}{CH_3CHO} + \underset{\text{Vapour}}{[I_2]} \longrightarrow \underset{\text{Gas}}{CH_4} + \underset{\text{Gas}}{CO} + [I_2]$$

(b) Examples of homogeneous catalysis in solution phase

Many reactions in solutions are catalysed by acids (H^+) and bases (OH^-).

(i) Decomposition of hydrogen peroxide (H_2O_2) in the presence of iodide ion (I^-) as catalyst.

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

(ii) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(iii) Hydrolysis of an ester in the presence of acid or alkali.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+/OH^-} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

[II] Heterogeneous Catalysis

When the catalyst is in a different phase than that of reactants, the phenomenon is known as heterogeneous catalysis.

Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are given below.

(a) Heterogeneous catalysis with gaseous reactants (contact catalysis)

(i) Oxidation of ammonia to nitric oxide (NO) in the presence of a platinum gauze (a stage in the manufacture of nitric acid).

$$\underset{\text{Gas}}{4NH_3} + \underset{\text{Gas}}{5O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 4NO + 6H_2O + [Pt]$$

(ii) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5, *(contact process for sulphuric acid).*

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2SO_3 + [Pt]$$

(iii) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.

$$\underset{\text{Ethene (gas)}}{H_2C{=}CH_2} + \underset{\text{Gas}}{H_2} + \underset{\text{Solid}}{[Ni]} \longrightarrow \underset{\text{Ethane}}{H_3C{-}CH_3} + [Ni]$$

Vegetable oils are tri-esters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the *vegetable oils* in presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield *solid fats (vanaspati ghee).*

(iv) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, *(Haber's process for ammonia).*

$$\underset{\text{Gas}}{N_2} + \underset{\text{Gas}}{3H_2} + \underset{\text{Solid}}{[Fe]} \longrightarrow 2NH_3 + [Fe]$$

(b) Heterogeneous catalysis with liquid reactants

(i) The decomposition of aqueous solutions of hydrogen peroxide (H_2O_2) is catalysed by manganese dioxide (MnO_2) or platinum in colloidal form.

$$\underset{\text{Liquid}}{2H_2O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2H_2O + O_2 + [Pt]$$

(ii) Benzene and ethanoyl chloride (CH_3COCl) react in the presence of anhydrous aluminium chloride to form phenyl methyl ketone ($C_6H_5COCH_3$).

$$\underset{\text{Liquid}}{C_6H_6} + \underset{\text{Liquid}}{CH_3COCl} + \underset{\text{Solid}}{[AlCl_3]} \longrightarrow C_6H_5COCH_3 + HCl + [AlCl_3]$$

(c) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ($KClO_3$) is catalysed by manganese dioxide (MnO_2).

$$\underset{\text{Solid}}{2KClO_3} + \underset{\text{Solid}}{[MnO_2]} \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

The above reaction is heterogeneous, though both reactants are in the same phase (solid), because every solid forms a new phase.

8·3. CLASSIFICATION OF CATALYSIS

Catalytic reactions are of the following four types :

(a) *Positive catalysis*

(b) *Negative catalysis*

(c) *Auto-catalysis*

(d) *Induced catalysis*

[I] Positive Catalysis

When the catalyst used accelerates the speed of a chemical reaction, it is known as a positive catalyst and the phenomenon is known as positive catalysis. For example, the rate of decomposition of hydrogen peroxide increases in the presence of colloidal platinum as catalyst.

(i) $2H_2O_2 \xrightarrow[\text{Catalyst}]{\text{Pt}} 2H_2O + O_2$

Other reactions are :

(ii) $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

(iii) $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

(iv) $2SO_2 + O_2 \xrightarrow{\text{Pt or NO}} 2SO_3$

[II] Negative Catalysis

When the foreign substance retards the speed of a chemical reaction, it is known as a negative catalyst and the phenomenon is known as negative catalysis. The following are examples of negative catalysts.

(i) Decomposition of hydrogen peroxide in presence of H_3PO_4.

$$2H_2O_2 \xrightarrow{H_3PO_4} 2H_2O + O_2$$

(ii) Oxidation of chloroform in presence of ethanol.

$$4CHCl_3 + 3O_2 \xrightarrow{C_2H_5OH} 4COCl_2 + 2Cl_2 + 2H_2O$$

(iii) Tetraethyl lead as antiknock. When tetraethyl lead, $Pb(C_2H_5)_4$ is added to petrol, it retards the too rapid or explosive combustion of the fuel which is responsible for the working of the engine.

Explanation of negative catalysis. The mechanism of negative catalysis could be different for different reactions, *e.g.*,

(1) **By poisoning a catalyst.** A negative catalyst may work by poisoning a catalyst which already happens to be present in the reaction mixture. For example, the traces of alkali dissolved from the glass of the container, catalyse the decomposition of hydrogen peroxide (H_2O_2). However, the addition of an acid would destroy the alkali catalyst and thus prevents decomposition.

(2) **By breaking a chain reaction.** In some cases, negative catalysts are believed to operate by breaking the chain of reactions. For example, the combination of H_2 and Cl_2, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl_3).

$$Cl_2 \longrightarrow \underset{\text{Free radicals}}{Cl\cdot + Cl\cdot}$$

$$H_2 + Cl\cdot \longrightarrow HCl + H\cdot$$

$$H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$$

NCl_3 breaks the chain of reactions by absorbing the propagating species ($Cl\cdot$) and so the reaction stops.

$$NCl_3 + Cl\cdot \longrightarrow \frac{1}{2}N_2 + 2Cl_2$$

[III] Auto-Catalysis

When one of the products formed in the reaction itself acts as a catalyst, the substance is known as an auto-catalyst and the phenomenon is known as auto-catalysis.

In auto-catalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (See fig. 1). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.

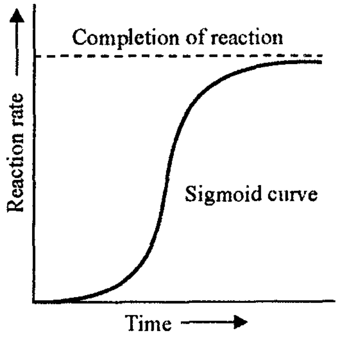


Fig. 1. Curve showing the rise of rate of reaction with time.

(i) Hydrolysis of ethyl acetate by water is an auto-catalytic reaction, since acetic acid liberated in this reaction acts as a catalyst.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{Auto-catalyst}}{CH_3COOH} + C_2H_5OH$$

(ii) The oxidation of oxalic acid by acidic $KMnO_4$ is catalysed by the presence of Mn^{2+} ions formed in the solution. In the beginning, the colour of $KMnO_4$ disappears slowly, but as Mn^{2+} is formed in the solution, the colour discharges rapidly. So, Mn^{2+} ions acts as auto-catalyst.

$$\underset{\text{Violet}}{2MnO_4^-} + 5C_2O_4^{2-} + 16H^+ \longrightarrow \underset{\substack{\text{Colourless} \\ \text{(Auto-catalyst)}}}{2Mn^{2+}} + 10CO_2 + 8H_2O$$

(iii) The free arsenic produced by the decomposition of arsine (AsH_3) auto-catalyses the reaction.

$$2AsH_3 \xrightarrow[\text{(Auto-catalyst)}]{} 2\underset{\text{Catalyst}}{As} + 3H_2$$

[IV] Induced Catalysis

When one reaction influences the speed of other, which is not possible under ordinary conditions, the phenomenon is known as induced catalysis.

For example, sodium sulphite solution is readily oxidised in air but sodium arsenite solution is not oxidised by passing a current of air through it. However, if air is passed through a mixture of sodium sulphite and sodium arsenite solution, the oxidation of both takes place. Here the oxidation of sodium sulphite acts as a catalyst for the oxidation of sodium arsenite solution.

8·4. CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them. These features are often referred to as the **criteria of catalysis.**

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction. Qualitative and quantitative analysis show that a catalyst undergoes no change in mass or chemical composition. However, it may undergo a physical change. Thus, granular manganese dioxide (MnO_2) used as a catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

(2) A small quantity of catalyst is generally needed to produce almost unlimited reaction. Sometimes, a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is, however, needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus, in Friedel-Craft's reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{\text{Anhy. AlCl}_3} C_6H_5C_2H_5 + HCl$$

anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 percent of the mass of benzene.

(3) A catalyst cannot, in general, initiate a reaction. In most cases, a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst *platinum black* in a few seconds.

$$H_2 + O_2 \xrightarrow{\text{Room temp.}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

It is thus now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energy for successful collisions. The molecules rebound from collisions without reacting at all.

(4) A catalyst is more effective when finely divided. In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine sub-division than when used in bulk. So, a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel, because former occupies greater surface area than the latter.

(5) A catalyst is specific in its action. While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, formic acid gives carbon dioxide and hydrogen when passed over hot copper.

$$\text{HCOOH} \xrightarrow{\text{Cu}} \text{CO}_2 + \text{H}_2$$

However, with hot aluminium oxide, formic acid gives carbon monoxide and water.

$$\text{HCOOH} \xrightarrow{\text{Al}_2\text{O}_3} \text{CO} + \text{H}_2\text{O}$$

(6) Change of temperature changes the rate of a catalytic reaction as it would do for the same reaction without a catalyst. We have already studied the effect of temperature change on reversible reactions under Le-Chatelier's principle. Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in temperature may cause their coagulation. In such a case, the rate of reaction increases up to a certain point and then gradually decreases. ***The rate of reaction is maximum at a particular temperature which is known as the optimum temperature.***

(7) A catalyst does not alter the final position of equilibrium, although it decreases the time required to establish it. It means that in a reversible reaction the catalyst accelerates the forward and the reverse reactions equally. Thus, the ratio of the rates of two opposing reactions, *i.e.*, the equilibrium constant, remains unchanged.

The effect of a catalyst on the time required for equilibrium to be established for the reaction

$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$$

is shown in figure (2). In the beginning, the concentrations of A and B are maximum and so the rate of forward reaction is maximum. As the time passes, the rate of the reaction decreases till the equilibrium

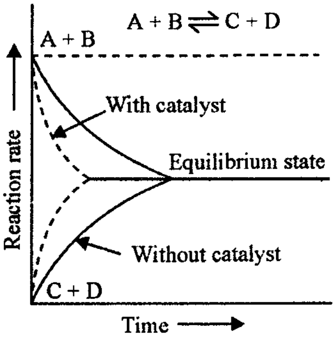


Fig. 2. The effect of a catalyst on the time required for the equilibrium to be established.

is established. For the reverse reaction, the initial concentrations of C and D are zero and the rate of reaction is lowest. As the time passes, the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are changed equally but the equilibrium is established in a much shorter time.

For example, in the Haber's process for ammonia, *i.e.*,

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$$

the reaction is very slow. In the presence of the catalyst, the equilibrium is reached much earlier but the percentage yield remains unchanged. The iron catalyst decreases the time to attain equilibrium but cannot change the percentage yield.

Energy considerations also show that the final state of equilibrium cannot be changed by the catalyst. Suppose the catalyst accelerates the forward reaction more than the reverse reaction. This will shift the equilibrium point, which cannot happen without the supply of energy to the system. But a catalyst unchanged in mass and composition at the end of the reaction, cannot supply the required energy.

8·5. CATALYTIC PROMOTERS

[I] Definition of Promoter

The activity of a catalyst can often be increased by the addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter or an activator.

[II] Examples of Promoters

(i) In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc oxide and chromium oxide is used as a catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$

(ii) Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber's synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \underset{+Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

[III] Explanation of Promoter's Action

The theory of promotion of a catalyst is not clearly understood. It may probably be due to :

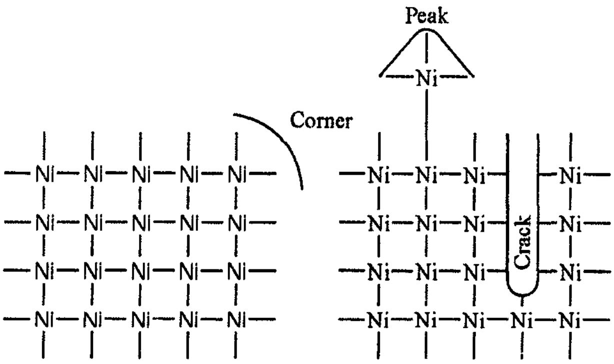


Fig. 3. Peaks, corners and cracks.

(1) ***Increase of peaks and cracks.*** The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

(2) ***Change of lattice spacing.*** The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The adsorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes the reaction go faster. The phenomenon of promotion is a common feature of heterogeneous catalysis.

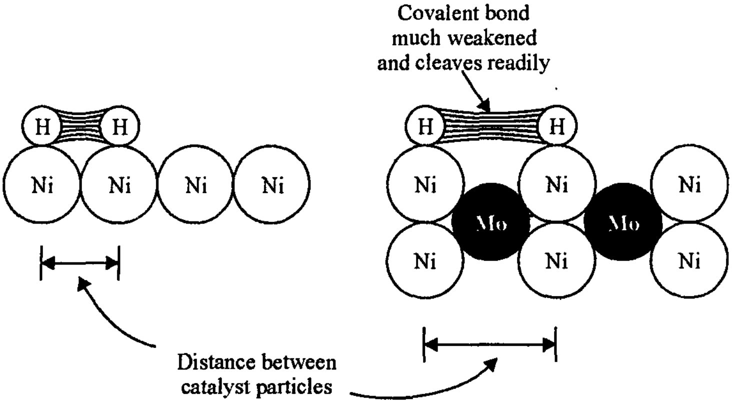


Fig. 4. How the change of crystal lattice spacing of catalyst makes the reaction go faster ?

8·6. CATALYTIC POISONS

[I] Definition of Poison

Very often a heterogeneous catalyst is rendered ineffective by the presence of small amounts of impurities in the reactants.

A substance which destroys the activity of the catalyst to accelerate a reaction, is called a catalytic poison and the process is called catalytic poisoning.

[II] Examples of Catalytic Poisoning

(1) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.

$$2H_2 + O_2 \xrightarrow[\substack{\text{Poisoned}\\ \text{by CO}}]{\text{Pt}} 2H_2O$$

(2) The platinum catalyst used in the oxidation of sulphur dioxide (contact process) is poisoned by arsenic oxide (As_2O_3).

$$2SO_2 + O_2 \xrightarrow[\substack{\text{Poisoned}\\ \text{by } As_2O_3}]{\text{Pt}} 2SO_3$$

(3) The iron catalyst used in the synthesis of ammonia (Haber's process) is poisoned by H_2S.

$$N_2 + 3H_2 \xrightarrow[\substack{\text{Poisoned}\\ \text{by } H_2S}]{\text{Fe}} 2NH_3$$

[III] Explanation of Catalytic Poisoning

(1) ***The poison is adsorbed on the catalyst surface in preference to the reactants*** : Even a monomolecular layer makes the surface unavailable for further adsorption of the reactants. The poisoning of platinum catalyst by CO comes in this class [Figure (5)].

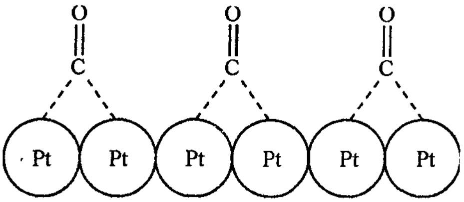


Fig. 5. Poisoning of platinum catalyst by carbon monoxide due to absorption.

(2) ***The catalyst may combine chemically with the impurity*** : The poisoning of iron catalyst by H_2S comes in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

8·7. THEORIES OF CATALYSIS

Many theories have been put forward to explain the catalytic activity of catalysts. A few important theories are given below :

[I] Intermediate Compound Formation Theory

According to this theory, a catalyst first combines with one of the reactants to form an intermediate compound of activity greater than that of the reactants. This intermediate compound then reacts with another reactant to form the product and so gives back the catalyst. If A and B are two reactants and C is a catalyst, then according to this theory.

$$\begin{array}{rcl} A + C & \longrightarrow & AC \\ AC + B & \longrightarrow & AB + C \\ \hline A + B + [C] & \longrightarrow & AB + [C] \end{array}$$

This theory can be fully explained by the following examples :

(1) In the oxidation of SO_2 by air, NO which acts as a catalyst, first combines with oxygen to form NO_2 (intermediate compound) which oxidises SO_2 and gives back nitric oxide.

$$\begin{array}{rcl} 2NO + O_2 & \longrightarrow & 2NO_2 \\ [SO_2 + NO_2 & \longrightarrow & SO_3 + NO] \times 2 \\ \hline 2SO_2 + O_2 + \underset{\text{Catalysis}}{[2NO]} & \longrightarrow & 2SO_3 + [2NO] \end{array}$$

(2) In the formation of ether from alcohol, H_2SO_4 which is used as catalyst first forms an intermediate compound $C_2H_5HSO_4$.

$$\begin{array}{rcl} C_2H_5OH + H_2SO_4 & \longrightarrow & C_2H_5HSO_4 + H_2O \\ C_2H_5HSO_4 + C_2H_5OH & \longrightarrow & C_2H_5OC_2H_5 + H_2SO_4 \\ \hline C_2H_5OH + C_2H_5OH + \underset{\text{Catalyst}}{[H_2SO_4]} & \longrightarrow & \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O + [H_2SO_4] \end{array}$$

(3) Formation of methylbenzene, $C_6H_5CH_3$ by reaction between benzene (C_6H_6) and methyl chloride (CH_3Cl) using anhydrous aluminium chloride, $AlCl_3$, as catalyst (Friedel-Craft's reaction).

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

Mechanism :

$$CH_3Cl + AlCl_3 \longrightarrow \underset{\substack{\text{Intermediate}\\\text{compound}}}{[CH_3]^+ [AlCl_4]^-}$$

$$C_6H_6 + [CH_3]^+ [AlCl_4]^- \longrightarrow C_6H_5CH_3 + AlCl_3 + HCl$$

(4) Thermal decomposition of potassium chlorate ($KClO_3$) in the presence of manganese dioxide (MnO_2).

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

Mechanism :

$$2KClO_3 + 6MnO_2 \longrightarrow \underset{\substack{\text{Intermediate}\\\text{compound}}}{6MnO_3} + 2KCl$$

$$6MnO_3 \longrightarrow 6MnO_2 + 3O_2$$

It may be noted that the actual isolation of intermediate compounds which would prove their existence is very difficult. As already stated, by their very nature they are unstable. In general, the intermediate compounds suggested as being formed are usually possible rather than proved.

[II] Adsorption Theory or Modern Theory of Heterogeneous Catalysis

Adsorption theory explains the mechanism of a reaction between two gases catalysed by a solid *(heterogeneous or contact catalysis).* According to this theory, the catalyst acts by adsorption of the reacting molecules on its surface. Generally speaking, four steps can be put forward for heterogeneous catalysis. For example, for the following reaction,

$$A(g) + B(g) \xrightarrow{\text{Catalyst}} C(g) + D(g)$$

the steps are as follows :

Step 1. Adsorption of reactant molecules. The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak vander Waals forces (physical adsorption) or by partial chemical bonds *(chemisorption).*

Step 2. Formation of activated complex. The particles of the reactants adjacent to one another join to form an *intermediate complex* (A – B). The activated complex is unstable. It has only a fleeting existence.

Step 3. Decomposition of activated complex. The activated complex breaks to form the products C and D. The separated particles of the products are held to the catalyst surface by partial chemical bonds.

Step 4. Desorption of products. The particles of the products are *desorbed* or released from the surface. They are stable and can lead to an independent existence.

The above four steps can diagrammatically be shown in figure (6).

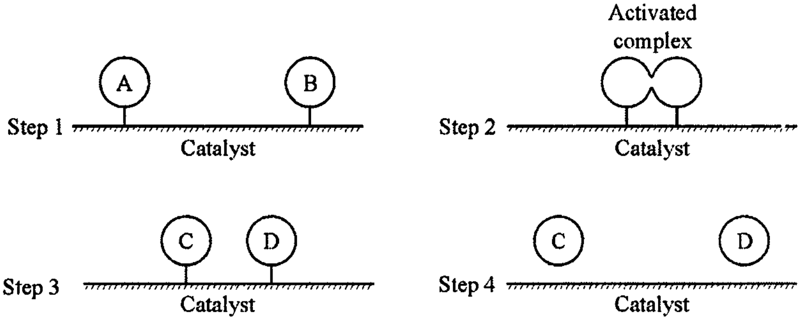
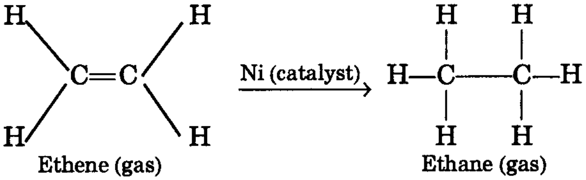


Fig. 6. Mechanism of contact catalyst.

The mechanism of contact catalysis may vary in details, depending on the nature of the reactants. Consider the example of hydrogenation of ethene in presence of nickel. In this case, ethene adds hydrogen in the presence of nickel as a catalyst to yield ethane.



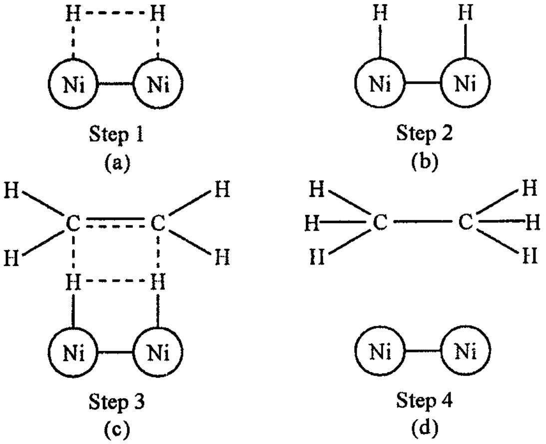


Fig. 7. Mechanism of the hydrogenation of ethene on nickel surface.

In the above reaction, catalyst functions according to the following steps.

Step 1. Adsorption of hydrogen molecules. Hydrogen molecules are adsorbed on the nickel surface due to the residual valence bonds of the nickel atoms [Figure (7a)].

Step 2. H—H bonds are broken. The H—H bond is smaller (0.74 Å) than Ni—Ni bond. Therefore, the H—H bond of the adsorbed hydrogen molecule is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the nickel surface by chemical bonds [Figure 7(b)].

Step 3. Formation of the activated complex. The chemisorbed hydrogen atoms then attach to ethene molecule by partial chemical bonds. Therefore, unstable activated complex is formed [Figure 7(c)].

Step 4. Decomposition of the activated complex and desorption of ethane molecule. The unstable activated complex decomposes to form ethane molecule. The freed catalyst surface is again available for further action [Figure 7(d)].

The adsorption theory explains the catalytic activity as follows :

(1) Metals in a state of fine sub-division or colloidal form are rich in free valence bonds and hence they are more efficient catalysts than the metal in lumps.

(2) A promoter increases the valence bonds on the catalyst surface by changing the crystal lattice and thereby increasing the active centres [Figure (8)].

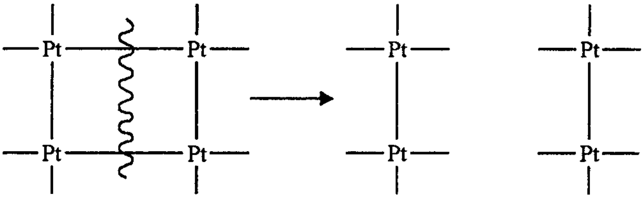


Fig. 8. Sub-division of a catalyst makes it more efficient due to the increase of free valence bonds.

(3) Catalytic poisoning occurs because the so-called poison blocks the free valence bonds on its surface by preferential adsorption or by chemical combination.

8·8. BIOCHEMICAL OR ENZYME CATALYSIS

Enzymes are complex nitrogeneous organic compounds. They are produced in the living cells of plants and animals. When dissolved in water they form colloidal solution, hence they behave as very active catalysts in certain biochemical reactions. They are thus known as **biochemical catalysts** and the phenomenon itself is known as **biochemical catalysis.**

[I] Characteristics of Enzyme Catalysts

(1) Enzymes form a colloidal solution in water and hence they are very active catalysts.
(2) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.
(3) They are highly specific in nature, *i.e.*, one catalyst cannot catalyse more than one reaction.
(4) They are highly specific to temperature. The optimum temperature of their activity is 35°C to 40°C. They are deactivated at 70°C.
(5) Their activity is increased in the presence of certain substances, known as co-enzymes.
(6) A small quantity of enzyme catalyst is sufficient for a large change.
(7) They are destroyed by U.V. rays.
(8) Their efficiency is decreased in the presence of electrolytes.

[II] Examples of Enzyme Catalysis

The following are some examples of biochemical or enzyme catalysis.

(1) Manufacture of ethyl alcohol from cane sugar.

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

(2) Manufacture of acetic acid from ethyl alcohol.

$$C_2H_5OH + O_2 \xrightarrow{\text{Mycoderma aceti}} CH_3COOH + H_2O$$

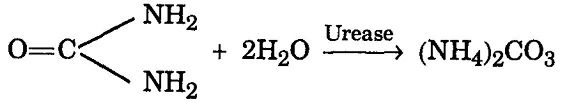
(3) Conversion of starch into maltose.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

(4) In the estimation of urea.

Urease enzyme completely converts urea into ammonium carbonate.



$$O{=}C\begin{matrix} NH_2 \\ NH_2 \end{matrix} + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3$$

(5) In digestive tract.

(a) In stomach, pepsin enzyme converts proteins into peptides, whereas in intestines, pancreas trypsin converts proteins into amino acids by hydrolysis. These amino acids are absorbed by blood and are used in the building of tissues.

(b) The enzyme ptyalin present in human saliva converts starch into glucose.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Ptyalin}} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

[III] Kinetics of Enzyme Catalysis

A reactant in an enzyme catalysed reaction is known as *substrate*. According to the mechanism of enzyme catalysis, the enzyme combines with the substrate to form a complex, as suggested by Henri (1903). He also suggested that this complex remains in equilibrium with the enzyme and the substrate. Later on in 1925, Briggs and Haldane showed that a steady state treatment could be easily applied to the kinetics of enzymes. Some photochemical reactions and some enzymic reactions are reactions of the zero order.

With S representing substrate, E the enzyme, ES an enzyme-substrate complex and P the products, the mechanism of the enzyme catalysed reaction is presumed to be adequately represented by

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P$$

where k_1, k_2, k_3 are the rate constants for the respective reactions.

The rate of formation of the complex ES is, evidently given by the following equation

$$\frac{d[ES]}{dt} = 0 = k_1 [E] [S] - k_2 [ES] - k_3 [ES]$$

$$= k_1 [E] [S] - (k_2 + k_3) [ES] \qquad \text{...(1)}$$

where [E], [S] and [ES] represent molar concentrations of the free enzyme, substrate and the complex, *i.e.*, bound or reacted enzyme, respectively.

Now [E] cannot be experimentally measured. The equilibrium between the free and bound enzyme is given by the enzyme conservation equation, *i.e.*,

$$[E]_0 = [E] + [ES]$$

where $[E]_0$ refers to the total enzyme concentration. So,

$$[E] = [E]_0 - [ES]$$

On substituting the value of [E] in equation (1), we get

$$\frac{d\,[ES]}{dt} = k_1 \{[E]_0 - [ES]\} [S] - (k_2 + k_3) [ES] = 0 \qquad \text{...(2)}$$

As the reaction proceeds, the intermediate complex formed in accordance with the suggested mechanism, decomposes instantaneously according to the same mechanism. On applying the steady state principle, we have

$$\frac{d\,[ES]}{dt} = 0$$

At the stationary state, equation (2) may be written as,

$$k_1 \{[E]_0 - [ES]\} [S] = (k_2 + k_3) [ES]$$

or

$$k_1 [E]_0 [S] = \{(k_2 + k_3) + k_1 [S]\} [ES]$$

$$[ES] = \frac{k_1 [E]_0 [S]}{(k_2 + k_3) + k_1 [S]}$$

$$= \frac{[E]_0 [S]}{\dfrac{k_2 + k_3}{k_1} + [S]}$$

The rate of formation of the product, P, *i.e.*, r is represented by the equation,

$$r = \frac{d[P]}{dt} = k_3 [ES] \qquad \text{...(3)}$$

Substituting the value of [ES] in equation (3), we get

$$r = \frac{d[P]}{dt} = \frac{k_3 [E]_0 [S]}{\dfrac{k_2 + k_3}{k_1} + [S]}$$

The quantity $\dfrac{(k_2 + k_3)}{k_1}$ is known as *Michaelis constant* and may be denoted by K_m. Therefore,

$$\frac{d[\mathrm{P}]}{dt} = \frac{k_3\,[\mathrm{E}]_0\,[\mathrm{S}]}{K_m + [\mathrm{S}]} \qquad \ldots(4)$$

Equation (4) is known as *Michaelis-Menten* equation.

Further simplification of equation (4) can be made. If it is assumed that all the enzyme has reacted with the substrate at high concentrations the reaction will be going on at maximum rate. No free enzyme will remain so that $[\mathrm{E}]_0 = [\mathrm{ES}]$. Thus, from equation (3), we get

$$r_{\max} = V_{\max} = k_3\,[\mathrm{E}]_0$$

where $V_{\max}$ refers to maximum rate, using the notation of enzymology. So, Michaelis-Menten equation (4) can also be written as,

$$r = \frac{V_{\max}\,[\mathrm{S}]}{K_m + [\mathrm{S}]}$$

If $r = V_{\max}/2$, *i.e.*, if the rate of formation of product is equal to half the maximum rate at which the reaction proceeds at high concentration of substrate, then

$$K_m = [\mathrm{S}]$$

Thus, ***Michaelis constant is equal to that concentration of substrate, S at which the rate of formation of the product is half the maximum rate obtained at a high concentration of substrate.***

From equation (4), we can draw the following conclusions :

(i) If [S] is very small as compared to K_m, the factor $K_m/[\mathrm{S}]$ will be very large as compared to unity and so the rate of formation of P, *i.e.*, $d[\mathrm{P}]/dt$ will be directly proportional to [S]. In other words, the reaction will be of *the first order with respect to S* (Fig. 9).

(ii) If [S] is very large as compared to K_m, the factor $K_m/[\mathrm{S}]$ will be negligibly small as compared to unity and so the rate of formation of P, *i.e.*, $d[\mathrm{P}]/dt$ will be independent of the concentration [S]. In other words, *the reaction will be of zero order with respect to S* (Fig. 9).

(iii) If [S] is very small or very large, the reaction remains of the first order with respect to the total concentration, $[\mathrm{E}]_0$ of the enzyme.

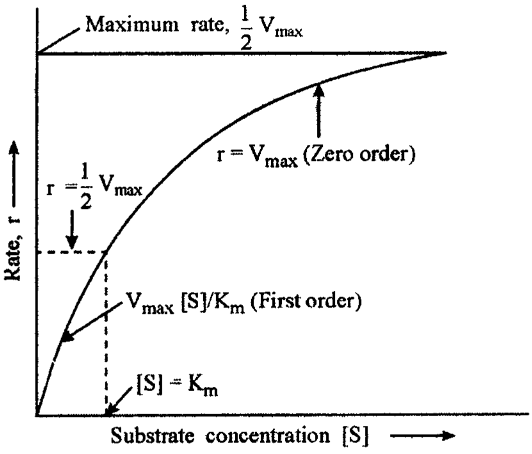


Fig. 9.

8·9. ACID-BASE CATALYSIS

Acids and bases catalyse several reactions. Suppose the rate of disappearance of a substance S (often called the substrate in a catalytic reaction) is first order in S, *i.e.*,

$$\frac{-d\,[S]}{dt} = k\,[S]$$

The first order rate constant k for the reaction in a buffer solution may be a linear function of $[H^+]$, $[OH^-]$, [HA] and $[A^-]$, when HA is the weak acid in the buffer and A^- is the corresponding conjugate base.

$$k = k_0 + k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{HA}[HA] + k_{A^-}[A^-] \qquad \text{... (1)}$$

In this equation, k_0 is the first order constant for the uncatalysed reaction. The so called catalytic coefficients, k_{H^+}, k_{OH^-}, k_{HA} and k_{A^-} may be evaluated from experiments with different concentrations of these species. If only the term $k_{H^+}[H^+]$ is important, the reaction is said to be subject to **specific hydrogen ion catalysis**. If the term k_{HA} [HA] is important, the reaction is said to be subject to **general acid catalysis** and if the term $k_{A^-}[A^-]$ is important, the reaction is said to be subject to **general base catalysis.**

By considering the two types of catalytic mechanisms, we can see how different types of terms arise in equation (1). In the first mechanism, a proton is transferred from an acid AH^+ to the substrate S and then the acid form of the substrate reacts with a water molecule to form the product P.

$$S + AH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A$$

$$SH^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P + H_3O^+$$

$$H_3O^+ + A \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} AH^+ + H_2O \qquad \text{... (2)}$$

The net reaction is S = P. Assuming that SH^+ to be in a steady state, then

$$\frac{d[SH^+]}{dt} = 0 = k_1\,[S]\,[AH^+] - (k_{-1}\,[A] + k_2)\,[SH^+] \qquad \text{... (3)}$$

The rate of appearance of product is given by

$$\frac{d[P]}{dt} = k_2\,[SH^+] = \frac{k_1 k_2\,[S]\,[AH^+]}{k_{-1}\,[A] + k_2} \qquad \text{... (4)}$$

where the second form is obtained by solving equation (3) for $[SH^+]$. If $k_2 >> k_{-1}$ [A], then

$$\frac{d[P]}{dt} = k_1\,[S]\,[AH^+] \qquad \text{... (5)}$$

The reaction is then said to be general acid catalysed. However, if $k_2 << k_{-1}$ [A], then

$$\frac{d[P]}{dt} = \frac{k_1 k_2\,[S]\,[AH^+]}{k_{-1}\,[A]} = \frac{k_1 k_2}{k_{-1} K}\,[S]\,[H^+] \qquad \text{... (6)}$$

where the second form is obtained by inserting $K = \frac{[A]\,[H^+]}{[AH^+]}$. In this case, the reaction is specifically hydrogen ion catalysed.

In the second mechanism, the acid form of the substrate reacts with a base A instead of a water molecule.

$$S + AH^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A\,; \qquad SH^+ + A \xrightarrow{k_1} P + AH^+ \qquad \dots (7)$$

The steady state treatment of this mechanism leads to

$$\frac{d[P]}{dt} = k_2\,[SH^+]\,[A] = \frac{k_1 k_2\,[S]\,[AH^+]}{k_{-1} + k_2} \qquad \dots (8)$$

This is an example of general acid catalysis.

For mechanisms of the type of equations (2) and (8), we might expect a relationship between the rate constant k_a for the acid catalysed reaction or k_b for the base catalysed reaction to depend on the strength of the acid or base. Bronsted found that the rate constant k_a for acid catalysis or k_b for base catalysis is proportional to the ionisation constant K_a for the acid or K_b for the base raised to some power.

$$k_a = C_A\,K_a^{\alpha}$$

$$k_b = C_B\,K_b^{\beta}$$

The exponents α and β are positive and have values between zero and one. The constants C_A, C_B, α and β apply to a single reaction at a particular temperature catalysed by different acids and bases.

In simpler terms, if a reaction is catalysed by an acid (S = P), then the rate becomes,

$$r = \frac{-d[S]}{dt} = k[S]$$

The rate law becomes

$$\frac{r}{[S]} = k + k_{H^+}\,[H^+]$$

For the same reaction to be catalysed by an acid and by a base, the rate law takes the form,

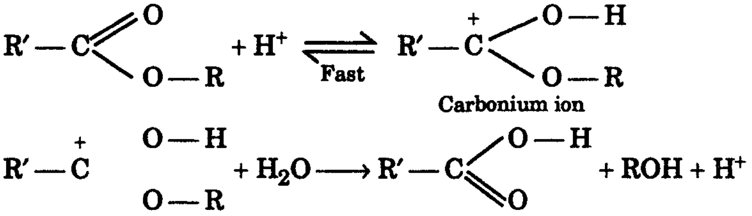
$$\frac{r}{[S]} = k + k_{H^+}\,[H^+] + k_{OH^-}\,[OH^-] \qquad \dots (9)$$

As $[H^+]\,[OH^-] = K_w$, the ionisation constant for water, equation (9) takes the form

$$\frac{r}{[S]} = k + k_{H^+}\,[H^+] + \frac{k_{OH^-}\,K_w}{[H^+]} \qquad \dots (10)$$

The term ***general acid-base catalysis*** refers to catalytic action by acids and bases according to Lowry-Bronsted definition. Reactions that are catalysed only by hydrogen or hydroxide ions arc said to be cases of ***specific acid-base catalysis.***

Mechanism. The first step in several acid or base catalysed raction is the fast transfer of proton to or from the substrate. The protonated or deprotonated species then undergoes the reaction that determines the overall reaction rate. During the subsequent stages of the reaction, acid or base is regenerated. For example, the acid catalysed hydrolysis of esters proceed in the following steps :



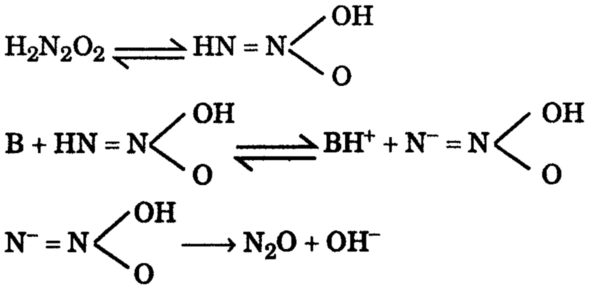
The rate of product formation is given by,

$$r = k' \text{ [Carbonium ion]} = k' K [H^+] \text{ [Ester]}$$

An example of a base catalysed reaction is given by the decomposition of nitramide :

$$H_2N_2O_2 \longrightarrow H_2O + N_2O$$

The suggested mechanism is,



$$OH^- + BH^+ \longrightarrow B + H_2O$$

The above mechanism is consistent with the rate law,

$$\frac{d\,[N_2O]}{dt} = \left(k + k_B\,[B] \right) [H_2N_2O_2]$$

8·10. INDUSTRIAL APPLICATIONS OF CATALYSTS

The presence of a catalyst is very useful in many industrially important reactions, which are either very slow or take place at a very high temperature. Hence, to decrease the cost of production it is essential to make use of a suitable catalyst. A few important examples of heterogeneous catalytic reactions of industrial applications are given as follows :

Reaction	Catalyst and other favourable conditions
1. **Haber's process** for the manufacture of ammonia. $N_2 + 3H_2 \longrightarrow 2NH_3$	Finely divided Fe + molybdenum (as promoter) 200 atm. pressure and temperature, 400°—450°C.
2. The manufacture of chlorine by **Deacon's process.** $4HCl + O_2 \longrightarrow 2H_2O + 2Cl_2$	Cupric chloride + excess of air at a temperature of 500°C.
3. **Ostwald's process** for the manufacture of HNO_3. $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ $2NO + O_2 \longrightarrow 2NO_2$ $4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$	Platinised asbestos + excess of air (as promoter) and temp. 300°C.
4. Manufacture of hydrogen by **Bosch's process.** $\underset{\text{Water gas}}{(CO + H_2)} + H_2O \longrightarrow CO_2 + 2H_2$	Ferric oxide + Cr_2O_3 (as a promoter) at a temp. of 400°—600°C.
5. Manufacture of methyl alcohol from water gas $\underbrace{CO + H_2}_{\text{Water gas}} + H_2 \longrightarrow CH_3OH$	$ZnO + Cr_2O_3$ (as a promoter), 200 atms. pressure and temp of 450°C.
6. **Chamber process** for the manufacture of H_2SO_4. $2SO_2 + O_2 + [NO] \longrightarrow 2SO_3 + [NO]$ $SO_3 + H_2O \longrightarrow H_2SO_4$	Nitric oxide
7. Acetic acid from acetaldehyde. $2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$	V_2O_5

EXERCISES

[I] Essay Type or Long Answer Type Questions

1. Write an essay on catalysis.
2. Describe the theories of catalysis.
3. What is enzyme catalysis? Derive Michaelis-Menten equation.
4. Write an essay on acid-base catalysis.
5. Mention the industrial applications of catalysis.
6. Discuss the important characteristics of catalysed reactions with examples.
7. Give a brief account of adsorption theory. How does this theory explain the characteristics of contact catalysis?

[II] Short Answer and Very Short Answer Type Questions

1. Define catalyst and catalysis.
2. Explain the terms, homogeneous catalysis and heterogeneons catalysis.
3. What do you understand by a promoter? Explain with one example.
4. Explain how a catalyst increases the rate of reaction?
5. Define the following terms :
   (a) Positive catalysis

(b) Negative catalysis
(c) Induced catalysis
(d) Auto catalysis
(e) Poisons
(f) Promoters.

6. What is an enzyme? Describe its characteristics.
7. Explain why solid catalysts are generally used in the finely divided state?
8. In the $KMnO_4$- oxalic acid titration, the decolorisation of $KMnO_4$ is very slow in the beginning but becomes quite rapid later, why ?
9. "Role of a catalyst is similar to the role of a whip to a horse." Comment.
10. What is the role of an inhibitor in a chemical reaction ?
11. The following mechanism has been proposed for the enzyme catalysis.

$$E + S \underset{k_2}{\overset{k_1}{\longrightarrow}} ES$$

$$ES \xrightarrow{k_2} P + E$$

Using steady-state approximation for [ES], show that the reaction rate is given by

$$r = k_2 [E]_0 [S]/(K_m + [S])$$

where the symbols have their usual meanings. Discuss the rate when $K_m < [S]$ and $K_m < [S]$.

12. Derive the rate equations for a general acid-catalyzed and a specifically hydrogen ion catalyzed reaction.
13. Explain with examples what is negative catalysis? Give one example of an industrially important catalytic reaction mentioning the specific catalyst used.
14. Give an account of the action of enzyme as catalyst choosing your example of everyday interest.
15. Derive Michaelis-Menten equation for enzyme catalysis.
16. Can a catalyst increase the yield in a chemical reaction?
17. Give a brief account of enzyme catalysis.
18. How does the concept of activation energy explain the role of catalysts in chemical reactions?
19. How does a catalyst act in a reversible reaction in equilibrium? Give reasons for your answer.
20. How does a catalyst act in a reaction involving collision of two molecules? On the basis of theory of adsorption explain :
    (i) How does a poison paralyse the activity of a catalyst?
    (ii) The specific action of a catalyst.
    (iii) The improved activity of a catalyst in a finer state of division.
21. Differentiate between homogeneous and hetergeneous catalysis. Explain both of these, giving one example each, with their mechanism.
22. Where are the following used as catalyst?
    (i) Finely divided nickel, (ii) Platinum gauze, (iii) Ferric oxide, (iv) Manganese dioxide.
23. Explain the following giving the relevant theory, wherever possible :
    (a) The fermentation of canesugar is slow in the absence of an enzyme.
    (b) The combination of nitrogen and hydrogen even at higher temperature is fast only in the presence of a solid catalyst.

(c) Why in a reaction catalysed by a metal, fine division of the metal increases its catalytic action.

(d) The action of a catalytic poison.

(e) Specificity in the action of a catalyst.

(f) The effect of addition of neutral salt on the velocity of an acid catalyst.

24. Write a note on adsorption theory of catalysis.

25. Define and explain the following terms :

(a) Catalyst (b) Catalysis

(c) Auto-catalysis (d) Promoters and poisons.

[III] Multiple Choice Questions

1. In the hydrogenation of oils the catalyst used is :

(a) Iron (b) Platinum

(c) Nickel (d) Molybdenum

2. The effect of a catalyst in a chemical reaction is to change the :

(a) Activation energy (b) Equilibrium concentration

(c) Heat of reaction (d) Final product

3. The catalyst used in the contact process of sulphuric acid manufacture is :

(a) Oxides of nitrogen (b) Nickel

(c) Vanadium pentoxide (d) Manganese dioxide

4. Which of the following is used as a contact catalyst?

(a) Boron (b) Germanium

(c) Nickel (d) Uranium

5. Which of the following statements is universally correct?

(a) A catalyst remains unchanged at the end of the reaction

(b) A catalyst physically changes at the end of the reaction

(c) A catalyst takes part in the chemical reaction

(d) A catalyst can induce chemical reaction

6. The catalyst used for the oxidation of ammonia to nitric acid is :

(a) Cupric chloride (b) Iron oxide

(c) Platinum (d) Manganese dioxide

7. A substance that retards the rate of chemical reaction in the presence of a catalyst is called :

(a) An inhibitor (b) A positive catalyst

(c) An auto-catalyst (d) A promoter

8. A catalyst poison is essentially :

(a) A homogeneous catalyst (b) A heterogeneous catalyst

(c) An inhibitor (d) An auto-catalyst

9. Catalyst poisons (temporary poisoning) act by :

(a) Chemically combining with the catalyst

(b) Getting adsorbed on the active centres on the catalyst surface

(c) Chemical combination with any one of the reactants

(d) Coagulating the catalyst

10. Which of the following types of the metal make the most efficient catalyst?

(a) Transition metals (b) Alkali metals

(c) Alkaline earth metals (d) Coloured metals

11. Which one of the following statements is incorrect?

(a) Presence of a catalyst does not alter the equilibrium concentration in a reversible reaction

(b) Change of temperature alter the rate of catalysed reaction in the same proportion as of the reaction without catalyst

(c) Homogeneous catalysis depends upon the nature and extent of the surface

(d) Change of a catalyst may change the nature of the reaction

12. Enzymes are :

(a) Micro-organisms (b) Proteins

(c) Inorganic compounds (d) Moulds

13. A photochemical reaction is :

(a) Catalysed by light

(b) Initiated by light

(c) Accompanied with emission of light

(d) Accompained with absorption of light

14. Platinised asbestos is used as catalyst in the manufacture of H_2SO_4. It is an example of :

(a) Homogeneous catalyst (b) Auto-catalyst

(c) Heterogeneous catalyst (d) Induced catalyst

15. The enzyme ptyalin used for digestion of food is present in :

(a) Saliva (b) Blood

(c) Intestine (d) Adrenal gland

16. A catalyst is a substance which :

(a) Increases the equilibrium concentration of the product

(b) Changes the equilibrium constant of the reaction

(c) Shortens the time to reach equilibrium

(d) Supplies energy to the reaction

17. An example of auto-catalytic reaction is :

(a) The decomposition of nitroglycerine

(b) Thermal decomposition of $KClO_3$, MnO_2 mixture

(c) Breakdown of $^{14}C_6$

(d) Hydrogenation of vegetable oils using nickel as catalyst

18. The efficiency of an enzyme in catalysing a reaction is due to its capacity :

(a) To form a strong enzyme-substrate complex

(b) To decrease the bond energies in the substrate molecule

(c) To change the shape of the substrate molecule

(d) To lower the activation energy of the reaction

19. A catalyst :

(a) Increases the energy change in a reaction

(b) Increases the free energy change in a reaction

(c) Neither decreases nor increases the free energy change in a reaction

(d) Can increase or decrease the free energy change in a reaction but it depends on the catalyst

20. Starch is converted into disaccharide in the presence of :

(a) Diastase (b) Maltase

(c) Lactase (d) Zymase

21. Glucose or fructose is converted into C_2H_5OH in the presence of :

(a) Invertase (b) Maltase

(c) Zymase (d) Diastase

22. A catalyst increases the rate of a chemical reaction by :

(a) Increasing the activation energy

(b) Decreasing the activation energy

(c) Reacting with reactants

(d) Reacting with products

23. Which of the following statement is correct?

(a) Enzymes are in colloidal state (b) Enzymes are catalysts

(v) Enzymes catalyse any reaction (d) Urease is an enzyme

24. A catalyst is used :

(a) To vaporise the compound (b) To kill the enzyme

(c) To alter the velocity of reaction (d) To balance the reaction

25. Enzymes are :

(a) Substances made by chemists to activate washing powder

(b) Very active vegetable catalysts

(c) Catalysts found in organisms

(d) Synthetic catalysts

26. Which of the following catalysts is used for preparing toluene by reacting benzene with CH_3Cl?

(a) Ni (b) Anhydrous $AlCl_3$ (c) Pd (d) Pt

27. The rusting of iron is catalysed by which of the following?

(a) Fe (b) O_2 (c) Zn (d) H^+

28. In which of the commerical process, a catalyst is not used?

(a) Haber's process (b) Deacon's process

(c) Solvay process (d) Lead chamber process

29. Which of the following statements is correct for a catalyst?

(a) It supplies energy to the system (b) It alters the rate of the reaction

(c) It alters the equilibrium constant (d) It is used up in the reaction

30. Organic catalysts differ from inorganic catalysts in :

(a) By acting at very high temperature

(b) By acting at low temperature

(c) Being used up

(d) Being proteinous in nature

31. Which one of the following statements regarding catalysts is not true?

(a) A catalyst can initiate a reaction

(b) A catalyst remains unchanged at the end of the reaction

(c) A catalyst does not alter the equilibrium in a reversible reaction

(d) Catalysts are sometimes very specific in terms of reactions

32. Which statement is incorrect for heterogeneous catalysis?

(a) Catalyst is absorbed on the surface

(b) Active centres are found on the surface of catalyst

(c) Catalyst increases the energy of activation

(d) None of these

33. Which of the following is used as a contact catalyst?
(a) Boron (b) Nickel (c) Germanium (d) Uranium

34. Which one of the following statements is incorrect in the case of heterogeneous catalyst?
(a) The catalyst lowers the energy of activation
(b) The catalyst actually forms a compound with the reactant
(c) The surface of the catalyst plays a very important role
(d) There is no change in the energy of activation

[IV] Fill in the Blanks

1. A substance which changes the rate of reaction is known as ....
2. The substance which retards the reaction rate is known as .... catalyst.
3. The .... of a catalyst increases when it is finely divided.
4. The substance which increases the efficiency of a catalyst is known as ....
5. In the conversion of urea into ammonium carbonate .... acts as a catalyst.
6. $2SO_2 + O_2 \xrightarrow{[NO]} 2SO_3$ is an example of .... catalysis.
7. $CH_3COOCH_3 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$ is an example of .... catalysis.
8. In $N_2 + 3H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$, M_0 acts as ....
9. A catalyst poison is essentially a ....
10. The presence of a catalyst .... the activation energy of the reaction.

[V] True or False

State whether the following statements are true (T) or false (F)?

1. A catalyst is a substance which can only increase the reaction rate.
2. When one of the products formed in the reaction itself acts as a catalyst, the phenomenon is called auto-catalysis.
3. A catalyst is specific in action.
4. A catalyst can change the position of equilibrium.
5. A catalyst remains unchanged in mass and chemical composition at the end of a reaction.
6. A large quantity of catalyst is required to bring about a reaction.
7. The substance which increases the activity of a catalyst is called an activator.
8. A promoter decreases the peaks and cracks on the catalyst surface.
9. Enzyme ptyalin present in human saliva changes starch into glucose.
10. The presence of a catalyst increases the activation energy of the reaction.
11. Transition metals are considered to be the most efficient catalysts.
12. In homogeneous catalysis, the intermediate compound is formed at lower activation energy.
13. Corners, peaks and cracks constitute the active centres on the surface of a catalyst.
14. The oxidation of oxalic acid by acidified $KMnO_4$ is catalysed by Mn^{2+} ions.
15. A catalyst cannot be recovered unchanged chemically at the end of the reaction.

ANSWERS

[III] Multiple Choice Questions

1. (c)
2. (a)
3. (c)
4. (c)
5. (a)
6. (c)
7. (a)
8. (c)
9. (b)
10. (a)
11. (c)
12. (b)
13. (b)
14. (c)
15. (a)
16. (c)
17. (a)
18. (d)
19. (d)
20. (a)
21. (c)
22. (b)
23. (c)
24. (c)
25. (c)
26. (b)
27. (d)
28. (c)
29. (b)
30. (d)
31. (a)
32. (c)
33. (d)
34. (d)

[IV] Fill in the Blanks

1. catalyst
2. negative
3. efficiency
4. promoter
5. urease
6. homogeneous
7. auto/homogeneous
8. promoter
9. inhibitor
10. decreases

[V] True or False

1. (F)
2. (T)
3. (T)
4. (F)
5. (T)
6. (F)
7. (T)
8. (F)
9. (T)
10. (F)
11. (T)
12. (T)
13. (T)
14. (T)
15. (F).

❑❑❑

SUBJECT INDEX

COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δ_m	1	2	3	4	5	6	7	8	9
											+	ADD								
10	.0000	0043	0086	0128	0170	0212					42	4	8	13	17	21	25	29	34	38
						0212	0253	0294	0334	0374	40	4	8	12	16	20	24	28	32	36
11	.0414	0453	0492	0531	0569	0607					39	4	8	12	16	19	23	27	31	35
						0607	0645	0682	0719	0755	37	4	7	11	15	19	22	26	30	33
12	.0792	0828	0864	0899	0934	0969					35	4	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	34	3	7	10	14	17	20	24	27	31
13	.1139	1173	1206	1239	1271	1303					33	3	7	10	13	16	20	23	26	30
						1303	1335	1367	1399	1430	32	3	6	10	13	16	19	22	26	29
14	.1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30	3	6	9	12	15	18	21	24	27
15	.1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28	3	6	8	11	14	17	20	22	25
16	.2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26	3	5	8	10	13	16	18	21	23
17	.2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25	2	5	7	10	12	15	17	20	22
18	.2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	24	2	5	7	10	12	14	17	19	22
19	.2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22	2	4	7	9	11	13	15	18	20
20	.3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21	2	4	6	8	11	13	15	17	19
21	.3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20	2	4	6	8	10	12	14	16	18
22	.3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19	2	4	6	8	10	11	13	15	17
23	.3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18	2	4	5	7	9	11	13	14	16
24	.3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18	2	4	5	7	9	11	13	14	16
25	.3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17	2	3	5	7	9	10	12	14	15
26	.4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16	2	3	5	6	8	10	11	13	14
27	.4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16	2	3	5	6	8	10	11	13	14
28	.4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15	2	3	5	6	8	9	11	12	14
29	.4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15	1	3	4	6	7	9	10	12	13
30	.4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14	1	3	4	6	7	8	10	11	13
31	.4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	14	1	3	4	6	7	8	10	11	13
32	.5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	13	1	3	4	5	7	8	9	10	12
33	.5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13	1	3	4	5	6	8	9	10	12
34	.5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	13	1	3	4	5	6	8	9	10	12
35	.5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	12	1	2	4	5	6	7	8	10	11
36	.5563	5573	5587	5599	5611	5623	5635	5647	5668	5670	12	1	2	4	5	6	7	8	10	11
37	.5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	12	1	2	4	5	6	7	8	10	11
38	.5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	11	1	2	3	4	6	7	8	9	10
39	.5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11	1	2	3	4	6	7	8	9	10
40	.6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	11	1	2	3	4	8	7	8	9	10
41	.6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	10	1	2	3	4	8	6	7	8	9
42	.6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	10	1	2	3	4	8	6	7	8	9
43	.6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10	1	2	3	4	8	6	7	8	9
44	.6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	10	1	2	3	4	8	6	7	8	9
45	.6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	10	1	2	3	4	8	6	7	8	9
46	.6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	9	1	2	3	4	8	5	6	7	8
47	.6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	9	1	2	3	4	8	5	6	7	8
48	.6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9	1	2	3	4	4	5	6	7	8
49	.6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	9	1	2	3	4	4	5	6	7	8

No.	log		No.	log
n = 3.14159	0.49715	$\ln x = \log_e x = (1/M) \log_{10} x$	(1/M) = 2.30259	0.36222
e = 2.71828	0.43429	$\log_x = \log_{10} x = M \log_e x$	M = 0.43429	1.63778

p	1	2	3	4	5	6	7	8	9	10
$\log e^p$	0.4343	0.8686	1.3029	1.7372	2.1715	2.6058	3.0401	3.4754	3.9087	4.3429
$\log e^{-p}$	1.5657	1.1314	2.6971	2.2628	3.8285	3.3942	4.9599	4.5256	4.0913	5.6571

COMMON LOGARITHMS $\log_{10} x$

x	0	1	2	3	4	5	6	7	8	9	Δm	1	2	3	4	5	6	7	8	9
											+	ADD								
50	.6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9	1	2	3	4	4	5	6	7	8
51	.7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8	1	2	2	3	4	5	6	6	7
52	.7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8	1	2	2	3	4	5	6	6	7
53	.7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8	1	2	2	3	4	5	6	6	7
54	.7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8	1	2	2	3	4	5	6	6	7
55	.7404	7412	7419	7427	7433	7443	7451	7459	7466	7474	8	1	2	2	3	4	5	6	6	7
56	.7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8	1	2	2	3	4	5	6	6	7
57	.7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8	1	2	2	3	4	5	6	6	7
58	.7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	8	1	2	2	3	4	5	6	6	7
59	.7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7	1	1	2	3	4	4	5	6	6
60	.7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7	1	1	2	3	4	4	5	6	6
61	.7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	7	1	1	2	3	4	4	5	6	6
62	.7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7	1	1	2	3	3	4	5	6	6
63	.7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7	1	1	2	3	3	4	5	6	6
64	.8062	8069	8075	8082	8089	8096	8101	8109	8116	8182	7	1	1	2	3	3	4	5	6	6
65	.8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7	1	1	2	3	3	4	5	6	6
66	.8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7	1	1	2	3	3	4	5	6	6
67	.8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6	1	1	2	2	3	4	4	5	5
68	.8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6	1	1	2	2	3	4	4	5	5
69	.8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6	1	1	2	2	3	4	4	5	5
70	.8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6	1	1	2	2	3	4	4	5	5
71	.8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	6	1	1	2	2	3	4	4	5	5
72	.8573	8579	8585	8691	8597	8603	8609	8615	8621	8627	6	1	1	2	2	3	4	4	5	5
73	.8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6	1	1	2	2	3	4	4	5	5
74	.8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	6	1	1	2	2	3	4	4	5	5
75	.8751	8756	8762	9768	8774	8779	8785	8791	8797	8802	6	1	1	2	2	3	4	4	5	5
76	.8808	8814	8820	8825	8831	8837	8842	8843	8854	8859	6	1	1	2	2	3	4	4	5	5
77	.8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	6	1	1	2	2	3	4	4	5	5
78	.8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	6	1	1	2	2	3	4	4	5	5
79	.8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	6	1	1	2	2	3	4	4	5	5
80	.9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	5	1	1	2	2	3	3	4	4	5
81	.9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5	1	1	2	2	3	3	4	4	5
82	.9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5	1	1	2	2	3	3	4	4	5
83	.9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5	1	1	2	2	3	3	4	4	5
84	.9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5	1	1	2	2	3	3	4	4	5
85	.9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5	1	1	2	2	3	3	4	4	5
86	.9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5	1	1	2	2	3	3	4	4	5
87	.9395	9400	9305	9410	9415	9420	9425	9430	9435	9440	5	0	1	1	2	2	3	3	4	4
88	.9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	5	0	1	1	2	2	3	3	4	4
89	.9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5	0	1	1	2	2	3	3	4	4
90	.9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5	0	1	1	2	2	3	3	4	4
91	.9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5	0	1	1	2	2	3	3	4	4
92	.9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5	0	1	1	2	2	3	3	4	4
93	.9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5	0	1	1	2	2	3	3	4	4
94	.9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5	0	1	1	2	2	3	3	4	4
95	.9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5	0	1	1	2	2	3	3	4	4
96	.9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4	0	1	1	2	2	2	3	3	4
97	.9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4	0	1	1	2	2	2	3	3	4
98	.9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4	0	1	1	2	2	2	3	3	4
99	.9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4	0	1	1	2	2	2	3	3	4

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δm	1	2	3	4	5	6	7	8	9
											+	ADD								
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	2	0	0	1	1	1	1	1	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	2	0	0	1	1	1	1	1	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	2	0	0	1	1	1	1	1	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	2	0	0	1	1	1	1	1	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	3	0	1	1	1	1	2	2	2	3
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	3	0	1	1	1	1	2	2	2	3
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	3	0	1	1	1	1	2	2	2	3
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	3	0	1	1	1	1	2	2	2	3
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	3	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	3	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	3	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	3	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	3	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	3	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	3	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	3	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	3	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	4	0	1	1	2	2	2	3	3	4
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	4	0	1	1	2	2	2	3	3	4
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	4	0	1	1	2	2	2	3	3	4
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	4	0	1	1	2	2	2	3	3	4
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	4	0	1	1	2	2	2	3	3	4
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	4	0	1	1	2	2	2	3	3	4
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	4	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	4	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	4	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	4	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	4	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	4	0	1	1	2	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	4	0	1	1	2	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	5	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	5	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	5	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	5	1	1	2	2	3	3	4	4	5
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	5	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	5	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	5	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	6	1	1	2	2	3	4	4	5	5
.38	2399	2404	2410	2415	2421	2427	2432	2338	2443	2449	6	1	1	2	2	3	4	4	5	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	6	1	1	2	2	3	4	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	6	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	6	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	6	1	1	2	2	3	4	4	5	5
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	6	1	1	2	2	3	4	4	5	5
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	6	1	1	2	2	3	4	4	5	5
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	7	1	1	2	3	3	4	5	6	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	7	1	1	2	3	3	4	5	6	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	7	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	7	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	7	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS 10^x

x	0	1	2	3	4	5	6	7	8	9	Δm	1	2	3	4	5	6	7	8	9
											+	ADD								
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	7	1	1	2	3	4	4	5	6	6
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	8	1	2	2	3	4	5	6	6	7
.52	3311	3319	3327	3334	3342	3550	3357	3365	3373	3381	8	1	2	2	3	4	5	6	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	8	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	8	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	8	1	2	2	3	4	5	6	6	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	8	1	2	2	3	4	5	6	6	7
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	9	1	2	3	4	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	9	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3926	3945	3954	3863	3972	9	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	9	1	2	3	4	5	5	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	10	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	10	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	10	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	10	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	10	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	11	1	2	3	4	5	7	8	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	11	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4883	11	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	11	1	2	3	4	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	12	1	2	4	5	6	7	8	10	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	12	1	2	4	5	6	7	8	10	11
.72	5248	560	5272	5284	5297	5309	5321	5335	5346	5358	12	1	2	4	5	6	7	8	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	12	1	2	4	5	6	7	8	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	13	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	13	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	13	1	3	4	5	7	8	9	10	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	14	1	3	4	6	7	8	10	11	13
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	14	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	14	1	3	4	6	7	8	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	15	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	15	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	15	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	16	2	3	5	6	8	10	11	13	14
.84	6918	6934	6950	6996	6982	6998	7015	7731	7047	7063	16	2	3	5	6	8	10	11	13	14
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	16	2	3	5	6	8	10	11	13	14
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	17	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7564	7482	7499	7516	7534	7551	7568	17	2	3	5	7	9	10	12	14	15
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	18	2	4	5	7	9	11	13	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	18	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	18	2	4	5	7	9	11	13	14	16
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	19	2	4	6	8	10	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	19	2	4	6	8	10	11	13	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	20	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	20	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	21	2	4	6	8	10	13	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	21	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	22	2	4	7	9	11	13	15	18	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	22	2	4	7	9	11	13	15	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	23	2	5	7	9	11	14	16	18	21