A

HANDBOOK

of

CHEMISTRY and PHYSICS

Edited and compiled by

M. V. GEORGE — J. MAHANTY — P. T. NARASIMHAN
C. N. R. RAO (*Editor in chief*)

Indian Institute of Technology, Kanpur

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THE EDITORS

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Alpha	$A\alpha$
Beta	$B\beta$
Gamma	$\Gamma\gamma$
Delta	$\Delta\delta$
Epsilon	$E\epsilon$
Zeta	$Z\zeta$
Eta	$H\eta$
Theta	$\Theta\theta$
Iota	$I\iota$
Kappa	$K\kappa$
Lambda	$\Lambda\lambda$
Mu	$M\mu$
Nu	$N\nu$
Xi	$\Xi\xi$
Omicron	Oo
Pi	$\Pi\pi$
Rho	$P\rho$
Sigma	$\Sigma\sigma$
Tau	$T\tau$
Upsilon	$\Upsilon\upsilon$
Phi	$\Phi\phi$
Chi	$X\chi$
Psi	$\Psi\psi$
Omega	$\Omega\omega$

A handbook forms an important and essential item in the personal library of students and teachers. The need of a handbook can only be compared to that of a slide rule. With the tremendous explosion in scientific knowledge in recent years, information in textbooks and journals is continually being transferred to handbooks and handbooks are getting bigger by the hour. In the present work, we have tried to present a new kind of handbook - one which is not merely a sourcebook of properties of substances, reference data and mathematical tables, but also serves as an instructional tool. For this purpose a considerable portion of this handbook is devoted to basic concepts, precise definitions, glossary of terms etc., chosen from the classical and modern aspects of physics and chemistry. With the enthusiasm evinced all over the world for newer and better approaches to science education and educational material, we have compiled this handbook with the hope that it would serve the changing needs of modern university curricula in physics and chemistry. It is expected that the material on mathematics in this handbook should satisfy the normal needs of most science students including undergraduate mathematics majors. We shall feel more than rewarded if this work is found useful by our colleagues and students.

In editing this handbook, we felt it important to limit the size so that the price is within the reach of most students and the work is still comprehensive(!). In compiling this work we have made use of several handbooks, compilations and texts and have exercised our best judgment in the choice of material; we beg to be excused for errors in judgment and ommissions which are likely to be present in this handbook.

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IITKanpur
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THE EDITORS

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I MATHEMATICS

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* The fundamental laws of algebra.

(a) Commutative law of addition: $a+b = b+a$.

(b) Commutative law of multiplication: $ab = ba$.

(c) Associative law of addition: $a+(b+c) = (a+b)+c$.

(d) Associative law of multiplication: $a(bc) = (ab)c$.

(e) Distributive law: $a(b+c) = ab+ac$.

(f) Laws of exponents:

$$a^x \cdot a^y = a^{x+y}, \qquad (ab)^x = a^x \cdot b^x.$$

$$(a^x)^y = a^{xy}, \qquad a^1 = a.$$

$$\frac{a^x}{a^y} = a^{x-y}, \qquad a^0 = 1.$$

$$a^{x/y} = \sqrt[y]{a^x}, \qquad a^{-x} = \frac{1}{a^x}, \text{ if } a \neq 0.$$

Factors and Expansions

$(a\pm b)^2 = a^2 \pm 2ab + b^2$.

$(a\pm b)^3 = a^3 \pm 3a^2 b + 3ab^2 \pm b^3$

$(a\pm b)^4 = a^4 \pm 4a^3 b + 6a^2 b^2 \pm 4ab^3 + b^4$.

$(a+b)^n = a^n + \binom{n}{1} a^{n-1} b + \binom{n}{2} a^{n-2} b^2 + \ldots + \binom{n}{n} b^n$.

$\qquad = a^n + na^{n-1} b + \dfrac{n(n-1)}{2!} a^{n-2} b^2 + \ldots + b^n$

$\qquad = \displaystyle\sum_{r=0}^{n} \binom{n}{r} a^{n-r} b^r$

Here the Binomial co-efficient $\binom{n}{r}$ means $\dfrac{n!}{r! \, (n-r)!}$

and $r! = \lfloor r = r(r-1)(r-2) \ldots 2.1$ is called "factorial r"

$$a^2 - b^2 = (a+b)(a-b).$$

$$a^3 \pm b^3 = (a \pm b)(a^2 \mp ab + b^2).$$

$$a^n - b^n = (a-b)(a^{n-1} + a^{n-2}b + \ldots + b^{n-1}).$$

$$a^n - b^n = (a+b)(a^{n-1} - a^{n-2}b + \ldots - b^{n-1}), \text{ for } n \text{ even.}$$

$$a^n + b^n = (a+b)(a^{n-1} - a^{n-2}b + \ldots + b^{n-1}), \text{ for } n \text{ odd.}$$

$$a^4 + a^2b^2 + b^4 = (a^2 + ab + b^2)(a^2 - ab + b^2).$$

$$(a+b+c+d\ldots)^n = \sum_{\text{all } r_i} \frac{n!}{r_1! r_2! r_3! \ldots} a^{r_1} b^{r_2} c^{r_3} d^{r_4} \ldots$$

$$\sum r_i = n$$

* **Ratio and Proportions**

If $\frac{a}{b} = \frac{c}{d}$, then $\frac{a+b}{b} = \frac{c+d}{d}$,

$$\frac{a-b}{b} = \frac{c-d}{d}, \quad \frac{a-b}{a+b} = \frac{c-d}{c+d}$$

If $\frac{a}{b} = \frac{c}{d} = \frac{e}{f} = \ldots = k$, then

$$k = \frac{a+c+e+\ldots}{b+d+f+\ldots} = \frac{pa+qc+re+\ldots}{pb+qd+rf+\ldots}$$

* **Sums of numbers**

$$\sum(n) = 1+2+3+ \ldots + n = \frac{n(n+1)}{2}.$$

$$\sum(n^2) = 1^2 + 2^2 + 3^2 + \ldots + n^2 = \frac{n(n+1)(2n+1)}{6}.$$

$$\sum(n^3) = 1^3 + 2^3 + 3^3 + \ldots + n^3 = \frac{n^2(n+1)^2}{4}.$$

$$\sum(n^4) = 1^4 + 2^4 + 3^4 + \ldots + n^4 = \frac{n^5}{5} + \frac{n^4}{2} + \frac{n^3}{3} - \frac{n}{30}.$$

$$\sum(n^s) = 1^s + 2^s + 3^s + \ldots + n^s = \frac{n^{s+1}}{s+1} + \frac{n^s}{2} + \frac{1}{2}\binom{s}{1}B_1 n^{s-1}$$
$$- \frac{1}{4}\binom{s}{3}B_2 n^{s-3} + \frac{1}{6}\binom{s}{5}B_3 n^{s-5} + \ldots$$

Where $B_1, B_2, \ldots$ are Bernoulli's numbers, $\binom{s}{n}$ are the

Binomial co-efficients. The series ends with the

term in n if s is even, and with the term in n^2 if s is odd.
The first few Bernoulli's numbers are

$$B_1 = \frac{1}{6}, \qquad B_6 = \frac{691}{2730},$$

$$B_2 = \frac{1}{30}, \qquad B_7 = \frac{7}{6},$$

$$B_3 = \frac{1}{42}, \qquad B_8 = \frac{3617}{510},$$

$$B_4 = \frac{1}{30}, \qquad B_9 = \frac{43867}{798},$$

$$B_5 = \frac{5}{66}, \qquad B_{10} = \frac{174611}{330}.$$

* Algebraic Series

Arithmetical progressions: If s is the sum,

a the first term, δ the common difference,

ℓ the last term and n the number of terms

$$S = a + (a+\delta) + (a+2\delta) + \ldots + [a+(n-1)\delta]$$

$$\ell = a + (n-1)\delta$$

$$S = \frac{n}{2}[2a+(n-1)\delta] = \frac{n}{2}(a+\ell).$$

Geometrical progressions:-

$$S = a+ap+ap^2+\ldots+ap^{n-1} = a\frac{p^n-1}{p-1}.$$

If $p < 1$ and $n = \infty$, then $S = \frac{a}{1-p}$.

Harmonical progressions: a, b, c, d, ... form an
harmonical progression if the reciprocals $\frac{1}{a}, \frac{1}{b}, \frac{1}{c}, \frac{1}{d}, \ldots$
form an arithmetical progression.

* Laws of Logarithms

If M, N, b are positive numbers and $b \neq 1$, then $\ell n_b M (\text{Or} \log_b M)$
called the logarithm of M to the base b is defined as the
numbers C, such that $b^c = M$.

$$\ell n_b MN = \ell n_b M + \ell n_b N, \quad \ell n_{\frac{M}{6N}} = \ell n_b M - \ell n_b N,$$

$$\ell n_b M^p = p. \ell n_b M, \quad \ell n_b \sqrt[q]{M} = \frac{1}{q}\ell n_b M,$$

$$\ell n_b \frac{1}{M} = -\ell n_b M, \quad \ell n_b b = 1, \quad \ell n_b 1 = 0.$$

Change of base.

$$\ell n_b M = \ell n_c M \cdot \ell n_b C = \frac{\ell n_c M}{\ell n_c b} .$$

The two basis commonly used are $b = 10$ (common logarithms) and $b = e = 2.71828 \cdots$ (Natural or Napierian logarithms). In natural logarithms the base is not usually indicated.

* **Complex numbers**

A complex number is of the form $a+ib$ where a and b are real and $i = \sqrt{-1}$.

$$i^2 = -1, \quad i^3 = -i, \quad i^4 = 1.$$

If $a+ib = c +id$, then $a=c$ and $b=d$.

$$(a+ib) + (c+id) = (a+c)+i (b+d) .$$

$$(a+ib) (c+id) = (ac-bd) + i(ad+bc).$$

$$\frac{a+ib}{c+id} = \frac{(a+ib)(c-id)}{(c+id)(c-id)} = \frac{ac+bd}{c^2+d^2} +i \frac{bc-ad}{c^2+d^2} .$$

$a-ib$ is called the complex conjugate of $a+ib$, and vice versa.

* **Algebraic Equations**

Quadratic equation: $ax^2+bx+c = 0 .$

The roots are $x = \dfrac{-b \pm \sqrt{b^2-4ac}}{2a} .$

If a, b and c are real, and then if b^2-4ac is positive, the roots are real and unequal;

if b^2-4ac is zero, the roots are real and equal;

if b^2-4ac is negative, the roots are complex and unequal (complex conjugate of each other).

Cubic equation: $z^3+ a_2 z^2 +a_1 z+a_0 = 0 .$

Let $q = \dfrac{1}{3} a_1 - \dfrac{1}{9} a_2^2$, $r = \dfrac{1}{6} (a_1 a_2 - 3a_0)- \dfrac{1}{27} a_2^3$,

and let $s = q^3 + r^2$

If $s > 0$, One real root and a pair of complex conjugate roots.

$s = 0$, all roots real and at least two are equal .

$s < 0$, all roots real.

Let $s_1 = \left[r + \sqrt{s}\right]^{1/3}$, $s_2 = \left[r - \sqrt{s}\right]^{1/3}$

Then the roots are

$$z_1 = s_1 + s_2 - \frac{a_2}{3}$$

$$z_2 = -\frac{1}{2}(s_1 + s_2) - \frac{a_2}{3} + i\frac{\sqrt{3}}{2}(s_1 - s_2)$$

$$z_3 = -\frac{1}{2}(s_1 + s_2) - \frac{a_2}{3} - i\frac{\sqrt{3}}{2}(s_1 - s_2).$$

* <u>Special series and formulae</u>:

Binomial series for $x^2 < 1$

$$(1 \pm x)^n = 1 \pm nx + \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 + \dots$$

$$(1 \pm x)^{-n} = 1 \mp nx + \frac{n(n+1)}{2!}x^2 \mp \frac{n(n+1)(n+2)}{3!}x^3 + \dots$$

$$(1 \pm x)^{-1} = 1 \mp x + x^2 \mp x^3 + x^4 \mp x^5 + \dots$$

$$(1 \pm x)^{-2} = 1 \mp 2x + 3x^2 \mp 4x^3 + 5x^4 \mp 6x^5 + \dots$$

Exponential Series

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \dots \quad = \lim_{n \to \infty}(1 + \frac{1}{n})^n = 2.71828 \dots$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad = \lim_{n \to \infty}(1 + \frac{x}{n})^n$$

$$a^x = 1 + x \ln a + \frac{(x \ln a)^2}{2!}$$

Logarithmic series:

$$\ln(1 \pm x) = \pm x - \frac{x^2}{2} \pm \frac{x^3}{3} - \frac{x^4}{4} \pm \dots \qquad (x^2 < 1)$$

$$\ln x = \frac{x-1}{x} + \frac{1}{2}\left(\frac{x-1}{x}\right)^2 + \frac{1}{3}\left(\frac{x-1}{x}\right)^3 + \dots \qquad (x > \frac{1}{2})$$

$$\ln x = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 + \dots \qquad (2 > x > 0)$$

$$\ln x = 2\left[\frac{x-1}{x+1} + \frac{1}{3}\left(\frac{x-1}{x+1}\right)^3 + \frac{1}{5}\left(\frac{x-1}{x+1}\right)^5 + \dots\right] \qquad (x > 0)$$

If a and b are much smaller than unity, then

$$(1 \pm a)^m \cong 1 \pm ma,$$

$$(1 \pm a)^n (1 \pm b)^m \cong 1 \pm ma \pm nb.$$

If n is nearly equal to m,

$$\sqrt{mn} \cong \frac{m+n}{2}.$$

If $y = a_1 x + a_2 x^2 + a_3 x^3 + \ldots$ $(a_1 \neq 0)$

then $x = A_1 + A_2 y + A_3 y^2 + \ldots$

where $A_1 = \dfrac{1}{a_1}$, $A_2 = -\dfrac{a_2}{a_1^3}$, $A_3 = \dfrac{1}{a_1^5}(2a_2^2 - a_1 a_3)$,

$A_4 = \dfrac{1}{a_1^7}(5a_1 a_2 a_3 - a_1^2 a_4 - 5a_2^3)$,

$A_5 = \dfrac{1}{a_1^9}(6a_1^2 a_2 a_4 + 3a_1^2 a_3^2 + 14a_2^4 - a_1^3 a_5 - 21a_1 a_2^2 a_3)$, etc.

$1 - \dfrac{1}{3} + \dfrac{1}{5} - \dfrac{1}{7} + \ldots$ $= \dfrac{\pi}{4}$.

$1 + \dfrac{1}{2^2} + \dfrac{1}{3^2} + \dfrac{1}{4^2} + \ldots$ $= \dfrac{\pi^2}{6} = B_1 \pi^2$.

$1 - \dfrac{1}{2^2} + \dfrac{1}{3^2} - \dfrac{1}{4^2} + \ldots$ $= \dfrac{\pi^2}{12} = \dfrac{B_1 \pi^2}{2}$.

$1 + \dfrac{1}{3^2} + \dfrac{1}{5^2} + \dfrac{1}{7^2} + \ldots$ $= \dfrac{\pi^2}{8} = \dfrac{3B_1 \pi^2}{4}$.

$\dfrac{1}{2^2} + \dfrac{1}{4^2} + \dfrac{1}{6^2} + \dfrac{1}{5^2} + \ldots$ $= \dfrac{\pi^2}{24} = \dfrac{1}{4} B_1 \pi^2$.

* Determinants

A determinant of the n-th order, with n^2 elements
is written

$$D = \begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1n} \\ a_{21} & a_{22} & a_{23} & \cdots & a_{2n} \\ a_{31} & a_{32} & a_{33} & \cdots & a_{3n} \\ \vdots & \vdots & \vdots & & \vdots \\ a_{n1} & a_{n2} & a_{n3} & & a_{nn} \end{vmatrix} = \begin{vmatrix} a_{ij} \end{vmatrix}$$

$(i, j = 1, 2, 3, \ldots n)$

A determinant is not changed in value by writing rows for
columns and columns for rows.

If two columns (or rows) of a determinant are interchanged,

the resulting determinant is unchanged in value but is of the opposite sign.

A determinant vanishes if it has two equal columns (or rows).

If each element of a row (or column) is multiplied by the same factor the determinant itself is multiplied by that factor.

The determinant is not changed in value if to each element of a row (or column) is added the corresponding element in another row (or column) multiplied by a common factor.

If each element of the l-th row (or column) consists of the sum of two or more terms the determinant splits up into the sum of two or more determinants having for elements of the l-th row (or column) the separate terms of the $l-\text{th}$ row (or column) of the given determinant.

If corresponding elements of two rows or columns of a determinant have a constant ratio the determinant vanishes.

If the ratio of the differences of corresponding elements in the pth and qth rows (or columns) to the differences of corresponding elements in the rth and sth rows (or columns) be constant the determinant vanishes.

If p rows (or columns) of a determinant whose elements are rational integral function of x become equal or proportional when $x = h$, the determinant is divisible by $(x - h)^{p-1}$.

The co-factor A_{ij} of the element a_{ij} is defined to be the product of $(-1)^{i+j}$ by the determinant obtained from D by deleting the i-th row and the j-th column.

$$D = a_{1j} A_{1j} + a_{2j} A_{2j} + \cdots + a_{nj} A_{nj}$$

$$= \sum_{i=1}^{n} a_{ij} A_{ij}. \quad \text{(Here j can be any number between 1 and n).}$$

The determinants of second and third orders are:

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = a_{11}\, a_{22} - a_{12}\, a_{21}.$$

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}\,a_{22}\,a_{33} + a_{12}\,a_{23}\,a_{31} + a_{13}\,a_{21}\,a_{32} \\ \qquad\qquad - a_{13}\,a_{22}\,a_{31} - a_{12}\,a_{21}\,a_{33} - a_{11}\,a_{23}\,a_{32}.$$

The solution of the system of equations

$$a_{11}\,x_1 + a_{12}\,x_2 + \;\cdots\; + a_{in}\,x_n = c_i, \; i = 1,2,3,\ldots n$$

is unique if $D \neq 0$, the solution is given by the equations

$$Dx_1 = C_1 \;,\quad Dx_2 = C_2, \quad \cdots\cdots \;,\quad Dx_n = C_n$$

where C_k is what D becomes when the elements of its k -th column are replaced by c_1, c_2, $\ldots$ c_n respectively.

* **Stirling's Formula**

    For large value of n,

    $$\sqrt{2n\pi}\left(\tfrac{n}{e}\right)^n < n! < \sqrt{2n\pi}\left(\tfrac{n}{e}\right)^n \left[1 + \frac{1}{12n-1}\right] \quad,$$

    where $\pi = 3.14159\cdots$, $e = 2.71828\cdots$

    $$\ln n! = \left(n + \tfrac{1}{2}\right)\ln n - n \ln e + \ln\sqrt{2\pi}\,.$$

I.2 Trigonometric and Mensuration formulae

* **Definition**

    If θ is the angle subtended by a line whose end point is P (x, y), with the x axis (see Fig.) ,   then
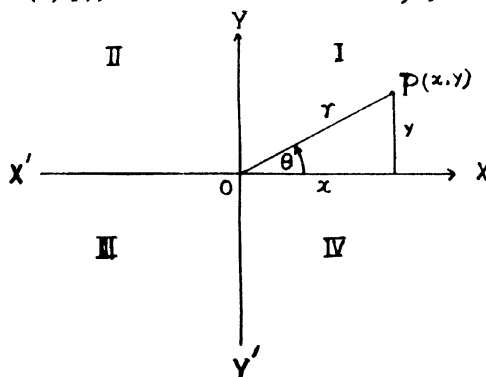
$$\text{sine } \theta \quad = \quad \sin \theta \quad = \frac{y}{r} \ .$$

$$\text{cosine } \theta \quad = \quad \cos \theta \quad = \frac{x}{r} \ .$$

$$\text{tangent } \theta \quad = \quad \tan \theta \quad = \frac{y}{x} \ .$$

$$\text{cotangent } \theta = \quad \text{ctn } \theta \quad = \frac{1}{\tan \theta} = \frac{x}{y} \ .$$

$$\text{secant } \theta \quad = \quad \sec \theta \quad = \frac{1}{\cos \theta} = \frac{r}{x} \ .$$

$$\text{cosecant } \theta \quad = \quad \csc \theta \quad = \frac{1}{\sin \theta} = \frac{r}{y} \ .$$

The angle θ is positive if it is measured counter clockwise or negative, if clockwise.

* Signs of Functions

Table

Quadrant	sin	cos	tan	ctn	sec	csc
I	+	+	+	+	+	+
II	+	-	-	-	-	+
III	-	-	+	+	-	-
IV	-	+	-	-	+	-

* **Functions of 0°, 30°, 45°, 60°, 90°, 180°, 270°, 360°**

Table

	0°	30°	45°	60°	90°	180°	270°	360°
sin	0	$\frac{1}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{\sqrt{3}}{2}$	1	0	-1	0
cos	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0	-1	0	1
tan	0	$\frac{1}{\sqrt{3}}$	1	$\sqrt{3}$	∞	0	∞	0
c'tn	∞	$\sqrt{3}$	1	$\frac{1}{\sqrt{3}}$	0	∞	0	∞
sec	1	$\frac{2}{\sqrt{3}}$	$\sqrt{2}$	2	∞	-1	∞	1
csc	∞	2	$\sqrt{2}$	$\frac{2}{\sqrt{3}}$	1	∞	-1	∞

Functions of Angles in any Quadrant in terms of Angles in First Quadrant.

Table

	$-\theta$	$90°\pm\theta$	$180°\pm\theta$	$270°\pm\theta$	$n(360°)\pm\theta$
sin	$-\sin\theta$	$+\cos\theta$	$\mp\sin\theta$	$-\cos\theta$	$\pm\sin\theta$
cos	$+\cos\theta$	$\mp\sin\theta$	$-\cos\theta$	$\pm\sin\theta$	$+\cos\theta$
tan	$-\tan\theta$	$\mp\text{ctn}\theta$	$\pm\tan\theta$	$\mp\text{ctn}\theta$	$\pm\tan\theta$
ctn	$-\cot\theta$	$\mp\tan\theta$	$\pm\cot\theta$	$\mp\tan\theta$	$\pm\text{ctn}\theta$
sec	$+\sec\theta$	$\mp\csc\theta$	$-\sec\theta$	$\pm\csc\theta$	$+\sec\theta$
csc	$-\csc\theta$	$+\sec\theta$	$\mp\csc\theta$	$-\sec\theta$	$\pm\csc\theta$

n = any integer .

* **Fundamental Identities**

$$\sin^2\theta + \cos^2\theta = 1, \quad 1+\tan^2\theta = \sec^2\theta , \quad 1+\text{ctn}^2\theta = \csc^2\theta$$

$$\sin(\alpha\pm\beta) = \sin\alpha \cos\beta \pm \cos\alpha \sin\beta ,$$

$\cos (\alpha \pm \beta) = \cos \alpha . \cos \beta \mp \sin \alpha . \sin \beta$,

$\tan (\alpha \pm \beta) = \dfrac{\tan \alpha \pm \tan \beta}{1 \mp \tan \alpha . \tan \beta}$,

$\sin 2\alpha = 2 \sin \alpha . \cos \alpha$,

$\cos 2\alpha = \cos^2 \alpha - \sin^2 \alpha = 2 \cos^2 \alpha - 1 = 1 - 2 \sin^2 \alpha$,

$\tan 2\alpha = \dfrac{2\tan \alpha}{1 - \tan^2 \alpha}$,

$\sin 3\alpha = 3 \sin \alpha - 4 \sin^3 \alpha$,

$\cos 3\alpha = 4 \cos^3 \alpha - 3 \cos \alpha$,

$\sin n\alpha = 2 \sin (n-1)\alpha . \cos \alpha - \sin (n-2)\alpha$,

$\cos n\alpha = 2 \cos (n-1)\alpha . \cos \alpha - \cos (n-2)\alpha$,

$\sin \alpha + \sin \beta = 2 \sin \frac{1}{2} (\alpha + \beta) . \cos \frac{1}{2} (\alpha - \beta)$,

$\sin \alpha - \sin \beta = 2 \cos \frac{1}{2} (\alpha + \beta) . \sin \frac{1}{2} (\alpha - \beta)$,

$\cos \alpha + \cos \beta = 2 \cos \frac{1}{2} (\alpha + \beta) . \cos \frac{1}{2} (\alpha - \beta)$,

$\cos \alpha - \cos \beta = -2\sin \frac{1}{2} (\alpha + \beta) . \sin \frac{1}{2} (\alpha - \beta)$,

$\sin \alpha . \sin \beta = \frac{1}{2} \cos (\alpha - \beta) - \frac{1}{2} \cos (\alpha + \beta)$,

$\cos \alpha . \cos \beta = \frac{1}{2} \cos (\alpha - \beta) + \frac{1}{2} \cos (\alpha + \beta)$,

$\sin \alpha . \cos \beta = \frac{1}{2} \sin (\alpha + \beta) + \frac{1}{2} \sin (\alpha - \beta)$.

* Inverse Trigonometric Functions

definition:- if $x = \sin y$, then the solution

is $y = (-1)^n \sin^{-1} x + n\pi$, $-\dfrac{\pi}{2} \leqslant \sin^{-1} x \leqslant \dfrac{\pi}{2}$.

$$n = 0, 1, \ldots$$

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

angle whose sin is x.

* Relation among Inverse functions

$\sin^{-1} x = \cos^{-1} \sqrt{1-x^2} = \tan^{-1} \dfrac{x}{\sqrt{1-x^2}}$,

$\cos^{-1} x = \sin^{-1} \sqrt{1-x^2} = \tan^{-1} \dfrac{\sqrt{1-x^2}}{x}$.

$$\tan^{-1}x = \sin^{-1}\frac{x}{\sqrt{1+x^2}} = \cos^{-1}\frac{1}{\sqrt{1+x^2}} \ .$$

$$\sec^{-1}x = \cos^{-1}\frac{1}{x} \ , \quad \csc^{-1}x = \sin^{-1}\frac{1}{x} \ ,$$

$$\operatorname{ctn}^{-1}x = \tan^{-1}\frac{1}{x}$$

* **Hyperbolic Functions**

Definitions: $\sinh x = \frac{1}{2}(e^x - e^{-x})$,

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

$\tanh x = \dfrac{e^x - e^{-x}}{e^x + e^{-x}} = \dfrac{\sinh x}{\cosh x}$.

$\operatorname{csch} x = \dfrac{1}{\sinh x}$; $\operatorname{sech} x = \dfrac{1}{\cosh x}$; $\operatorname{ctnh} x = \dfrac{1}{\tanh x}$.

If $x = \sinh y$, then y is the inverse hyperbolic

sine of x, i.e. $y = \sinh^{-1}x$ or arc sinh x.

$\sinh^{-1}x = \ln(x + \sqrt{x^2 + 1})$, $\cosh^{-1}x = \ln(x + \sqrt{x^2 - 1})$

$\tanh^{-1}x = \frac{1}{2}\ln\left(\dfrac{1+x}{1-x}\right)$, $\operatorname{ctnh}^{-1}x = \frac{1}{2}\ln\left(\dfrac{x+1}{x-1}\right)$,

Fundamental Identities

$\cosh^2 x - \sinh^2 x = 1$,

$\operatorname{sech}^2 x + \tanh^2 x = 1$,

$\operatorname{csch}^2 x - \operatorname{ctnh}^2 x = -1.$

$\sinh(x{\pm}y) = \sinh x . \cosh y \pm \cosh x . \sinh y$,

$\cosh(x{\pm}y) = \cosh x . \cosh y \pm \sinh x . \sinh y$,

$\tanh(x{\pm}y) = \dfrac{\tanh x \pm \tanh y}{1 \pm \tanh x . \tanh y}$.

$\sinh 2x = 2\sinh x . \cosh x.$

$\cosh 2x = \cosh^2 x + \sinh^2 x$,

$2\sinh^2 \frac{x}{2} = \cosh x - 1$,

$2\cosh^2 \frac{x}{2} = \cosh x + 1.$

$\sinh x + \sinh y = 2\sinh \frac{1}{2}(x+y) . \cosh \frac{1}{2}(x-y)$,

$$\sinh x - \sinh y = 2\cosh \frac{1}{2}(x+y) \cdot \sinh \frac{1}{2}(x-y),$$

$$\cosh x + \cosh y = 2\cosh \frac{1}{2}(x+y) \cdot \cosh \frac{1}{2}(x-y),$$

$$\cosh x - \cosh y = 2\sinh \frac{1}{2}(x+y) \cdot \sinh \frac{1}{2}(x-y).$$

* <u>Connection between Hyperbolic and Circular Functions</u>.

$$2i\sin x = e^{ix} - e^{-ix},$$

$$2\cos x = e^{ix} + e^{-ix}. \qquad i = \sqrt{-1}.$$

$$\sin x = -i\sinh ix, \quad \cos x = \cosh ix,$$

$$\tan x = -i\tanh ix,$$

$$\sin ix = i\sinh x, \cos ix = \cosh x, \tan ix = i\tanh x.$$

$$\sinh(x\pm iy) = \sinh x \cdot \cos y \pm i\cosh x \cdot \sin y,$$

$$\cosh(x\pm iy) = \cosh x \cdot \cos y \pm i\sinh x \cdot \sin y,$$

$$(\cos\theta + i\sin\theta)^n = \cos n\theta + i\sin n\theta, \text{ for all } n.$$

$$\left(\cos\frac{2\pi k}{n} + i\sin\frac{2\pi k}{n}\right)^n = 1, \quad k = 0, 1, \ldots n-1.$$

$$x+iy = re^{i\theta}, \text{ where } r = +\sqrt{x^2+y^2}, \quad \theta = \tan^{-1}\frac{y}{x}.$$

$$\log(x\pm iy) = \frac{1}{2}\ln(x^2+y^2) \pm i\tan^{-1}\frac{y}{x}.$$

* <u>Trigonometric series</u>

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots,$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots,$$

$$\tan x = x + \frac{x^3}{3} + \frac{2x^5}{15} + \frac{17x^7}{315} + \cdots, \quad x^2 < \frac{\pi^2}{4},$$

$$\sin^{-1}x = x + \frac{x^3}{6} + \frac{1}{2}\cdot\frac{3}{4}\cdot\frac{x^5}{5} + \frac{1}{2}\cdot\frac{3}{4}\cdot\frac{5}{6}\cdot\frac{x^7}{7} + \cdots, \quad x^2 < 1,$$

$$\tan^{-1}x = x - \frac{1}{3}x^3 + \frac{1}{5}x^5 - \frac{1}{7}x^7 + . \qquad , x^2 < 1,$$

$$= \frac{\pi}{2} - \frac{1}{x} + \frac{1}{3x^3} - \frac{1}{5x^5} + \cdots \qquad , x^2 > 1,$$

$$\sinh x = x + \frac{x^3}{3!} + \frac{x^5}{5!} + \frac{x^7}{7!} + \cdots$$

$$\cosh x = 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \frac{x^6}{6!} + \cdots$$

$$\tanh x = x - \frac{x^3}{3} + \frac{2x^5}{15} - \frac{17x^7}{315} + \cdots \quad ,$$

$$\sinh^{-1} x = x - \frac{1}{2}\frac{x^3}{3} + \frac{1.3}{2.4} \cdot \frac{x^5}{5} - \frac{1.3.5}{2.4.6}\frac{x^7}{7} + \cdots \quad , \quad x^2 < 1,$$

$$\sinh^{-1} x = \ln 2x + \frac{1}{2}\frac{1}{2x^2} - \frac{1.3}{2.4} \cdot \frac{1}{4x^4} + \frac{1.3.5}{2.4.6} \cdot \frac{1}{6x^6} \cdots , x > 1,$$

$$\cosh^{-1} x = \ln 2x - \frac{1}{2} \cdot \frac{1}{2x^2} - \frac{1.3}{2.4} \cdot \frac{1}{4x^4} - \frac{1.3.5}{2.4.6} \cdot \frac{1}{6x^6} \cdots \quad ,$$

$$\tanh^{-1} x = x + \frac{x^3}{3} + \frac{x^5}{5} + \frac{x^7}{7} + \cdots \qquad , \quad x^2 < 1.$$

* <u>Triangles, Polygons etc.</u>

     A denotes area and V denotes volume

Triangle: $A = \frac{1}{2} bh = \sqrt{s(s-a)(s-b)(s-c)}$,   b = base

            h = height, a & c are other two sides and

            $s = \frac{1}{2}(a+b+c)$.

Rectangle: $A = ab$, a and b are the lengths of the sides.

Parallelogram: $A = ah = ab\sin\theta$, a and b are the
                      sides, h is the altitude and θ is
                      the angle between the sides.

* <u>Trapezoid</u> (four sides, two parallel) : $A = \frac{1}{2}h(a+b)$

            a, b are the parallel sides and
            h the altitude.

* <u>Regular polygon</u> of n sides, each of length a:

            $A = \frac{1}{4} na^2 \cot \frac{180°}{n}$ (Radius of inscribed

            circle $= \frac{a}{2} \cot \frac{180°}{n}$, and that of

            circumscribed circle is $\frac{a}{2} \csc \frac{180°}{n}$).

* <u>Circle:</u> c = circumference;   R = radius

         D = diameter;   L = length of arc subtended by θ;

         l = chord subtended by arc L , h = rise;

θ = central angle in radians.

(180° = π radians).

$$C = 2\pi R = \pi D; \qquad L = R\theta = \frac{D\theta}{2} = D\cos^{-1}\frac{d}{R} \; ;$$

$$(d \neq R-h)$$

$$l = 2\sqrt{R^2-d^2} = 2R \sin\frac{\theta}{2} = 2d\tan\frac{\theta}{2} \; ;$$

$$d = \frac{1}{2}\sqrt{4R^2-l^2} = R\cos\frac{\theta}{2} = \frac{1}{2} l \cot\frac{\theta}{2} \; ;$$

$$\theta = \frac{L}{R} = \frac{2L}{D} = 2 \cos^{-1}\frac{d}{R} = 2 \tan^{-1}\frac{l}{2d}$$

$$= 2 \sin^{-1}\frac{l}{D} \; ;$$

$$A_{circle} = \pi R^2 = \frac{\pi}{4} D^2, \quad A_{sector} = \frac{1}{2} RL = \frac{1}{2} R^2\theta \; ;$$

$$A_{segment} = A_{sector} - A_{triangle} = \frac{1}{2} R^2 (\theta - \sin\theta)$$

$$= R^2 \cos^{-1}\left(\frac{R-h}{R}\right) - (R-h)\sqrt{2Rh - h^2}.$$

The radii of the circles inscribed in and circumscribed about a triangle (of sides a, b, c) respectively are

$$r = \sqrt{\frac{(s-a)(s-b)(s-c)}{s}}$$

$$R = \frac{abc}{4\sqrt{s(s-a)(s-b)(s-c)}} \qquad .$$

* **Ellipse:** $A = \pi ab$, a, b are lengths of semi-major and semi-minor axes respectively.

Perimeter = $4a\, E(k, \pi/2)$

where $k = \sqrt{1 - \frac{b^2}{a^2}}$ and $E(k, \pi/2)$ is the elliptic integral of second kind.

* **Cube:** $A = 6a^2$ = Total surface area

$V = a^3$

d = diagonal = $a\sqrt{3}$, a = length of the side .

* __Rectangular Parallelopiped:__

   A = Total surface area = $2(ab+bc+ca)$

   V = abc

   d = diagonal = $\sqrt{a^2+b^2+c^2}$, a,b,c are the lengths of
                                          the sides .

* __Prism or Cylinder:__

   V = (area of base) . (altitude)

   Lateral area = (perimeter of right section) . (lateral edge).

* __Pyramid or Cone:__

   $V = \frac{1}{3}$ (area of base) . (altitude)

   Lateral area of regular pyramid = $\frac{1}{2}$ (perimeter of base).
                                          (slant height).

* __Sphere:__

   $V = \frac{4\pi}{3} R^3$,

   $A = 4\pi R^2$, R = Radius .

I.3 __Analytic Geometry and vectors__

* Cartesian co-ordinates

   Any point $P(x,y)$ is specified
   by x (abscissa) and y (ordinate)
   measured from the origin O.
   x is positive to the right and
   negative to the left of the
   y'y-axis, and y is positive
   above and negative below the
   x'x-axis.
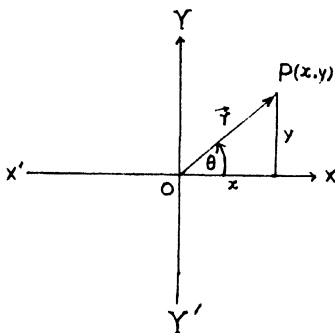
* __Polar coordinates:__

   Any point $P(r,\theta)$ is specified by the distance $\vec{r}$(radius vector)
   from the origin O (Pole) and θ(Vectorial angle) measured from
   the reference line OX, θ is positive if measured counterclockwise,
   and negative if measured clockwise.

* <u>Relations between the two systems:</u>

$$x = r\cos\theta \; , \quad r = \sqrt{x^2 + y^2}$$

$$y = r\sin\theta \; , \quad \theta = \tan^{-1}\frac{y}{x}$$

* <u>Transformation of co-ordinates</u>: (Rectangular systems).

  (i) old axis parallel to new axes.

  The co-ordinates of new origin in terms of old
  system are (h,k)

  $$x = x' + h \; ,$$

  $$y = y' + k \; .$$

  (ii) the new system (x'y') which is rotated through
  an angle θ about the origin from the old system
  (x,y)

  $$x = x' \cos\theta - y' \sin\theta \; ,$$

  $$y = x' \sin\theta + y' \cos\theta \; .$$

* <u>Points and Slopes:</u>

  If $P(x_1, y_1)$ and $Q(x_2, y_2)$ are two points, and α is the
  angle measured   counter-clockwise from OX to PQ, then
  the distance between P & Q

  $$= PQ = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}.$$

  and $\tan\alpha = m = \dfrac{y_2 - y_1}{x_2 - x_1}$
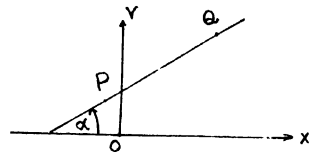
  The angle θ between two straight
  lines whose slopes are m_1 and m_2
  respectively is given by

  $$\theta = \tan^{-1}\frac{m_2 - m_1}{1 + m_1 m_2} \; .$$

  So two lines are $\perp$ to each other if
  $m_1 m_2 = -1$, and parallel if $m_1 = m_2$.

* <u>Straight line</u>: The equation of a straight line can be
  written in the following forms.

(a) $y = mx + c$.

      ($m = \tan\theta =$ slope

      $c =$ intercept on the

      y axis.)
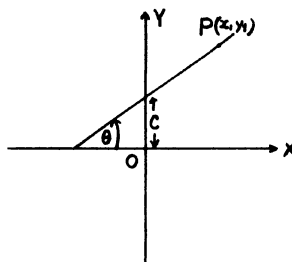
(b) $y - y_1 = m(x - x_1)$. ($m =$ slope and
                          the st. line
                          passes through
                          a given point).

(c) $\dfrac{y - y_1}{x - x_1} = \dfrac{y - y_2}{x - x_2}$. [line passes through two-given points
                                    $(x_1 y_1)$ and $(x_2 y_2)$] .

(d) $\dfrac{x}{a} + \dfrac{y}{b} = 1$.   (a, b are the intercepts on x and y axes,
                     respectively) .

(e) $x\cos\alpha + y\sin\alpha = p$.(p is distance from the origin to the line,
                      α is the angle that the normal makes with
                      x-axis) .

(f) $Ax + By + C = 0$. (General form from which all other forms
                    can be obtained)

* **Circle**:- General equation to a circle of radius r
             with its centre at (a,b) is

$$(x - a)^2 + (y - b)^2 = r^2$$

            for centre at the origin the equation becomes

$$x^2 + y^2 = r^2$$

* **Conic**:- The locus of a point P which moves so that its
             distance from a fixed point F (focus) bears a
             constant ratio e (eccentricity) to its distance
             from a fixed straight line (directrix) is a conic.

The focus is at the origin

x + d = distance from the
      point P(x,y) to
      the directrix.

r = distance of P(x,y) from
    the origin.

Then $e = \dfrac{r}{x + d}$ or $r = \dfrac{de}{1 - e\cos\theta}$.
                        directrix
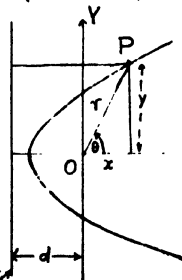
* **Parabola:** The conic is a parabola if e = 1.

(1) $(y-k)^2 = 4a(x-h)$, the
vertex V is at (h,k)
and axis parallel to
OX (Fig) distance from
the vertex to focus =
VF = a, distance from the
vertex to directrix = a
Laturs rectum = PQ = 4a.
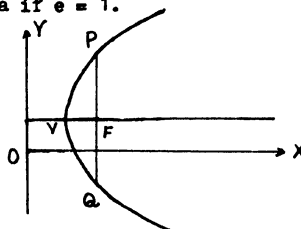
(ii) $(x-h)^2 = 4a(y-k)$, vertex at (h,k) and axis
parallel to OY.

* **Ellipse:** The conic is an ellipse of e < 1.

(1) $\dfrac{(x-h)^2}{a^2} + \dfrac{(y-k)^2}{b^2} = 1$, the

centre is at (h,k) and
major axis ‖ OX (Fig)
Length of the semi major axis = a
Length of the semi minor axis = b

Eccentricity = e = $\sqrt{\dfrac{a^2-b^2}{a}}$
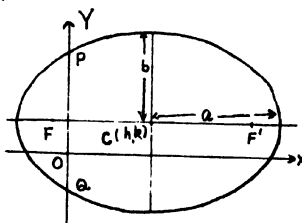
Distance from centre to either focus = ae
Distance from centre to either directrix = $\dfrac{a}{e}$

Latus ructum = PQ $= \dfrac{2b^2}{a}$.

PF + PF' = 2a where P is any point on the ellipse.

(ii) $\dfrac{(y-k)^2}{a^2} + \dfrac{(x-h)^2}{b^2} = 1$, centre at (h,k), major
axis ‖ OY.

* **Hyperbola:** The conic is a hyperbola if e > 1.
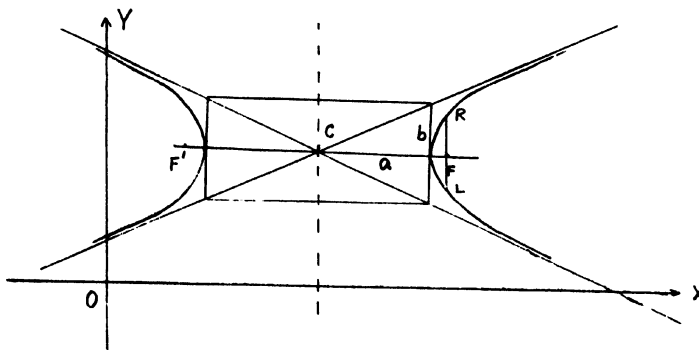
$$\frac{(x-h)^2}{a^2} + \frac{(y-k)^2}{b^2} = 1 \ .$$ Centre at C (h,k) and
transverse axis parallel to OX
(Fig)

Slopes of the asymptotes = $\pm$ b/a

Transverse axis = 2a

Conjugate axis = 2b

Distance from centre to either focus = $\sqrt{a^2+b^2}$

Distance from centre to either directrix = $\frac{a}{e}$

Eccentricity = e = $\frac{\sqrt{a^2+b^2}}{a}$

Difference of distances of any point on hyperbola from
the foci = 2a

Latus ructum = RL = $2b^2/a$

* **Vectors :**

    A physical quantity possessing both magnitude and
    direction is called a vector. If $\hat{e}_x$, $\hat{e}_y$, $\hat{e}_z$
    represent three vectors of unit magnitude along the
    three mutually perpendicular axes OX, OY, OZ, respectively,
    then any vector A in space can be written as

    $$\vec{A} = \hat{e}_x \ A_x + \hat{e}_y \ A_y + \hat{e}_z \ A_z \ .$$

    Where A_x, A_y and A_z are the magnitudes of the projections
    of $\vec{A}$ along the three axes respectively. The magnitude of
    $\vec{A} = |\vec{A}| = \sqrt{A_x^2 + A_y^2 + A_z^2}$ and direction Cosines of $\vec{A}$
    are such that $\cos\alpha : \cos\beta : \cos\gamma = A_x : A_y : A_z$.

* **Vector Algebra:**

    (a) Commutative law of addition: $\vec{A}+\vec{B} = \vec{B}+\vec{A}$.

    (b) Associative law of addition: $\vec{A}+(\vec{B}+\vec{C}) = (\vec{A}+\vec{B})+\vec{C}$.

    (c) multiplication of a vector by a scaler : $\vec{B} = C\vec{A}$.

    where C, is a scaler and the magnitude of $\vec{B}$ is c
    times as that of $\vec{A}$. The direction of $\vec{B}$ is same
    or opposite to that of $\vec{A}$ depending on whether
    C is + ve or - ve .

    (d) Scaler product of two vectors $\vec{A}$ and $\vec{B}$ is defined as

    (i) $\vec{A} \ . \ \vec{B} = |\vec{A}| |\vec{B}| \cos\theta = \vec{B} \ . \ \vec{A}$.

    Where, θ = angle between $\vec{A}$ $\notin$ $\vec{B}$.

    (ii) $\vec{A} \ . \ \vec{B} = A_x B_x + A_y B_y + A_z B_z$

(iii) $\vec{A} \cdot \vec{A} = |A|^2$

(iv) $\vec{A} \cdot (\vec{B} + \vec{C}) = \vec{A} \cdot \vec{B} + \vec{A} \cdot \vec{C}$

(v) $\hat{e}_x \cdot \hat{e}_y = \hat{e}_y \cdot \hat{e}_z = \hat{e}_z \cdot \hat{e}_x = 0.$

(vi) $\hat{e}_x \cdot \hat{e}_x = \hat{e}_y \cdot \hat{e}_y = \hat{e}_z \cdot \hat{e}_z = 1.$

(e) Vector product of two vectors $\vec{A}$ and $\vec{B}$ is defined as

   (i) $\vec{A} \times \vec{B} = |\vec{A}| \, |\vec{B}| \sin\theta \, \hat{a}$, where θ = angle between $\vec{A}$ and $\vec{B}$ and $\hat{a}$ is the unit vector $\perp$ r to the plane containing $\vec{A}$ and $\vec{B}$ in the sense of advance of a right-handed screw rotated from $\vec{A}$ to $\vec{B}$.

   (ii) $\vec{A} \times \vec{B} = \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_z \\ A_x & A_y & A_z \\ B_x & P_y & P_z \end{vmatrix} = -\vec{B} \times \vec{A}$.

   (iii) $\vec{A} \times \vec{A} = 0$.

   (iv) $\vec{A} \times (\vec{B} + \vec{C}) = \vec{A} \times \vec{B} + \vec{A} \times \vec{C}.$

   (v) $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$

   (vi) $\vec{A} \cdot (\vec{B} \times \vec{C}) = \vec{B} \cdot (\vec{C} \times \vec{A}) = \vec{C} \cdot (\vec{A} \times \vec{B}).$

     This is the volume of a parallelopiped whose edges are $\vec{A}, \vec{B}, \vec{C}.$

   (vii) $\hat{e}_x \times \hat{e}_y = \hat{e}_z, \; \hat{e}_y \times \hat{e}_z = \hat{e}_x, \; \hat{e}_z \times \hat{e}_x = \hat{e}_y$

   (viii) $\hat{e}_x \times \hat{e}_x = \hat{e}_y \times \hat{e}_y = \hat{e}_z \times \hat{e}_z = 0.$

* **Vector Calculus:**

(i) $\dfrac{d\vec{A}}{dt} = \hat{e}_x \dfrac{dA_x}{dt} + \hat{e}_y \dfrac{dA_y}{dt} + \hat{e}_z \dfrac{dA_z}{dt}$.

(ii) $\dfrac{d}{dt}(\vec{A} + \vec{B}) = \dfrac{d\vec{A}}{dt} + \dfrac{d\vec{B}}{dt}$

(iii) $\dfrac{d}{dt}(\vec{A} \cdot \vec{B}) = \dfrac{d\vec{A}}{dt} \cdot \vec{B} + \vec{A} \cdot \dfrac{d\vec{B}}{dt}$.

(iv) $\dfrac{d}{dt}(\vec{A} \times \vec{B}) = \dfrac{d\vec{A}}{dt} \times \vec{B} + \vec{A} \times \dfrac{d\vec{B}}{dt}$.

(v) $\dfrac{d}{dt}(c\vec{A}) = \dfrac{dc}{dt}\vec{A} + c\dfrac{d\vec{A}}{dt}$ (c = scaler)

(vi) $\text{grad } \phi = \nabla\phi = \hat{e}_x \dfrac{\partial\phi}{\partial x} + \hat{e}_y \dfrac{\partial\phi}{\partial y} + \hat{e}_z \dfrac{\partial\phi}{\partial z}$ = a vector

    where ϕ is a scaler, $\vec{\nabla} = \hat{e}_x \dfrac{\partial}{\partial x} + \hat{e}_y \dfrac{\partial}{\partial y} + \hat{e}_z \dfrac{\partial}{\partial z}$ (called del)

(vii) div $\vec{A} = \vec{\nabla}\cdot\vec{A} = \dfrac{\partial A_x}{\partial x} + \dfrac{\partial A_y}{\partial y} + \dfrac{\partial A_x}{\partial z}$ = a scaler

(viii) Curl $\vec{A} = \vec{\nabla} \times \vec{A} = \begin{vmatrix} \hat{e}_x & \hat{e}_y & \hat{e}_z \\[6pt] \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\[6pt] A_x & A_y & A_z \end{vmatrix}$ = a vector

* Some Important Relations of Vector Analysis:

(i) div Curl $\vec{A} = \vec{\nabla}\cdot(\vec{\nabla}\times\vec{A}) = 0$.

(ii) div grad $\vec{\phi} = \vec{\nabla}\cdot(\vec{\nabla}\phi) = \nabla^2\vec{\phi} = \dfrac{\partial^2\phi}{\partial x^2} + \dfrac{\partial^2\phi}{\partial y^2} + \dfrac{\partial^2\phi}{\partial z^2}$

(iii) Curl grad $\vec{\phi} = \vec{\nabla}\times(\vec{\nabla}\phi) = 0$.

(iv) Curl Curl $\vec{A} = \vec{\nabla}\times(\vec{\nabla}\times\vec{A}) = \vec{\nabla}(\vec{\nabla}\cdot\vec{A}) - \nabla^2\vec{A}$
$$= \text{grad div }\vec{A} - \text{del}^2\vec{A}.$$

Theorems on Vector Analysis:

* Gauss Theorem: The volume integral of the divergenence of a vector field $\vec{A}$ is taken over any volume V is equal to the surface integral of A taken over the closed surface surrounding the volume i.e.

$$\int_V (\vec{\nabla}\cdot\vec{A})dV = \int_S \vec{A}\cdot\vec{ds}$$

* Green's Theorem:

If $\vec{A} = u\vec{\nabla}w$, then the Gauss theorem becomes

$$\int_V (u\,\nabla^2 w - w\,\nabla^2 u)dV = \int_S (u\vec{\nabla}w - w\vec{\nabla}u)\cdot\vec{ds}$$

* Stokes Theorem: The surface integral of the Curl of a vector field $\vec{A}$ taken over any surface S is equal to the line integral of $\vec{A}$ around the peripheri of $\vec{A}$ i.e.

$$\oint_c \vec{A}\cdot\vec{dl} = \int_S (\vec{\nabla}\times\vec{A})\cdot\vec{ds}$$

* ∇^2 in different co-ordinates:

(i) Cartesian , $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

(ii) Cylindrical, $\nabla^2 = \frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial}{\partial r}) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2}$

(iii) Spherical Polar

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} (\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \varphi^2}$$

I.4 Complex Variables.

* Analytic Functions:- A function $f(z)$ of the complex variable $z = x+iy$ is called analytic in a region R if it possesses a continuous derivative throughout the region R. If $f(z) = u(x,y) + iv(x,y)$ then, the condition for analyticity are

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y} \quad \text{and} \quad \frac{\partial v}{\partial x} = -\frac{\partial u}{\partial y} \qquad (1)$$

which are also called the Cauchey - Riemann equations.

* Cauchy Integral Theorem:- If $f(z)$ is analytic function within and a closed contour C, then

$$\oint_C f(z)\, dz = 0 \qquad (2)$$

* Singularities:- Suppose a function $f(z)$ is analytic throughout a closed region R, except possibly at a finite number of exceptional points, those points are called the singular points or singularities of the function. If there are no singularities within the domain R, the function is said to be regular in the domain. If a circle can be drawn about the singular point as centre, so as to enclose no other singularity of the function, the singularity is said to be isolated.

One type of singularity is known as a branch point. A point $z = \alpha$ is a branch point of $f(z)$ if $f(z)$ fails to return to its original value when z moves around α in a circle of arbitrary small (non zero) radius. For example, the function $f(z) = z^{1/2}$ where $z = \rho e^{i\theta}$ has two values namely

$$f_1(z) = \rho^{\frac{1}{2}} (\cos \frac{\theta}{2} + i \sin \frac{\theta}{2}) \qquad (3)$$

$$f_2(z) = \rho^{\frac{1}{2}} \cos (\frac{\theta+2\pi}{2}) + i \sin (\frac{\theta+2\pi}{2}) = -f_1(z)$$

Another type of singularity is known as a pole. Let $f(z)$ be analytic throughout a region R, except at a single point α inside the region and let

$$f(z) = \frac{a_{-m}}{(z-\alpha)^m} + \frac{a_{-m+1}}{(z-\alpha)^{m-1}} + \cdots + \frac{a_{-1}}{(z-\alpha)} + \phi(z) \qquad (4)$$

where $a_{-m} \neq 0$ and $\phi(z)$ is analytic within R.

Then $f(z)$ is said to have a pole of order m at α . The terms containing negative powers of $(z -\alpha)$ are in the aggregate called the principal part of $f(z)$ near α . If α is a pole of order m, then $\underset{z \to \alpha}{Lt} \ (z-\alpha)^m \ f(z) \ = a_{-m}$.

* **The theorem of Residues:-**

Consider a function $f(z)$ which has a pole of order m at $z=\alpha$, then using equation (2)

$$\oint f(z)dz = a_{-1}\oint \frac{dz}{z-\alpha} + \sum_{n=2}^{m} a_{-n}\oint \frac{dz}{(z-\alpha)^n} + \oint \phi(z)dz \quad (5)$$

the last term is zero by Cauchy Integral formula (3) and putting $z -\alpha = \rho \ e^{i\theta}$, we have

$$\oint f(z)dz = 2\pi i \ a_{-1} \quad\quad\quad ... \quad (6)$$

So the integral depends on the co-efficient of $(z-\alpha)^{-1}$ in the principal part and this co-efficient is called the residue of the function at the pole.

* **Evaluation of some Integrals :-**

(i) Very often we come across integrals of the form

$$I = \oint \frac{f(z)}{S(z)} \ dz$$

Where $f(z)$ is analytic within the closed contour and $s(z)$ is a polynomial in z. In this case $1/S(z)$ is written in terms of its partial fractions and integration is carried out term by term. For example if $s(z) = (z-a)(z-b)$, then

$$I = \oint \frac{f(z)}{(z-a)(z-b)} \ dz \ = \frac{1}{a-b} \oint f(z)\left[\frac{1}{z-a} - \frac{1}{z-b} \right] dz$$

$$= \frac{2\pi i}{(a-b)} \ Res = \frac{2\pi i}{a-b} \left[f(a) - f(b) \right]$$

(ii) $\ I = \int_{-\infty}^{+\infty} F(x) \ e^{ixt} \ dx = \int_{c} F(z) \ e^{izt} \ dz = \pm \ 2\pi i \sum Res.$

Where $\sum Res$ means the sum of the residues of $F(z)e^{izt}$ at all its poles enclosed by the contour C and the sign is + if the contour is described in the counterclockwise direction and minus if clockwise direction. For example

$$I = \int_{-\infty}^{+\infty} \frac{e^{ixt}}{x^2+a^2} \, dx = \frac{\pi}{a} e^{-at} \quad \text{if } (t > 0)$$
$$= \frac{\pi}{a} e^{at} \quad \text{if } (t < 0)$$

where the poles lie at $\pm$ ia and if $t > 0$ the contour is completed in counter clockwise direction.

I.5 Special Functions

* **Bessel Functions:**

Bessel function of order n of first kind is given by

$$J_n(x) = \sum_{s=0}^{\infty} \frac{(-1)^s}{\pi(s)\pi(n+s)} \left(\frac{x}{2}\right)^{n+2s}$$

and $J_{-n}(x) = \sum_{s=0}^{\infty} \frac{(-1)^s}{\pi(s)\pi(s-n)} \left(\frac{x}{2}\right)^{2s-n}$

where $\pi(n+s) = (n+s)!$

Integral representations for $J_n(x)$

$$J_n(x) = \frac{i^{-n}}{2\pi} \int_0^{2\pi} e^{i(x\cos\theta+n\theta)} \, d\theta$$
$$= \frac{i^{-n}}{\pi} \int_0^{\pi} e^{ix\cos\theta} \cos n\theta \, d\theta$$
$$J_n(x) = \frac{1}{\pi} \int_0^{\pi} \cos(n\theta - x\sin\theta) \, d\theta$$

where n is any integer positive or negative.

The differential equation satisfied by $J_n(x)$ is

$$x^2 \frac{d^2y}{dx^2} + x \frac{dy}{dx} + (x^2-n^2)y = 0 .$$

The generating function for $J_n(x)$ is given by

$$F(h,x) = e^{\frac{x}{2}(h-\frac{1}{h})} = \sum_n h^n(x) J_n(x)$$

Some important Relations of Bessel functions

(i) $J_n(-x) = (-1)^n J_n(x)$

(ii) $\frac{2n}{x} J_n(x) = J_{n-1}(x) + J_{n+1}(x)$

(iii) $\frac{d}{dx}(x^n J_n(x)) = x^n J_{n-1}(x)$

(iv) $\frac{d}{dx}(x^{-n} J_n(x)) = -x^{-n} J_{n+1}(x).$

(v) $\cos(x\sin\theta) = J_0(x) + 2J_2(x)\cos2\theta + 2J_4(x)\cos4\theta + \ldots$

$\sin(x\sin\theta) = 2\left[\ J_1(x)\sin\theta + J_3(x)\sin3\theta + J_5(x)\sin5\theta + \ldots\right]$.

(vi) $J_n(x) = \sqrt{\dfrac{2}{\pi x}}\ \cos\left(x - \dfrac{\pi}{4} - \dfrac{n\pi}{2}\right)$.

$x \rightarrow \infty$

* Legendre Functions or polynomials

Definition

(a) Series expansion

$$P_n(x) = \sum_{r=0}^{} (-1)^r \frac{(2n-2r)!}{2^n r!(n-r)!(n-2r)!} x^{n-2r}$$

where $N = \dfrac{n}{2}$ for $n =$ even and $N = (n-1)/2$ for n odd

(b) Rodrigues' formula for $P_n(x)$ is

$$P_n(x) = \frac{1}{2^n n!}\ \frac{d^n}{dx^n}(x^2 - 1)^n\ .$$

(c) Associated Legendre Polynomials

$$P_n^m(x) = (1-x^2)^{m/2}\ \frac{d^m}{dx^m}\ P_n(x)$$

The differential equation satisfied by $P_n^m(x)$ is

$$(1-x^2)\frac{d^2y}{dx^2} - 2x(m+1)\frac{dy}{dx} + (n-m)(n+m+1)y = 0\ .$$

For $m = 0$, the resulting equation is Legendre's differential equation.

The generating function $F(h,x)$ for Legendre polynomials is

$$F(h,x) = \frac{1}{\sqrt{1-2hx+h}} = \sum_{n=0}^{\infty} h^n P_n(x)$$

(d) Some values of $P_n(x)$ and $P_n^m(x)$

$P_0(x) = 1$, $P_4(x) = \dfrac{1}{8}(35x^4 - 30x^2 + 3)$

$P_1(x) = x$, $P_5(x) = \dfrac{1}{8}(63x^5 - 70x^3 + 15x)$,

$P_2(x) = \dfrac{1}{2}(3x^2 - 1), P_6(x) = \dfrac{1}{16}(231x^6 - 315x^4 + 105x^2 - 5)$,

$$P_3(x) = \frac{1}{2}(5x^3 - 3x) ,$$

$$P_1^1(x) = (1-x^2)^{1/2} , \qquad\qquad P_3^3(x) = 15(1-x^2)^{3/2} ,$$

$$P_2^1(x) = 3(1-x^2)^{1/2}x , \qquad\qquad P_4^1(x) = \frac{5}{2}(1-x^2)^{1/2}(7x^3 - 3x) ,$$

$$P_2^2(x) = 3(1-x^2) , \qquad\qquad P_4^2(x) = \frac{15}{2}(1-x^2)(7x^2 - 1) ,$$

$$P_3^1(x) = \frac{3}{2}(1-x^2)^{1/2}(5x^2 - 1), \quad P_4^3(x) = 105(1-x^2)^{3/2} ,$$

$$P_3^2(x) = 15(1-x^2)x \qquad , \qquad P_4^4(x) = 105(1-x^2)^2 .$$

(e) Properties

Orthogonality of $P_n(x)$ and $P_n^m(x)$

$$\int_{-1}^{+1} P_m(x) P_n(x) \, dx = \frac{2}{2n+1} \delta nm , \quad n = 0, 1, 2 \ldots .$$

$$\int_{-1}^{+1} P_n^m(x) P_1^m(x) \, dx = \frac{2}{2n+1} \cdot \frac{(n+m)!}{(n-m)!} \delta nl , \quad n=0, 1, 2, \ldots$$

Further,

$$P_n(-x) = (-1)^n P_n(x) , \quad P_n(x) = P_{-n-1}(x) .$$

$$P_n^m(-x) = (-1)^{n-m} P_n^m(x) , \quad P_n^m(x) = P_{-n-1}^m(x) .$$

* Elliptic Integrals

Definition

$$F(k,\varphi) = \int_0^\varphi \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}} , \quad \text{elliptic integral of the first kind .}$$

$$E(k,\varphi) = \int_0^\varphi d\theta \sqrt{1-k^2\sin^2\theta} \quad \text{elliptic integral of the second kind}$$

$\varphi = \pi/2$, gives the "complete" elliptic integrals.

$$F(k, \pi/2) = K(k) , \quad E(k, \pi/2) = E(k)$$

Some Properties of E and F

$$F(-\varphi) = -F(\varphi), \quad E(-\varphi) = -E(\varphi)$$

$$F(n\pi \pm \varphi) = 2nK \pm F(\varphi)$$

$$E(n \pm \varphi) = 2nE \pm E(\varphi) .$$

I.6   <u>Statistics</u>

* <u>Probability</u>

   Let p be the probability of occurence of an event E in a single
trial (such as the occurence of the head in the tossing of a coin),
and q = (1-p) be that of the non-occurence of that event in a single
trial.   Then the probability P(r) that E will occur <u>exactly</u> r times
in n trials is $\binom{n}{r}$ $p^r q^{n-r}$. This is called the <u>binomial distribution</u>
function.   For the binomial distribution the <u>mean</u> number of
favourable events is

$$a \ = \ \sum_{r=0}^{n} \ r \quad P(r) = np$$

The <u>standard deviation</u> is given by

$$\sigma \ = \ \left[\sum_{r=0}^{n} r^2 P(r) - a^2 \right]^{\frac{1}{2}} \ = \ \sqrt{pqn}$$

If n is large, Stirling's formula can be used for the factorials n!
in ($\frac{n}{r}$) to give us (with a substitution $p = \frac{a}{n}$),

$$P(r) = \frac{a^r e^{-a}}{r!}$$

This is called the <u>Poisson distribution</u>. The mean of r is 'a' in this
distribution.   The standard deviation $\sigma = \sqrt{a}$.

   If r and a are also large, P(r) becomes highly peaked in the
neighbourhood of r = a, and using Stirling's formula for r! we get
(after some manipulations),

$$P(r) \cong \frac{1}{\sqrt{2\pi a}} \ e^{-\frac{1}{2}\frac{(r-a)^2}{a}} \ = \ \frac{1}{\sigma\sqrt{2\pi}} e^{-(r-a)^2/2\sigma^2}$$

This is called <u>the normal or Gaussian distribution</u>. For normal distri-
bution, averages of functions of r are obtained by integration rather
than by summation. For instance, the probability that r will be bet-
ween r_1 and r_2 is

$$P = \int_{r_1}^{r_2} p(y)dy, \quad \text{where} \quad p(r) = \frac{1}{\sigma\sqrt{2\pi}} \ e^{-(r-a)^2/2\sigma^2}$$

a is the mean and σ is the standard deviation of the distribution. In
terms of a variable $x = \frac{r-a}{\sigma}$, $P = \int_{x_1}^{x_2} \phi(x)dx$ where $\phi(x) = \frac{1}{\sqrt{2\pi}}e^{-x^2/2}$
(called the <u>normal function</u>). The modulus of precision is $h = \frac{1}{\sigma\sqrt{2}} = \frac{0.7071}{\sigma}$. The <u>mean absolute error</u> (m.a.e.) = <u>mean deviation</u>(MD) =
$\sigma\sqrt{2/\pi}$ = 0.7979 σ. The <u>probable error</u> (p.e.) = semi - inter -
quartile range = 0.6745σ = 0.8453 MD. The variance = σ^2. The mean

values of various functions of r can be obtained by using the formula

$$\overline{f} = \int_{-\infty}^{\infty} f(r)P(r)dr = \int_{-\infty}^{\infty} F(x)\,\phi(x)\,dx \quad \text{(using the transformation}$$

$$x = \frac{r-a}{\sigma}).$$

Often one needs incomplete integrals over $\phi(x)$, of the form $\int_{x_1}^{x_2} F(x)$

$\phi(x)$ dx. For instance, the sum of those terms of $(p+q)^n = \sum_{t=a}^{b} \binom{n}{t} p^t q^{n-t}$

(with $p + q = 1$) in which t ranges from a to b, a and b being integers, is (if n is large enough) approximately

$$\int_{x_1}^{x_2} \phi(x)dx + \left[\frac{q-p}{6\sigma} \phi^{(2)}(x) + \frac{1}{24}\left(\frac{1}{\sigma^2} - \frac{6}{n}\right)\phi^{(3)}(x) \right]_{x_1}^{x_2}$$

where $x_1 = (a - \tfrac{1}{2} - nq)/\sigma$, $x_2 = (b + \tfrac{1}{2} - nq)/\sigma$, $\sigma = \sqrt{npq}$, and $\phi^{(k)}(x)$ is the k-th derivative of $\phi(x)$. Tables of $\phi(x)$ are given later.

* Probable Error

The errors in a series of observations generally satisfy a Gaussian distribution about the mean value. The following results can be established from this presumption. The probable error ϵ of a single observation in a series of n measurements t_1, $t_2 \cdots t_n$, the arithmatic mean of which is $m = \frac{1}{n}\sum_{j=1}^{n} t_j$, is

$$\epsilon = 0.6745\,\sigma = \frac{0.6745}{\sqrt{n-1}}\sqrt{(m-t_1)^2 + (m-t_2)^2 + \ldots + (m-t_n)^2}$$

σ is the standard deviation. The standard deviation σ_m of the arithmetic mean m is $m = / n$. The probable error E of the arithmetic mean is

$$E = 0.6745\,\sigma_m = \frac{0.6745}{\sqrt{n(n-1)}}\sqrt{(m-t_1)^2 + (m-t_2)^2 + \ldots + (m-t_n)^2}.$$

Approximate values of ϵ and E are

$$\epsilon = \frac{0.8453}{\sqrt{n(n-1)}} D, \qquad E = \frac{0.8453}{n\sqrt{n-1}} D$$

where

$$D = |m-t_1| + |m-t_2| + \ldots + |m-t_n|$$

Factors for Computing

Probable Errors

n	$\frac{1}{\sqrt{n}}$	$\frac{1}{\sqrt{n(n-1)}}$	$\frac{.6745}{\sqrt{n-1}}$	$\frac{.6745}{\sqrt{n(n-1)}}$	$\frac{.8453}{n\sqrt{n-1}}$	$\frac{.8453}{\sqrt{n(n-1)}}$
2	.707 107	.707 107	.6745	.4769	.4227	.5978
3	.577 350	.408 248	.4769	.2754	.1993	.3451
4	.500 000	.288 675	.3894	.1947	.1220	.2440
5	.447 214	.223 607	.3372	.1508	.0845	.1890
6	.408 248	.182 574	.3016	.1231	.0630	.1543
7	.377 964	.154 303	.2754	.1041	.0493	.1304
8	.353 553	.133 631	.2549	.0901	.0399	.1130
9	.333 333	.117 851	.2385	.0795	.0332	.0996
10	.316 228	.105 409	.2248	.0711	.0282	.0891
11	.301 511	.095 346	.2133	.0643	.0243	.0806
12	.288 675	.087 039	.2034	.0587	.0212	.0736
13	.277 350	.080 064	.1947	.0540	.0188	.0677
14	.267 261	.074 125	.1871	.0500	.0167	.0627
15	.258 199	.069 007	.1803	.0465	.0151	.0583
16	.250 000	.064 550	.1742	.0435	.0138	.0546
17	.242 536	.060 634	.1686	.0409	.0124	.0513
18	.235 702	.057 166	.1636	.0386	.0114	.0483
19	.229 416	.054 074	.1590	.0365	.0105	.0457
20	.223 607	.051 299	.1547	.0346	.0097	.0434

* Least Squares

The normal equations for finding coefficients, a_0, a_1,..., a_m, in fitting a curve of the form $y = a_0 + a_1 x + \ldots + a_m x^m$ to data (X_1, Y_1), $i = 1, \ldots, n$, $(n > m)$, are $m + 1$ in number as follows:

$$\sum Y_i = a_0 n + a_1 \sum X_i + a_2 \sum X_i^2 + \ldots + a_m \sum X_i m,$$

$$\sum X_i Y_i = a_0 \sum X_i + a_1 \sum X_i^2 + a_2 \sum X_i^3 + \ldots + a_m \sum X_i^{m+1},$$

$$\sum X_i^m Y_i = a_0 \sum X_i^m + a_1 \sum X_i^{m+1} + a_2 \sum X_i^{m+2} + \ldots + a_m \sum X_i^{2m}.$$

<u>Deviation</u> from fitted curve, $d_i = Y_i - (a_0 + a_1 X_i + \ldots + a_m X_i^m)$.

For $z = ab^x$, use/$y = \log z$, $a_0 = \log a$, $a_1 = \log b$.

For $z = at^p$, use/$y = \log z$, $a_0 = \log a$, $a_1 = p$, $x = \log t$.

S_y, <u>standard error of estimate,</u> = root-mean-square of the y-deviations about a fitted curve $= \sqrt{\sum d_i^2 / n}$, where $\sum d_i^2 = \sum Y_i^2 - (a_0 \sum Y_i^2 + a_1 \sum X_i Y_i + \ldots)$.

* "t" test of significance between two sample means $(\bar{x}_1$ and $\bar{x}_2)$.

Paired variates: $t = \dfrac{\bar{d}}{\sqrt{\dfrac{\sum(d_i - \bar{d})^2}{N(N - 1)}}}$ with $N - 1$ degrees of freedom

where $\bar{d} = \bar{x}_1 - \bar{x}_2$, $d_1 = x_{11} - x_{21}$, $d_2 = x_{12} - x_{22}$ etc. and N = sample size.

Unpaired variates: $t = \dfrac{\bar{x}_1 - \bar{x}_2}{\sqrt{\dfrac{\sum_i(x_1 - \bar{x}_1)^2 + \sum_i(x_{21} - \bar{x}_2)^2}{N_1 + N_2 - 2}\left(\dfrac{1}{N_1} + \dfrac{1}{N_2}\right)}}$

with $N_1 + N_2 - 2$ degrees of freedom where N_1 = size of sample 1 and $N_2 \doteq$ size of sample 2

* F test for equality of variances

$$F = \frac{\sigma_1^2}{\sigma_2^2}$$

where σ_1^2 = variance of sample with size N_1 and σ_2^2 = variance of sample with size N_2 with $N_1 - 1$ = degrees of freedom for numberator $N_2 - 1$ = degrees of freedom for denominator.

I.7 Computational Methods

* **Numerical Integration**

    Evaluation of an integral of the form $I = \int_a^b y(x)dx$ can be done numerically to a fair degree of accuracy by dividing the interval from a to b into n equal segments each of length h and using any of the formulae.

$$I_T = h\left[\tfrac{1}{2}(y_0 + y_n) + y_1 + y_2 + \ldots + y_{n-1}\right] \quad \text{(Trapezoidal rule)}$$

$$I_D = h\left[0.4(y_0 + y_n) + 1.1(y_{n-1} + y_1) + y_2 + y_3 + \ldots + \ldots + y_{n-2}\right]$$

$$\text{(Durand's rule)}$$

$$I_S = \frac{h}{3}\left[(y_0 + y_n) + 4(y_1 + y_3 + \ldots y_{n-1})\right.$$
$$\left. + 2(y_2 + y_4 + \ldots + y_{n-2})\right] \quad \text{(n even, Simpson's rule).}$$

y_1 is the value of y at the point separating the l-th segment from the $(1 + 1)$-th segment. In general Simpson's rule gives the best results, and the accuracy increases with decrease in the value of h.

* **Numerical Solution of Ordinary Differential Equations**

    For ordinary differential equations of first order, of the form $y' = f(x,y)$, the simplest way of obtaining the solution is to start from the initial value y_0 at $x = x_0$, divide the range of values of x (in which the form of the solution is desired) into a large number of equal segments each of width h, and obtain the sequence of points on the graph of y versus x by successive use of the formula

$$y_{n+1} = y_n + h\, y_n'$$

The accuracy of the method improves with decrease in h. A better procedure is to start with

$$y_1 = y_0 + \tfrac{1}{2} h\left(y_0' + y_1'\right) - \frac{h^2}{12}\left(y_1'' - y_0''\right)$$

where the second dervative can be obtained by differentiating the original equation and using the numerical values of x, y and y' in the resulting expression. One first evaluates $y_1 = y_0 + y'h$ and uses this to evaluate y_1' and y_1''. These values when substituted in the above equation give the next value of y_1 which can be used again in the same way to obtain a still better value of y_1. Usually a couple of iterations suffice to give a reasonably good value of y_1. Then one proceeds to the next point and gets a good value of y_2 following the same iterative method with y_2 and y_1. Following this up one can get the complete curve.

    For a second order differential equation of the form $y'' = f(x,y,y')$ with the initial values y_0 and y_0' given, one can proceed as in the above case first to obtain $y'(x)$ as a function of x, and then another repetition of the above process leads to $y(x)$ as a function of x. For

other boundary conditions and other forms of second order equations the procedure is more involved.

* Solution of Transcendental Equations

Transcendental equations of the form $f(x) = 0$ where $f(x)$ is not an algebraic function of x, but involves functions such as logarithmic, exponential, trigonometric, hyperbolic functions etc. can be solved numerically by an iteration method (Newton's method). Suppose x_0 is the initial estimate of the root (based on guess work or drawing a graph of of the function), a better approximation to the root in given by

$$x_1 = x_0 - f(x_0)/f'(x_0)$$

Similarly a still better approximation is

$$x_2 = x_1 - f(x_1)/f'(x_1),$$

and in general,

$$x_n = x_{n-1} - f(x_{n-1})/f'(x_{n-1})$$

This method works for ordinary equations also.

The few topics and methods discussed above are for ordinary computations not requiring great accuracy. More extensive computational techniques are given in Handbook of Mathematical Functions - M. Abramowitz and L.A. Stegun (U.S. National Bureau of Standards).

* A Note on Computers

Most of the numerical computations a student requires in the course of his studies can be handled through the use of slide rules and desk calculators. More elaborate and longer computations are best tackled using an electronic digital computer.

An electronic digital computer has a memory section, an arithmetic section and a logic section. Hence it can remember numbers, perform arithmetic operations and take decisions involving the use of logic In effect it behaves as an individual who needs instructions for what it should do with the numbers it deals with. Such instructions are provided through a "programme", and the computer performs elaborate sequential calculations following the instructions in the programme. The machine is versatile enough to process information, besides performing operations with numbers. In order to solve a computational problem by an electronic computer, the problem has to be programmed in a language that the computer understands. A commonly used programme language is FORTRAN, which is accepted by all IBM computers, and with slight modifications by other computers. Details of programming procedures can be obtained from the staff of the various computer centers in the country.

A small computer (such as IBM-1620) can perform more than 1000 additions and 100 multiplications of 8 digit decimal numbers per second, and has storage capacity in the memory part of between 20000 to 40000 digits. A large computer (such as IBM-7090, IBM-7044, or CDC-3600) can be 500 times faster in operation, and has storage capacities of the order of 40000 words (each word = 9 digits). This indicates the scale of performance of a modern electronic computer.

Some of the Computer Centers in India	Computer Models
1. Tata Institute of Fundamental Research, Colaba, Bombay	CDC-3600
2. Physical Research Laboratory, Ahmedabad	IBM-1620
3. Indian Institute of Technology, Kanpur	IBM-7044 IBM-1620
4. University of Delhi, Delhi	IBM-1620
5. Planning Commission, Delhi	IBM-1620
6. Indian Agricultural Research Institute, Delhi	IBM-1620
7. Indian Institute of Technology, Delhi	ICT-1609
8. Structural Engineering Research Institute, Roorkee	IBM-1620
9. Indian Statistical Institute, Calcutta	IBM-1620
10. Indian Institute of Technology, Kharagpur	IBM-1620
11. Union Carbide (India) Co., Calcutta	IBM-1401
12. Engineering College, Guindy, Madras	IBM-1620
13. Hindustan Aeronautics Ltd., Bangalore	ELLIOT

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I.8 Calculus and Integral Tables

(i) Differentials

$d(au) = a\ du$

$d(u + v - w) = du + dv - dw$

$d(uv) = u\ dv + v\ du$

$d(\frac{u}{v}) = \dfrac{v\ du - u\ dv}{v^2}$

$d(u^n) = nu^{n-1}du$

$d(u^v) = vu^{v-1}\ du + u^v(\log_e u)\ dv$

$d(e^u) = e^u\ du$

$d(e^{au}) = ae^{au}\ du$

$d(a^u) = a^u(\log_e a)\ du$

$d(\log_e u) = u^{-1}du$

$d(\log_a u) = u^{-1}(\log_a e)\ du$

$d(u^v) = u^u(1 + \log_e u)\ du$

$d \sin u = \cos u\ du$

$d \cos u = -\sin u\ du$

$d \tan u = \sec^2 u\ du$

$d \cot u = -\csc^2 u\ du$

$d \sec u = \tan u \sec u\ du$

$d \csc u = -\cot u \cdot \csc u\ du$

$d \sin^{-1} u = (1 - u^2)^{-\frac{1}{2}}\ du$

$d \cos^{-1} u = -(1 - u^2)^{-\frac{1}{2}}\ du$

$d \tan^{-1} u = (1 + u^2)^{-1}\ du$

$d \cot^{-1} u = -(1 + u^2)^{-1}\ du$

$d \sec^{-1} u = u^{-1}(u^2 - 1)^{-\frac{1}{2}}\ du$

$d \csc^{-1} u = -u^{-1}(u^2 - 1)^{-\frac{1}{2}}\ du$

$d \sinh u = \cosh u\ du$

$d \cosh u = \sinh u\ du$

$d \tanh u = \text{sech}^2 u\ du$

$d \coth u = -\text{csch}^2 u\ du$

$d \text{sech}\ u = -\text{sech}\ u \tanh u\ du$

$d \text{csch}\ u = -\text{csch}\ u \coth u\ du$

$d \sinh^{-1} u = (u^2 + 1)^{-\frac{1}{2}}\ du$

$d \cosh^{-1} u = (u^2 - 1)^{-\frac{1}{2}}\ du$

$d \tanh^{-1} u = (1 - u^2)^{-1}\ du$

$d \coth^{-1} u = -(u^2 - 1)^{-1}\ du$

$d \text{sech}^{-1} u = -u^{-1}(1 - u^2)^{-\frac{1}{2}}\ du$

$d \text{csch}^{-1} u = -u^{-1}(u^2 + 1)^{-\frac{1}{2}}\ du$

(ii) <u>Indefinite</u> <u>Integrals</u>

1. $\int (ax + b)^n dx = \dfrac{(ax + b)^{n+1}}{a(n + 1)}$, $n = -1$.

2. $\int \dfrac{dx}{ax+b} = \dfrac{1}{a} \log (ax + b)$.

3. $\int \dfrac{x^2\,dx}{ax + b} = \dfrac{1}{a^3} [\tfrac{1}{2} (ax + b)^2 - 2b (ax + b) + b^2 \log(ax+b)]$.

4. $\int x^m (ax + b)^n\,dx = \dfrac{1}{a(m+n+1)} [x^m (ax+b)^{n+1}$

$\qquad\qquad\qquad\qquad\qquad -mb \int x^{m-1}(ax+b)^n\,dx]$,

$\qquad = \dfrac{1}{m+n+1} [x^{m+1}(ax+b)^n + nb \int x^m(ax+b)^{n-1}\,dx]$,

$\qquad\qquad m > 0, \quad m + n + 1 \ne 0.$

5. $\int \dfrac{dx}{x(ax+b)} = \dfrac{1}{b} \log \dfrac{x}{ax+b}$.

6. $\int \dfrac{dx}{x(ax+b)^2} = - \dfrac{d}{db} \int \dfrac{dx}{x(ax+b)}$.

7. $\int \sqrt{ax + b}\,dx = \dfrac{2}{3a} (ax + b)^{3/2}$.

8. $\int x^n \sqrt{(ax+b)}\,dx = \dfrac{2}{a^{n+1}} \int u^2(u^2 - b)^n du$, $u = ax+b$.

9. $\int \dfrac{\sqrt{ax + b}}{x}\,dx = 2 \sqrt{ax + b} + b \int \dfrac{dx}{x \sqrt{ax+b}}$.

10. $\int \dfrac{dx}{\sqrt{ax+b}} = \dfrac{2 \sqrt{ax+b}}{a}$.

11. $\int \dfrac{x^n\,dx}{\sqrt{ax + b}} = \dfrac{2}{a^{n+1}} \int (u^2-b)^n\,du$, $u = \sqrt{ax+b}$

12. $\int \dfrac{dx}{x \sqrt{ax+b}} = \dfrac{1}{\sqrt{b}} \log \dfrac{\sqrt{ax+b} - \sqrt{b}}{\sqrt{ax+b} + \sqrt{b}}$, for $b > 0$.

13. $\int \dfrac{dx}{x\sqrt{ax+b}} = \dfrac{2}{\sqrt{-b}}\ \tan^{-1}\sqrt{\dfrac{ax+b}{-b}}\ ,\quad b < 0\ ;$

$\qquad\qquad = \dfrac{-2}{\sqrt{-b}}\ \tanh^{-1}\sqrt{\dfrac{ax+b}{b}}\ ,\quad b > 0.$

14. $\int \dfrac{dx}{x^n(ax+b)^m} = -\dfrac{1}{b^{m+n-1}}\int \dfrac{(u-a)^{m+n-2}}{u^m}\ du,\ u = \dfrac{ax+b}{x}\ .$

15. $\int (ax+b)^{\pm\frac{n}{2}}\ dx = \dfrac{2(ax+b)^{\frac{2+n}{2}}}{a(2\pm n)}\ .$

16. $\int x(ax+b)^{\pm\frac{n}{2}}\ dx = \dfrac{2}{a^2}\ [\ \dfrac{(ax+b)^{\frac{4\pm n}{2}}}{4\pm n} - \dfrac{b(ax+b)^{\frac{2\pm n}{2}}}{2\pm n}\ ]$

17. $\int \dfrac{dx}{x(ax+b)^{\frac{n}{2}}} = \dfrac{1}{b}\int \dfrac{dx}{x(ax+b)^{\frac{n-2}{2}}} - \dfrac{a}{b}\int \dfrac{dx}{(ax+b)^{\frac{n}{2}}}\ .$

18. $\int \dfrac{x^m dx}{\sqrt{ax+b}} = \dfrac{2x^m\sqrt{ax+b}}{(2m+1)a} - \dfrac{2mb}{(2m+1)a}\int \dfrac{x^{m-1}\ dx}{\sqrt{ax+b}}\ .$

19. $\int \dfrac{dx}{x^n\sqrt{ax+b}} = \dfrac{-\sqrt{ax+b}}{(n-1)b\ x^{n-1}} - \dfrac{(2n-3)a}{(2n-2)b}\int \dfrac{dx}{x^{n-1}\sqrt{ax+b}}$

20. $\int \dfrac{(ax+b)^{\frac{n}{2}}}{x}\ dx = a\int (ax+b)^{\frac{n-2}{2}}\ dx + b\int \dfrac{(ax+b)^{\frac{n-2}{2}}}{x}\ dx$

21. $\int \dfrac{dx}{(ax+b)(cx+d)} = \dfrac{1}{bc - ad}\ \log\dfrac{cx + d}{ax + b}\ ,\ bc - ad \neq 0.$

22. $\int (ax+b)^n\ (cx+d)^m\ dx = \dfrac{1}{(m+n+1)a}\ [\ (ax+b)^{n+1}(cx+d)^m$

$\qquad\qquad - m(bc-ad)\int (ax+b)^n\ (cx+d)^{m-1}\ dx\ ].$

23. $\displaystyle\int \frac{dx}{(ax+b)^n(cx+d)^m} = \frac{-1}{(m-1)(bc-ad)} \left[\frac{1}{(ax+b)^{n-1}(cx+d)^{m-1}} \right.$

$$+ a(m+n-2) \int \frac{dx}{(ax+b)^n(cx+d)^{m-1}} \Big] \ , \ m > 1, \ n > 0;$$

$$bc - ad \neq 0$$

24. $\displaystyle\int \frac{(ax+b)^n}{(cx+d)^m} \, dx = - \frac{1}{(m-1)(bc-ad)} \left[\frac{(ax+b)^{n+1}}{(cx+d)^{m-1}} + \right.$

$$(m-n-2)a \int \frac{(ax+b)^n \, dx}{(cx+d)^{m-1}} \Big] \ ,$$

$$= \frac{-1}{(m-n-1)c} \left[\frac{(ax+b)^n}{(cx+d)^{m-1}} + n (bc-ad) \int \frac{(ax+b)^{n-1}}{(cx+d)^m} \, dx \right].$$

25. $\displaystyle\int \frac{(cx+d)}{\sqrt{ax+b}} \, dx = \frac{2}{3a^2} (3ad - 2bc + acx) \sqrt{ax+b} \ .$

26. $\displaystyle\int \frac{\sqrt{(ax+b)}}{cx+d} \, dx = \frac{2\sqrt{ax+b}}{c} - \frac{2}{c} \sqrt{\frac{ad-bc}{c}} \tan^{-1} \sqrt{\frac{c(ax+b)}{ad-bc}} \ ,$

$$c > 0, \quad ad > bc$$

$$= \frac{2\sqrt{ax+b}}{c} + \frac{1}{c} \sqrt{\frac{bc-ad}{c}} \ x$$

$$\log \frac{\sqrt{c(ax+b)} - \sqrt{bc-ad}}{\sqrt{c(ax+b)} + \sqrt{bc-ad}} \ , \ c > 0, \quad bc > ad.$$

27. $\displaystyle\int \frac{dx}{(cx+d)\sqrt{ax+b}} = \frac{2}{\sqrt{c}\sqrt{ad-bc}} \tan^{-1} \sqrt{\frac{c(ax+b)}{ad-bc}}, \ c > 0, ad > bc.$

28. $\displaystyle\int \frac{dx}{(cx+d)\sqrt{ax+b}}$

$$= \frac{1}{\sqrt{c}\sqrt{bc-ad}} \log \frac{\sqrt{c(ax+b)} - \sqrt{bc-ad}}{\sqrt{c(ax+b)} + \sqrt{bc-ad}} \ , \ c > 0, \ bc > ad.$$

29. $\int \dfrac{dx}{p^2+x^2} = \dfrac{1}{p} \tan^{-1} \dfrac{x}{p}$, Or $- \dfrac{1}{p} \operatorname{ctn}^{-1} \dfrac{x}{p}$.

30. $\int \dfrac{dx}{p^2-x^2} = \dfrac{1}{2p} \log \dfrac{p+x}{p-1}$, Or $\dfrac{1}{p} \tanh^{-1} \dfrac{x}{p}$.

31. $\int \dfrac{dx}{ax^2+b} = \dfrac{1}{\sqrt{ab}} \tan^{-1} (x\sqrt{\tfrac{a}{b}})$; a, c > 0 .

32. $\int \dfrac{dx}{ax^2+b} = \dfrac{1}{2\sqrt{-ab}} \log \dfrac{x\sqrt{a} - \sqrt{-b}}{x\sqrt{a}+\sqrt{-b}}$; a >0, b <0.

$\qquad = \dfrac{1}{2\sqrt{-ab}} \log \dfrac{\sqrt{b} + x \sqrt{-a}}{\sqrt{b} - x \sqrt{-a}}$; a < 0, b > 0.

33. $\int \dfrac{dx}{(ax^2+b)^n} = \dfrac{1}{2(n-1)b} \cdot \dfrac{x}{(ax^2+b)^{n-1}}$

$\qquad + \dfrac{2n-3}{2(n-1)b} \int \dfrac{dx}{(ax^2+b)^{n-1}}$, n a positive integer, n >1 .

34. $\int x(ax^2+b)^n dx = \dfrac{1}{2a} \dfrac{(ax^2+b)^{n+1}}{n+1}$, n $\neq$ -1 .

35. $\int \dfrac{x}{ax^2+b} dx = \dfrac{1}{2a} \log (ax^2+b)$.

36. $\int \dfrac{dx}{x(ax^2+b)} = \dfrac{1}{2b} \log \dfrac{x^2}{ax^2+b}$.

37. $\int \dfrac{x^n dx}{ax^2+b} = \dfrac{x^{n-1}}{a(n-1)} - \dfrac{b}{d} \int \dfrac{x^{n-2} dx}{ax^2 + b}$, n $\neq$ 1 .

38. $\int \dfrac{x^2 dx}{(ax^2+b)^n} = - \dfrac{1}{2(n-1)a} \cdot \dfrac{x}{(ax^2+b)^{n-1}}$

$\qquad + \dfrac{1}{2(n-1)a} \int \dfrac{dx}{(ax^2+b)^{n-1}}$

39. $\displaystyle\int \frac{dx}{x^2(ax^2+b)^n} = \frac{1}{b}\int \frac{dx}{x^2(ax^2+b)^{n-1}} - \frac{a}{b}\int \frac{dx}{(ax^2+b)^n}$.

40. $\displaystyle\int \sqrt{x^2 \pm p^2}\ dx = \frac{1}{2}\left[\ x\sqrt{x^2 \pm p^2} \pm p^2 \log(x+\sqrt{x^2\pm p^2})\ \right]$.

41. $\displaystyle\int \sqrt{p^2 - x^2}\ dx = \frac{1}{2}\left[\ x\sqrt{p^2 - x^2} + p^2 \sin^{-1}\left(\frac{x}{p}\right)\ \right]$.

42. $\displaystyle\int \frac{dx}{\sqrt{x^2 \pm p^2}} = \log(x + \sqrt{x^2 \pm p^2})$.

43. $\displaystyle\int \frac{dx}{\sqrt{p^2 - x^2}} = \sin^{-1}\left(\frac{x}{p}\right)\ \text{Or}\ - \cos^{-1}\left(\frac{x}{p}\right)$.

44. $\displaystyle\int \sqrt{ax^2+b}\ dx = \frac{x}{2}\sqrt{ax^2 + b} + \frac{c}{2\sqrt{a}}\log(x\sqrt{a}+\sqrt{ax^2+b})$,
$$a > 0$$
$$= \frac{x}{2}\sqrt{ax^2+b} + \frac{b}{2\sqrt{-a}}\sin^{-1}\left(x\sqrt{\frac{-a}{b}}\right),\ a < 0.$$

45. $\displaystyle\int \frac{dx}{\sqrt{ax^2+b}} = \frac{1}{\sqrt{a}}\log(x\sqrt{a} + \sqrt{ax^2 + b}),\quad a > 0.$
$$= \frac{1}{\sqrt{-a}}\sin^{-1}\left(x\sqrt{\frac{-a}{b}}\right),\quad a < 0.$$

46. $\displaystyle\int x\sqrt{ax^2+b}\ dx = \frac{1}{3a}(ax^2 + b)^{3/2}$.

47. $\displaystyle\int x^2\sqrt{ax^2+b}\ dx = \frac{x}{4a}(ax^2+b)^{3/2} - \frac{bx}{8a}\sqrt{ax^2+b}$
$$- \frac{b^2}{8\sqrt{a^3}}\log(x\sqrt{a} + \sqrt{ax^2+b}),\ a > 0.$$
$$= \frac{x}{4a}(ax^2+b)^{3/2} - \frac{bx}{8a}\sqrt{ax^2+b}$$

$$- \frac{b^2}{8a\sqrt{-a}} \sin^{-1}(x\sqrt{\tfrac{-a}{b}}), \quad a < 0.$$

48. $\displaystyle\int \frac{x\, dx}{\sqrt{ax^2+b}} = \frac{1}{a} \sqrt{ax^2 + b}$.

49. $\displaystyle\int \frac{\sqrt{ax^2+b}}{x} = \sqrt{ax^2+b} + \sqrt{b} \log \frac{\sqrt{ax^2+b}-\sqrt{b}}{x}, \quad c > 0.$

$$= \sqrt{ax^2+b} - \sqrt{-b} \tan^{-1} \frac{\sqrt{ax^2+b}}{\sqrt{-b}}, \quad b < 0.$$

50. $\displaystyle\int \frac{dx}{x\sqrt{p^2 \pm x^2}} = -\frac{1}{p} \log \frac{p+\sqrt{p^2+x^2}}{x})$.

51. $\displaystyle\int \frac{dx}{x\sqrt{x^2-p^2}} = \frac{1}{p} \cos^{-1}(\tfrac{p}{x})' \quad \text{or} \quad -\frac{1}{p} \sin^{-1}(\tfrac{p}{x}).$

52. $\displaystyle\int \frac{dx}{x\sqrt{ax^2+b}} = \frac{1}{\sqrt{b}} \log \frac{\sqrt{ax^2+b}-\sqrt{b}}{x}, \quad b > 0.$

$$= \frac{1}{\sqrt{-b}} \sec^{-1}(x\sqrt{\tfrac{-a}{b}}), \quad b < 0.$$

53. $\displaystyle\int \frac{x^n\, dx}{\sqrt{ax^2+b}} = \frac{x^{n-1}\sqrt{ax^2+b}}{na} - \frac{(n-1)b}{na} \int \frac{x^{n-2}dx}{\sqrt{ax^2+b}}, \quad n > 0.$

54. $\displaystyle\int x^n \sqrt{ax^2+b}\, dx = \frac{x^{n-1}(ax^2+b)^{3/2}}{(n+2)a}$

$$- \frac{(n-1)b}{(n+2)a} \int x^{n-2} \sqrt{ax^2+b}\, dx, \quad n > 0.$$

55. $\displaystyle\int \frac{\sqrt{ax^2+b}}{x^n}\,dx \;=\; -\;\frac{(ax^2+b)^{3/2}}{b(n-1)x^{n-1}} \;-\; \frac{(n-4)a}{(n-1)b}\int \frac{\sqrt{ax^2+b}}{x^{n-2}}\,dx,$

$$n > 1.$$

56. $\displaystyle\int \frac{dx}{x^n\,\sqrt{ax^2+b}} \;=\; \frac{-\sqrt{ax^2+b}}{b(n-1)x^{n-1}} \;-\; \frac{(n-2)a}{(n-1)b}\int \frac{dx}{x^{n-2}\,\sqrt{ax^2+b}}\,,$$

$$n > 1.$$

57. $\displaystyle\int (ax^2+b)^{3/2}\,dx = \frac{x}{8}\,(2ax^2+5b)\,\sqrt{ax^2+b}$

$$+\;\frac{3b^2}{8\sqrt{a}}\,\log\,(x\sqrt{a} + \sqrt{ax^2+b}),\quad a > 0.$$

$$=\;\frac{x}{8}\,(2ax^2+5b)\,\sqrt{ax^2+b}$$

$$+\;\frac{3b^2}{8\sqrt{-a}}\,\sin^{-1}\,(x\,\sqrt{\tfrac{-a}{b}}),\quad a < 0\,.$$

58. $\displaystyle\int (ax^2+b)^{3/2}\,x^n dx \;=\; \frac{x^{n+1}(ax^2+b)^{3/2}}{n+4} \;+$

$$\frac{3b}{n+4}\int x^n\,\sqrt{ax^2+b}\,dx.$$

59. $\displaystyle\int \frac{dx}{(ax^2+b)^{3/2}} \;=\; \frac{x}{c\sqrt{ax^2+b}}\,.$

60. $\displaystyle\int \frac{dx}{(ax^n+b)^m} \;=\; \frac{1}{b}\,\frac{dx}{(ax^n+c)^{m-1}} \;-\; \frac{a}{b}\int \frac{x^n\,dx}{(ax^n+b)^m}\,.$

61. $\displaystyle\int \frac{dx}{x\sqrt{ax^n+b}} \;=\; \frac{1}{n\sqrt{c}}\,\log\,\frac{\sqrt{ax^n+b}-\sqrt{c}}{\sqrt{ax^n+b}+\sqrt{c}}\,,\quad b < 0\,,$

$$= \frac{2}{n\sqrt{-b}} \sec^{-1} \frac{\sqrt{-ax^n}}{b} , \quad b < 0 .$$

62. $$\int x^{m-1}(ax^n+b)^p dx = \frac{1}{mb} [x^m(ax^n+b)^{p+1}$$

$$- (m+np+n) \int x^{m+n-1}(ax^n+b)^p dx].$$

63. $$\int \frac{x^m dx}{(ax^n+b)^p} = \frac{1}{a} \frac{x^{m-n} dx}{(ax^n+b)^{p-1}} - \frac{b}{a} \int \frac{x^{m-n} dx}{(ax^n+b)^p} .$$

64. $$\int \frac{dx}{x^m(ax^n+b)^p} = \frac{1}{b} \int \frac{dx}{x^m(ax^n+b)^{p-1}} - \frac{a}{b} \int \frac{dx}{x^{m-n}(ax^n+b)^p} .$$

65. $$\int \frac{dx}{ax^2+bx+c} = \frac{1}{\sqrt{b^2-4ac}} \log \frac{2ax+b - \sqrt{b^2-4ac}}{2ax+b + \sqrt{b^2-4ac}} , \quad b^2 > 4ac .$$

66. $$\int \frac{dx}{ax^2+bx+c} = \frac{2}{\sqrt{4ac-b^2}} \tan^{-1} \frac{2ax+b}{\sqrt{4ac-b^2}} , \quad b^2 < 4ac ;$$

$$= - \frac{2}{2ax+b} , \quad b^2 = 4ac$$

67. $$\int \frac{dx}{(ax^2+bx+c)^{n+1}} = \frac{2ax+b}{n(4ac-b^2)(ax^2+bx+c)^n}$$

$$+ \frac{2(2n-1)a}{n(4ac-b^2)} \int \frac{dx}{(ax^2+bx+c)^n} .$$

68. $$\int \frac{x^n dx}{ax^2+bx+c} = \frac{x^{n-1}}{(n-1)a} - \frac{c}{a} \int \frac{x^{n-2} dx}{ax^2+bx+c} - \frac{b}{a} \int \frac{x^{n-1} dx}{ax^2+bx+c} .$$

69. $\displaystyle\int \frac{x^m dx}{(ax^2+bx+c)^{n+1}} = - \frac{x^{m-1}}{a(2n-m+1)(ax^2+bx+c)^n}$

$\displaystyle - \frac{(n-m+1)}{(2n-m+1)} \cdot \frac{b}{a} \int \frac{x^{m-1}dx}{(ax^2+bx+c)^{n+1}} - \frac{(m-1)}{(2n-m+1)} \cdot \frac{c}{a} \int \frac{x^{m-2}dx}{(ax^2+bx+c)^{n+1}}$

70. $\displaystyle\int \frac{dx}{x^m(ax^2+bx+c)^{n+1}} = - \frac{1}{(m-1)c\ x^{m-1}(ax^2+bx+c)^n}$

$\displaystyle - \frac{(n+m-1)}{m-1} \cdot \frac{b}{c} \int \frac{dx}{x^{m-1}(ax^2+bx+c)^{n+1}}$

$\displaystyle - \frac{(2n+m-1)}{m-1} \cdot \frac{a}{c} \int \frac{dx}{x^{m-2}(ax^2+bx+c)^{n+1}} \quad .$

71. $\displaystyle\int \frac{dx}{\sqrt{ax^2+bx+c}} = \frac{1}{\sqrt{a}} \log\,(2ax+b+2\sqrt{a(ax^2+bx+c)}),\quad a > 0.$

$\displaystyle = \frac{1}{\sqrt{-a}}\ \sin^{-1} \frac{-2ax-b}{\sqrt{b^2-4ac}}\ ,\quad a < 0.$

72. $\displaystyle\int \frac{x^n\ dx}{\sqrt{ax^2+bx+c}} = \frac{x^{n-1}}{an}\ \sqrt{ax^2+bx+c}\quad .$

$\displaystyle - \frac{b(2n-1)}{2an} \int \frac{x^{n-1}dx}{\sqrt{ax^2+bx+c}} - \frac{c(n-1)}{an} \int \frac{x^{n-2}\ dx}{\sqrt{ax^2+bx+c}}\quad .$

73. $\displaystyle\int \sqrt{ax^2+bx+c}\quad dx = \frac{2ax+b}{4a} \sqrt{ax^2+bx+c} + \frac{4ac-b^2}{8a} \int \frac{dx}{\sqrt{ax^2+bx+c}}\,.$

74. $\displaystyle\int \frac{dx}{x^n\ \sqrt{ax^2+bx+c}} = - \frac{\sqrt{ax^2+bx+c}}{c(n-1)x^{n-1}}$

$\displaystyle + \frac{b(3-2n)}{2c(n-1)} \int \frac{dx}{x^{n-1}\sqrt{ax^2+bx+c}} + \frac{a(2-n)}{c(n-1)} \int \frac{dx}{x^{n-2}\sqrt{ax^2+bx+c}}\quad .$

75. $\displaystyle\int \frac{dx}{x\sqrt{ax^2+bx+c}} = -\frac{1}{\sqrt{c}}\log\left(\frac{\sqrt{ax^2+bx+c}+\sqrt{c}}{x} + \frac{b}{2\sqrt{c}}\right),\ c > 0,$

$\displaystyle = \frac{1}{\sqrt{-c}}\sin^{-1}\frac{bx+2c}{x\sqrt{b^2-4ac}},\ c < 0.$

76. $\displaystyle\int \frac{dx}{(ax^2+bx+c)^{3/2}} = -\frac{2(2ax+b)}{(b^2-4ac)\sqrt{ax^2+bx+c}},\ b^2 \neq 4ac.$

$\displaystyle = -\frac{1}{2\sqrt{a^3}(x+b/2a)^2},\ b^2 = 4ac.$

77. $\displaystyle\int \sqrt{2px-x^2}\ dx = \frac{1}{2}\left[(x-p)\sqrt{2px-x^2} + p^2\sin^{-1}\left(\frac{x-p}{p}\right)\right].$

78. $\displaystyle\int \frac{dx}{\sqrt{2px-x^2}} = \cos^{-1}\left(\frac{p-x}{p}\right).$

79. $\displaystyle\int \frac{dx}{\sqrt{ax+b}\ \sqrt{cx+d}} = \frac{2}{\sqrt{-ac}}\tan^{-1}\sqrt{\frac{-c(ax+b)}{a(cx+d)}},$

$\displaystyle\text{Or}\ \frac{2}{\sqrt{ac}}\tanh^{-1}\sqrt{\frac{c(ax+b)}{a(cx+d)}}.$

80. $\displaystyle\int \sqrt{ax+b}\ \sqrt{cx+d}\ dx = \frac{(2acx+bc+ad)\sqrt{ax+b}\cdot\sqrt{cx+d}}{4ac}$

$\displaystyle + \frac{(ad-bc)^2}{8ac}\int \frac{dx}{\sqrt{ax+b}\ \sqrt{cx+d}}.$

81. $\displaystyle\int \sqrt{\frac{cx+d}{ax+b}}\,dx = \frac{\sqrt{ax+b}\ \sqrt{cx+d}}{a} + \frac{(ad-bc)}{2a}\int \frac{dx}{\sqrt{ax+b}\ \sqrt{cx+d}}.$

❋ Trigonometric Expressions

82. $\displaystyle\int \sin ax\ dx = -\frac{1}{a}\cos ax$.

83. $\displaystyle\int \sin^n ax\ dx = -\frac{\sin^{n-1}ax \cos ax}{na} + \frac{n-1}{n}\int \sin^{n-2}ax\ dx$,

                                          n positive integer .

84. $\displaystyle\int \frac{dx}{\sin ax} = \frac{1}{a}\log \tan \frac{ax}{2} = \frac{1}{a}\log (\csc ax - \text{ctn } ax)$.

85. $\displaystyle\int \frac{dx}{\sin^n ax} = -\frac{1}{a(n-1)}\ \frac{\cos ax}{\sin^{n-1}ax} + \frac{n-2}{n-1}\int \frac{dx}{\sin^{n-2}ax}$,

                                          n integer > 1.

86. $\displaystyle\int \frac{dx}{1\pm \sin ax} = \mp \frac{1}{a}\tan \left(\frac{\pi}{4} \mp \frac{ax}{2} \right)$.

87. $\displaystyle\int \frac{dx}{b+c\ \sin ax} = -\frac{2}{a\sqrt{b^2-c^2}}\tan^{-1}\left[\sqrt{\frac{b-c}{b+c}}\tan \left(\frac{\pi}{4} - \frac{ax}{2}\right) \right]$,

                                          $b^2 > c^2$

88. $\displaystyle\int \frac{dx}{b+c\ \sin ax} = -\frac{1}{a\sqrt{c^2-b^2}}\log \frac{c+b\ \sin ax + \sqrt{c^2-b^2}\ \cos ax}{b+c\ \sin ax}$,

                                          $c^2 > b^2$.

89. $\displaystyle\int \sin ax\ \sin bx = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)}$, $a^2 \neq b^2$.

90. $\displaystyle\int \sqrt{1+\sin x}\ dx = \pm 2\left(\sin \frac{x}{2} - \cos \frac{x}{2}\right)$;

    Use + sign when $(8k-1)\frac{\pi}{2} < x \leqslant (8k+3)\frac{\pi}{2}$

    Otherwise − sign, k an integer.

91. $\displaystyle\int \sqrt{1-\sin x}\ dx = \pm 2\left(\sin \frac{x}{2} + \cos \frac{x}{2}\right)$,

Use + sign when $(8k - 3) \frac{\pi}{2} < x \leqslant (8k+1) \frac{\pi}{2}$,

Otherwise − sign, k an integer.

92. $\int \cos ax \, dx = \frac{1}{a} \sin ax$

93. $\int \cos^n ax \, dx = \frac{\cos^{n-1} ax \sin ax}{na} + \frac{n-1}{n} \int \cos^{n-2} ax \, dx$,

$\qquad\qquad\qquad\qquad\qquad$ n positive integer .

94. $\int \frac{dx}{\cos ax} = \frac{1}{a} \log \tan (\frac{ax}{2} + \frac{\pi}{4}) = \frac{1}{a} \log (\tan ax + \sec ax)$.

95. $\int \frac{dx}{\cos^n ax} = \frac{1}{a(n-1)} \frac{\sin ax}{\cos^{n-1} ax} + \frac{n-2}{n-1} \int \frac{dx}{\cos^{n-2} ax}$.

$\qquad\qquad\qquad\qquad\qquad$ n integer > 1.

96. $\int \frac{dx}{1+\cos ax} = \frac{1}{a} \tan \frac{ax}{2}$.

97. $\int \frac{dx}{1-\cos ax} = -\frac{1}{a} \operatorname{ctn} \frac{ax}{2}$.

98. $\int \frac{dx}{b+c \cos ax} = \frac{1}{a\sqrt{b^2-c^2}} \tan^{-1} \left(\frac{\sqrt{b^2-c^2} \sin ax}{c+b \cos ax} \right), b^2 > c^2$.

99. $\int \frac{dx}{b+c \cos x} = \frac{1}{a\sqrt{c^2-b^2}} \tanh^{-1} [\frac{\sqrt{c^2-b^2} \sin ax}{c+b \cos ax}], c^2 > b^2$.

100. $\int \cos ax \cos bx = \frac{\sin(a-b)x}{2(a-b)} + \frac{\sin(a+b)x}{2(a+b)}$, $a^2 \neq b^2$.

101. $\int \sqrt{1+\cos x} \, dx = \pm 2\sqrt{2} \sin \frac{x}{2}$.

$\qquad\qquad$ Use + sign when $(4k-1)\pi < x \leqslant (4k+1)\pi$,

$\qquad\qquad$ Otherwise − sign, k an integer.

102. $\int \sqrt{1-\cos x} \, dx = \mp 2\sqrt{2} \cos \frac{x}{2}$.

$\qquad\qquad$ Use − sign when $4\pi k < x \leqslant (4k+2)\pi$,
Otherwise + sign.

103. $\int \dfrac{\cos ax\ dx}{b+c\ \sin ax} = \dfrac{1}{ac}\ \log\ (b+c\ \sin ax).$

104. $\int \dfrac{\sin ax\ dx}{b+c\ \cos ax} = -\ \dfrac{1}{ac}\ \log\ (b+c\ \cos ax).$

105. $\int \dfrac{dx}{b\ \sin ax + c\ \cos ax} = \dfrac{1}{a\sqrt{b^2+c^2}}\ [\ \log\tan\tfrac{1}{2}\ (ax+\tan^{-1}\tfrac{c}{b})\ ].$

106. $\int \dfrac{dx}{b+c\ \cos ax + d\ \sin ax} = \dfrac{-1}{a\sqrt{b^2-c^2-d^2}}\ \sin^{-1} U$

$U = [\ \dfrac{c^2+d^2+b(c\ \cos ax + a\ \sin ax)}{\sqrt{c^2+d^2}\ (b+c\ \cos ax + d\ \sin ax)}\ ]\ ,\ b^2 \neq c^2+d^2,$

$-\pi < ax < \pi$

107. $\int \dfrac{dx}{b+c\ \cos ax + d\ \sin ax} = \dfrac{1}{ab}\ [\ \dfrac{b-(c+d)\cos ax + (c-d)\sin ax}{b+(c-d)\cos ax + (c+d)\sin ax}\ ],$

$b^2 = c^2+d^2$

108. $\int \dfrac{\sin^2 ax\ dx}{b+c\ \cos^2 ax} = \dfrac{1}{ac}\ \tan^{-1} (\sqrt{\dfrac{b}{b+c}}\ \tan ax) - \dfrac{x}{c}\ .$

109. $\int \dfrac{\sin ax\ \cos ax\ dx}{b\ \cos^2 ax + c\ \sin^2 ax} = \dfrac{1}{2a(c-b)}\ \log\ (b\ \cos^2 ax + c\ \sin^2 ax).$

110. $\int \dfrac{dx}{b^2\ \cos^2 ax - c^2 \sin^2 ax} = \dfrac{1}{2abc}\ \log\ \dfrac{b\ \cos ax + c\ \sin ax}{b\ \cos ax - c\ \sin ax}\ .$

111. $\int \dfrac{dx}{b^2\ \cos^2 ax + c^2\ \sin^2 ax} = \dfrac{1}{abc}\ \tan^{-1} (\dfrac{c\tan ax}{b}).$

112. $\int \sin^m ax\ \cos^n ax\ dx = -\ \dfrac{\sin^{m-1} ax\ \cos^{n+1} ax}{a(m+n)}$

$+\ \dfrac{m-1}{m+n}\ \int \sin^{m-2} ax\ \cos^n ax\ dx,\ m,\ n > 0.$

$=\ \dfrac{\sin^{m+1} ax\ \cos^n ax}{a(m+n)} + \dfrac{n-1}{m+n} \int \sin^m ax\ \cos^{n-2} ax\ dx,$

$m,\ n > 0.$

113. $\int \dfrac{\sin^m ax}{\cos^n ax}\ dx = \dfrac{\sin^{m+1} ax}{a(n-1)\cos^{n-1} ax} - \dfrac{m-n+2}{(n-1)} \int \dfrac{\sin^m ax}{\cos^{n-2} ax}\ dx,$

$m,\ n > 0,\ n \neq 1.$

114. $\int \dfrac{\cos^n ax}{\sin^m ax}\, dx \;=\; -\;\dfrac{\cos^{n+1}ax}{a(m-1)\sin^{m-1}ax} + \dfrac{m-n-2}{(m-1)}\int \dfrac{\cos^n ax}{\sin^{m-2}ax}\, dx\;,$

$$m,n,>0;\quad m\neq 1.$$

115. $\int \dfrac{dx}{\sin^m ax\,\cos^n ax} \;=\; \dfrac{1}{a(n-1)\sin^{m-1}ax\,\cos^{n-1}ax}$

$$+\;\dfrac{m+n-2}{n-1}\int\dfrac{dx}{\sin^m ax\,\cos^{n-2}ax}\;.$$

$$=\;-\;\dfrac{1}{a(m-1)\sin^{m-1}ax\,\cos^{n-1}ax} + \dfrac{m+n-2}{m-1}\int\dfrac{dx}{\sin^{m-2}ax\,\cos^n ax}\;\cdot$$

116. $\int \tan ax\, dx = -\dfrac{1}{a}\log\cos ax$

117. $\int \tan^n ax\, dx = \dfrac{1}{a(n-1)}\tan^{n-1}ax - \int\tan^{n-2}ax\, dx,$

$$n \text{ integer} > 1.$$

118. $\int \operatorname{ctn} x\, dx = \log\sin x$

119. $\int \operatorname{ctn}^n ax\, dx = -\dfrac{1}{a(n-1)}\operatorname{ctn}^{n-1}ax - \int\operatorname{ctn}^{n-2}ax\, dx,$

$$n \text{ integer} > 1.$$

120. $\int \dfrac{dx}{b+c\,\tan ax} = \dfrac{1}{b^2+c^2}\left[\,bx+\dfrac{c}{a}\log\,(b\cos ax+ c\sin ax)\right].$

121. $\int \dfrac{dx}{b+c\,\operatorname{ctn} ax} = \dfrac{1}{b^2+c^2}\left[\,bx-\dfrac{c}{a}\log\,(b\sin ax +c\cos ax)\right].$

122. $\int \dfrac{dx}{\sqrt{b+c\,\tan^2 ax}} = \dfrac{1}{a\sqrt{b-c}}\;\sin^{-1}\left(\sqrt{\dfrac{b-c}{b}}\,\sin ax\right),$ b positive,

$$b^2 > c^2\;.$$

123. $\int \sec ax\, dx = \dfrac{1}{a}\log\tan\left(\dfrac{ax}{2}+\dfrac{\pi}{4}\right).$

124. $\int \sec^n ax\, dx = \dfrac{1}{a(n-1)}\dfrac{\sin ax}{\cos^{n-1}ax}+\dfrac{n-2}{n-1}\int\sec^{n-2}ax\, dx,$

$$n \text{ integer} > 1.$$

125. $\int \csc ax\, dx = \dfrac{1}{a}\log\tan\dfrac{ax}{2}\;.$

126. $\int \csc^n ax\, dx = -\dfrac{1}{a(n-1)}\dfrac{\cos ax}{\sin^{n-1}ax}+\dfrac{n-2}{n-1}\int\csc^{n-2}ax\, dx,$

$$n \text{ integer} > 1.$$

127. $\int \tan ax \ \sec ax \ dx = \frac{1}{a} \sec ax.$

128. $\int \operatorname{ctn} u \ \csc u \ du \ = \ - \csc u,$ where it is any function of x.

129. $\int \frac{\csc^2 ax \ dx}{\operatorname{ctn} ax} = \ - \frac{1}{a} \log \operatorname{ctn} ax.$

130. $\int x^n \sin ax \ dx = - \frac{1}{a} x^n \cos ax + \frac{n}{a} \int x^{n-1} \cos ax \ dx.$

131. $\int \frac{\sin ax}{x} \ dx \ = \ ax - \frac{(ax)^3}{3 \cdot 3!} + \frac{(ax)^5}{5 \cdot 5!} - \ \ldots$

132. $\int \frac{\sin ax}{x^m} \ dx \ = - \frac{1}{(m-1)} \ \frac{\sin ax}{x^{m-1}} + \frac{a}{(m-1)} \int \frac{\cos ax}{x^{m-1}} \ dx.$

133. $\int x^n \cos ax \ dx = \frac{1}{a} x^n \sin ax - \frac{n}{a} \int x^{n-1} \sin ax \ dx,$

   n positive .

134. $\int \frac{\cos ax}{x} \ dx \ = \ \log ax - \frac{(ax)^2}{2 \cdot 2!} + \frac{(ax)^4}{4 \cdot 4!} - \ldots$

135. $\int \frac{\cos ax}{x^m} \ dx \ = \ - \frac{1}{(m-1)} \ \frac{\cos ax}{x^{m-1}} - \frac{a}{(m-1)} \int \frac{\sin ax}{x^{m-1}} \ dx.$

＊ Exponential and Logarithmic Expressions

136. $\int e^{ax} \ dx \ = \ \frac{1}{a} e^{ax} \ .$

137. $\int b^{ax} \ dx = \frac{b^{ax}}{a \log b} \ .$

138. $\int x^n e^{ax} \ dx = \frac{1}{a} \ x^n \ e^{ax} - \frac{n}{a} \int x^{n-1} e^{ax} \ dx,$ n positive.

139. $\int \frac{dx}{b+c \ e^{ax}} = \frac{1}{ab} \left[ax - \log (b + c \ e^{ax}) \right].$

140. $\int \frac{dx}{b \ e^{ax} + c \ e^{-ax}} = \frac{1}{a\sqrt{bc}} \tan^{-1} \left(e^{ax} \sqrt{\frac{b}{c}} \right),$ b and c positive.

141. $\int e^{ax} \sin bx \; dx = \dfrac{a^{ax}}{a^2+b^2} \; (a \sin bx - b \cos bx).$

142. $\int e^{ax} \cos bx \; dx = \dfrac{e^{ax}}{a^2+b^2} \; (a \cos bx + b \sin bx).$

143. $\int x \, e^{ax} \sin bx \; dx = \dfrac{d}{da} \int e^{ax} \sin bx \; dx$

$$= \dfrac{xe^{ax}}{a^2+b^2} \; (a \sin bx - b \cos bx) - \dfrac{e^{ax}}{(a^2+b^2)^2}[(a^2-b^2)\sin bx$$

$$- 2ab \cos bx].$$

144. $\int e^{ax} \sin^n bx \; dx = \dfrac{e^{ax} \sin^{n-1} bx(a \sin bx - nb \cos bx)}{a^2 + n^2 b^2}$

$$+ \dfrac{n(n-1)b^2}{a^2+n^2b^2} \int e^{ax} \sin^{n-2} bx \; dx.$$

145. $\int \log ax \; dx = x \log ax - x.$

146. $\int x^n \log ax \; dx = x^{n+1} \left[\dfrac{\log ax}{n + 1} - \dfrac{1}{(n+1)^2}\right], \; n \neq -1 \; .$

147. $\int (\log ax)^n \; dx = x \, (\log ax)^n - n \int (\log ax)^{n-1} \, dx, \; n \text{ pos.}$

148. $\int x^n \, (\log ax)^m \; dx = \dfrac{x^{n+1}}{n+1} \; (\log ax)^m - \dfrac{m}{n+1} \int x^n (\log ax)^{m-1} dx$

149. $\int \dfrac{dx}{x \, \log x} = \log (\log ax).$

150. $\int \dfrac{dx}{x(\log ax)^n} = - \dfrac{1}{(n-1)(\log ax)^{n-1}}$

151. $\int \dfrac{x^n \, dx}{(\log ax)^m} = \dfrac{-x^{n+1}}{(m-1)(\log ax)^{m-1}} + \dfrac{n+1}{m-1} \int \dfrac{x^n dx}{(\log ax)^{m-1}}, m \neq 1.$

152. $\int \dfrac{x^n dx}{\log ax} = \dfrac{1}{a^{n+1}} \int \dfrac{e^y dy}{y}$, $\quad y = (n+1) \log ax$ $\quad$.

153. $\int \dfrac{x^n dx}{\log ax} = \dfrac{1}{a^{n+1}} [\log |\log ax| + (n+1) \log ax$

$\qquad + \dfrac{(n+1)^2 (\log ax)^2}{2.2 !} + \dfrac{(n+1)^3 (\log ax)^3}{3.3 !} + ..].$

154. $\int \dfrac{dx}{\log ax} = \dfrac{1}{a} [\log |\log ax| + \log ax + \dfrac{(\log ax)^2}{2.2!} + ..].$

155. $\int \sin (\log ax) \, dx = \dfrac{x}{2} [\sin (\log ax) - \cos(\log ax)].$

156. $\int \cos (\log ax) \, dx = \dfrac{x}{2} [\sin (\log ax) + \cos(\log ax)].$

157. $\int e^{ax} \log bx \, dx = \dfrac{1}{a} e^{ax} \log bx - \dfrac{1}{a} \int \dfrac{e^{ax}}{x} \, dx$.

✳ Inverse Trigonometric Functions

158. $\int \sin^{-1} ax \, dx = x (\sin^{-1} ax) + \dfrac{1}{a} \sqrt{1-a^2 x^2}$.

159. $\int x^n \sin^{-1} ax \, dx = \dfrac{x^{n+1}}{n+1} \sin^{-1} ax - \dfrac{a}{n+1} \int \dfrac{x^{n+1} dx}{\sqrt{1-a^2 x^2}}$,

$\qquad\qquad n \neq -1.$

160. $\int \dfrac{\sin^{-1} ax}{x} \, dx = ax + \dfrac{(ax)^3}{2.3.3} + \dfrac{1.3}{2.4.5.5} (ax)^5$

$\qquad\qquad + \dfrac{1.3.5}{2.4.6.7.7} (ax)^7 + .. ; \ a^2 x^2 < 1.$

161. $\int \dfrac{\sin^{-1} ax}{x^2} \, dx = \dfrac{1}{x} \sin^{-1} ax - a \log \left| \dfrac{1+ \sqrt{1-a^2 x^2}}{ax} \right|$

162. $\int \cos^{-1} ax \, dx = x \cos^{-1} ax - \dfrac{1}{a} \sqrt{1-a^2 x^2}$

163. $\int x^n \cos^{-1} ax \, dx = \dfrac{x^{n+1}}{n+1} \cos^{-1} ax + \dfrac{a}{n+1} \int \dfrac{x^{n+1} dx}{\sqrt{1-a^2 x^2}}$,

$\qquad\qquad n \neq -1$.

164. $\int \dfrac{\cos^{-1}ax}{x}\,dx = \dfrac{\pi}{2}\log\left|ax\right| - ax - \dfrac{1}{2.3.3}(ax)^3$

$$- \dfrac{1.3}{2.4.5.5}(ax)^5 - \dfrac{1.3.5}{2.4.6.7.7}(ax)^7 - \dots$$

$$a^2x^2 < 1.$$

165. $\int \dfrac{\cos^{-1}ax}{x^2}\,dx = -\dfrac{1}{x}\cos^{-1}ax + a\log\left|\dfrac{1+\sqrt{1-a^2x^2}}{ax}\right|.$

166. $\int \tan^{-1}ax\,dx = x\tan^{-1}ax - \dfrac{1}{2a}\log(1+a^2x^2).$

167. $\int x^n\,\tan^{-1}ax\,dx = \dfrac{x^{n+1}}{n+1}\tan^{-1}ax - \dfrac{a}{n+1}\int\dfrac{x^{n+1}dx}{1+a^2x^2}$, $n \neq -1.$

168. $\int \dfrac{\tan^{-1}ax\,dx}{x^2} = \dfrac{1}{x}\tan^{-1}ax - \dfrac{a}{2}\log\left(\dfrac{1+a^2x^2}{a^2x^2}\right).$

169. $\int \operatorname{ctn}^{-1}ax\,dx = x\operatorname{ctn}^{-1}ax + \dfrac{1}{2a}\log(1+a^2x^2).$

170. $\int x^n\operatorname{ctn}^{-1}ax\,dx = \dfrac{x^{n+1}}{n+1}\operatorname{ctn}^{-1}ax + \dfrac{a}{n+1}\dfrac{x^{n+1}dx}{1+a^2x^2}$, $n \neq -1.$

171. $\int \dfrac{\operatorname{ctn}^{-1}ax}{x^2}\,dx = -\dfrac{1}{x}\operatorname{ctn}^{-1}ax + \dfrac{a}{2}\log\left(\dfrac{1+a^2x^2}{a^2x^2}\right).$

172. $\int \sec^{-1}ax\,dx = x\sec^{-1}ax - \dfrac{1}{a}\log(ax+\sqrt{a^2x^2-1}).$

173. $\int x^n\sec^{-1}ax\,dx = \dfrac{x^{n+1}}{n+1}\sec^{-1}ax \pm \dfrac{1}{n+1}\int\dfrac{x^n dx}{\sqrt{a^2x^2-1}}$, $n \neq -1.$

Use + sign when $\dfrac{\pi}{2} < \sec^{-1}ax < \pi$,

    − sign when $0 < \sec^{-1}ax < \dfrac{\pi}{2}$.

174. $\int \csc^{-1}ax\,dx = x\csc^{-1}ax + \dfrac{1}{a}\log(ax + \sqrt{a^2x^2-1}).$

175. $\int x^n\csc^{-1}ax\,dx = \dfrac{x^{n+1}}{n+1}\csc^{-1}ax \pm \dfrac{1}{n+1}\int\dfrac{x^n dx}{\sqrt{a^2x^2-1}}$, $n \neq -1.$

Use + sign when $0 < \csc^{-1}ax < \dfrac{\pi}{2}$,

    − sign when $\dfrac{-\pi}{2} < \csc^{-1}ax < 0.$

(iii) <u>Definite Integrals</u>

176. $\int_0^\infty \dfrac{a\ dx}{a^2+x^2} = \dfrac{\pi}{2}$, if $a > 0$,

$= 0$, if $a = 0$,

$= -\dfrac{\pi}{2}$, if $a < 0$.

177. $\int_0^\infty x^{n-1}\ e^{-x}\ dx = \quad [\ \log_e(1/x)]^{n-1}\ dx = \Gamma(n).$

$\Gamma(n+1) = n.\,\Gamma(n)$, if $n > 0$. $\Gamma(2) = \Gamma(1) = 1$

$\Gamma(\tfrac{1}{2}) = \sqrt{\pi}$

$\Gamma(n+1) = n!$, if n is an integer.

$\Gamma(n) = \pi(n-1)$.

$Z(1) = -\ 0.5772157 \dots$ $Z(Y) = D_y\ [Log_e\ \Gamma(y)].$

178. $\int_0^\infty e^{-zx}\,.\,z^n.\,x^{n-1}\ dx = \Gamma(n)$, $z > 0$.

179. $\int_0^1 x^{m-1}\ (1-x)^{n-1}dx = \int_0^\infty \dfrac{x^{m-1}dx}{(1+x)^{m+n}} = \dfrac{\Gamma(m)\Gamma(n)}{\Gamma(m+n)}$.

180. $\int_0^\infty \dfrac{x^{n-1}}{1+x}dx = \dfrac{\pi}{\sin n\pi}$, $0 < n < 1$.

181. $\int_0^{\pi/2} \sin^n x\ dx = \int_0^{\pi/2} \cos^n x\ dx = \dfrac{1}{2}\ \sqrt{\pi}\ \dfrac{\Gamma(\tfrac{n}{2}+\tfrac{1}{2})}{\Gamma(\tfrac{n}{2}+1)}$, If $n > -1$.

$= \dfrac{1.3.5\ ..(n-1)}{2.4.6\ ..(n)}\,.\,\dfrac{\pi}{2}$, if n is even integer

$= \dfrac{2.4.6\ ..(n-1)}{1.3.5.7..\ n}$, if n is odd integer.

182. $\int_0^\infty \dfrac{\sin^2 x}{x^2}\ dx = \dfrac{\pi}{2}$.

183. $\int_0^\infty \dfrac{\sin\ ax}{x}\ dx = \dfrac{\pi}{2}$, if $a > 0$.

184. $\displaystyle\int_0^\infty \frac{\sin x \cos ax}{x}\,dx$ $= 0$, if $a < -1$, Or $a > 1$;

$= \frac{\pi}{4}$, if $a = -1$, Or $a = 1$;

$= \frac{\pi}{2}$, if $-1 < a < 1$.

185. $\displaystyle\int_0^\pi \sin^2 ax\,dx = \int_0^\pi \cos^2 ax\,dx = \frac{\pi}{2}$.

186. $\displaystyle\int_0^{\pi/a} \sin ax \cdot \cos ax\,dx = \int_0^\pi \sin ax \cos ax\,dx = 0$.

187. $\displaystyle\int_0^\pi \sin ax \cdot \sin bx\,dx = \int_0^\pi \cos ax \cdot \cos bx\,dx = 0$, $a \neq b$.

188. $\displaystyle\int_0^\pi \sin ax \cdot \cos bx\,dx = \frac{2a}{a^2 - b^2}$, if $a-b$ is odd,

$= 0$, if $a-b$ is even.

189. $\displaystyle\int_0^\infty \frac{\sin ax \sin bx}{x^2}\,dx = \frac{1}{2}\,\pi a$, if $a < b$.

190. $\displaystyle\int_0^\infty \cos(x^2)\,dx = \int_0^\infty \sin(x^2)\,dx = \frac{1}{2}\sqrt{\frac{\pi}{2}}$.

191. $\displaystyle\int_0^\infty e^{-a^2 x^2}\,dx = \frac{\sqrt{\pi}}{2a} = \frac{1}{2a}\,\Gamma(\tfrac{1}{2})$, if $a > 0$.

192. $\displaystyle\int_0^\infty x^n \cdot e^{-ax}\,dx = \frac{\Gamma(n+1)}{a^{n+1}}$, $= \frac{n!}{a^{n+1}}$, if n is a positive integer, $a > 0$.

193. $\displaystyle\int_0^\infty x^{2n}\, e^{-ax^2}\,dx = \frac{1.3.5 \ldots (2n-1)}{2^{n+1}\,a^n}\sqrt{\frac{\pi}{a}}$.

194. $\displaystyle\int_0^\infty \sqrt{x}\, e^{-ax}\,dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$.

195. $\displaystyle\int_0^\infty \frac{e^{-ax}}{\sqrt{x}}\,dx = \sqrt{\frac{\pi}{a}}$.

196. $\displaystyle\int_0^\infty e^{(-x^2 - a^2/x^2)}\,dx = \frac{1}{2}\,e^{-2a}\sqrt{\pi}$, if $a > 0$.

197. $\displaystyle\int_0^\infty e^{-ax} \cos bx\,dx = \frac{a}{a^2 + b^2}$, if $a > 0$.

198. $\displaystyle\int_0^\infty e^{-ax} \sin bx \, dx = \frac{b}{a^2+b^2}$, if $a > 0$.

199. $\displaystyle\int_0^\infty \frac{e^{-ax} \sin x}{x} \, dx = \text{ctn}^{-1} a, \quad a > 0$.

200. $\displaystyle\int_0^\infty e^{-a^2 x^2} \cos bx \, dx = \frac{\sqrt{\pi}. \, e^{-b^2/4a^2}}{2a}$, if $a > 0$.

201. $\displaystyle\int_0^1 (\log x)^n \, dx = (-1)^n . n!$, n positive integer.

202. $\displaystyle\int_0^1 \frac{\log x}{1-x} \, dx = -\frac{\pi^2}{6}$.

203. $\displaystyle\int_0^1 \frac{\log x}{1+x} \, dx = -\frac{\pi^2}{12}$.

204. $\displaystyle\int_0^1 \frac{\log x}{1-x^2} \, dx = -\frac{\pi^2}{8}$.

205. $\displaystyle\int_0^1 \frac{\log x}{\sqrt{1-x^2}} \, dx = -\frac{\pi}{2} \log 2$.

206. $\displaystyle\int_0^1 \log\left(\frac{1+x}{1-x}\right) \frac{dx}{x} = \frac{\pi^2}{4}$.

207. $\displaystyle\int_0^1 \log\left(\frac{e^x+1}{e^x-1}\right) dx = \frac{\pi^2}{4}$.

208. $\displaystyle\int_0^1 \frac{dx}{\sqrt{\log(1/x)}} = \sqrt{\pi}$.

209. $\displaystyle\int_0^1 \log |\log x| \, dx = \int_0^\infty e^{-x} \log x \, dx = -\gamma = -0.5772157..$

210. $\displaystyle\int_0^{\pi/2} \log \sin x \, dx = \int_0^{\pi/2} \log \cos x \, dx = -\frac{\pi}{2} \log_e 2$.

211. $\displaystyle\int_0^\pi x \log \sin x \, dx = -\frac{\pi^2}{2} \log_e 2$.

212. $\displaystyle\int_0^1 \left(\log \frac{1}{x}\right)^{\frac{1}{2}} dx = \frac{\sqrt{\pi}}{2}$.

213. $\displaystyle\int_0^1 \left(\log \frac{1}{x}\right)^{-\frac{1}{2}} dx = \sqrt{\pi}$.

214. $\displaystyle\int_0^1 x^m \log\left(\frac{1}{x}\right)^n dx = \frac{\Gamma(n+1)}{(m+1)^{m+1}}$, if $m+1 > 0$, $n+1 > 0$.

215. $\int_0^\pi \log (a\pm b \cos x) \, dx = \pi \log (\frac{a+\sqrt{a^2-b^2}}{2}), \, a \gg b.$

216. $\int_0^\pi \frac{\log (1+\sin a \cos x)}{\cos x} \, dx = \pi a.$

217. $\int_0^1 \frac{x^b-x^a}{\log x} \, dx = \log \frac{1+b}{1+a}.$

218. $\int_0^\pi \frac{dx}{a+b \cos x} = \frac{\pi}{\sqrt{a^2-b^2}}, \, \text{if } a > b > 0.$

219. $\int_0^{\pi/2} \frac{dx}{a+b \cos x} = \frac{\cos^{-1}(\frac{b}{a})}{\sqrt{a^2-b^2}}, \, a > b.$

220. $\int_0^\infty \frac{\cos ax \, dx}{1+x^2} = \frac{\pi}{2} e^{-a}, \, \text{if } a > 0;$

$= \frac{\pi}{2} e^a, \, \text{if } a < 0.$

221. $\int_0^\infty \frac{\cos x \, dx}{\sqrt{x}} = \frac{\sin x \, dx}{\sqrt{x}} = \sqrt{\frac{\pi}{2}}.$

222. $\int_0^\infty \frac{e^{-ax}- e^{-bx}}{x} \, dx = \log \frac{b}{a}.$

223. $\int_0^\infty \frac{\tan^{-1} ax - \tan^{-1} bx}{x} \, dx = \frac{\pi}{2} \log \frac{a}{b}.$

224. $\int_0^\infty \frac{\cos ax - \cos bx}{x} \, dx = \log \frac{b}{a}.$

225. $\int_0^{\pi/2} \frac{dx}{a^2 \cos^2 x+b^2 \sin^2 x} = \frac{\pi}{2ab}.$

226. $\int_0^{\pi/2} \frac{dx}{(a^2 \cos^2 x +b^2 \sin^2 x)^2} = \frac{\pi(a^2+b^2)}{4a^3 b^3}.$

227. $\int_0^\pi \frac{(a-b \cos x) \, dx}{a^2-2ab \cos x+b^2} = 0, \, \text{if } a^2 < b^2 \, ; \, = \frac{\pi}{a}, \, \text{if } a^2 > b^2 \, ;$

$= \frac{\pi}{2a}, \, \text{if } a = b.$

228. $\int_0^1 \dfrac{1+x^2}{1+x^4}\,dx = \dfrac{\pi}{4}\sqrt{2}\ .$

229. $\int_0^1 \dfrac{\log(1+x)}{x}\,dx = \dfrac{1}{1^2} - \dfrac{1}{2^2} + \dfrac{1}{3^2} - \dfrac{1}{4^2} + \ldots = \dfrac{\pi^2}{12}\ .$

230. $\int_{+\infty}^1 \dfrac{e^{-xu}}{u}\,du = \gamma + \log x - x + \dfrac{x^2}{2.2!} - \dfrac{x^3}{3.3!} + \dfrac{x^4}{4.4!} - \ldots$

where $\gamma = \text{Lim}\ (1 + \tfrac{1}{2} + \tfrac{1}{3} + \ldots + \tfrac{1}{t} - \log t)$

$= 0.5772157\ \ldots\ ,\ \ 0 < x < \infty.$

231. $\int_{+\infty}^1 \dfrac{\cos xu}{u}\,du = \gamma + \log x - \dfrac{x^2}{2.2!} + \dfrac{x^4}{4.4!} - \dfrac{x^6}{6.6!} + \ldots$

where $\gamma = 0.5772157\ \ldots\ ,\ 0 < x < \infty\ .$

232. $\int_0^1 \dfrac{e^{xu} - e^{-xu}}{u}\,du = 2\left(x + \dfrac{x^3}{3.3!} + \dfrac{x^5}{5.5!} + \ldots\right),\ \ 0 < x < \infty$

233. $\int_0^1 \dfrac{1-e^{-xu}}{u}\,du = x - \dfrac{x^2}{2.2!} + \dfrac{x^3}{3.3!} - \dfrac{x^4}{4.4!} + \ldots\ ,\ 0 < x < \infty\ .$

234. $\int_0^{\pi/2} \dfrac{dx}{\sqrt{1-k^2\sin^2 x}} = \dfrac{\pi}{2}\Big[1 + (\tfrac{1}{2})^2 k^2 + (\tfrac{1.3}{2.4})^2 k^4$

$+ \left(\tfrac{1.3.5}{2.4.6}\right)^2 k^6 + \ldots\Big],\ \text{if}\ k^2 < 1.$

255. $\int_0^{\pi/2} \sqrt{1-k^2\sin^2 x}\,dx = \dfrac{\pi}{2}\Big[1 - (\tfrac{1}{2})^2 k^2 - \left(\tfrac{1.3}{2.4}\right)^2 \dfrac{k^4}{3}$

$- \left(\tfrac{1.3.5}{2.4.6}\right)^2 \dfrac{k^6}{5} - \ldots\Big],\ \text{if}\ k^2 < 1.$

236. $\int_0^\infty e^{-ax}\cosh bx\,dx = \dfrac{a}{a^2-b^2}\ ,\ \ a > 0,\ \ a^2 \neq b^2\ .$

237. $\int_0^\infty e^{-ax}\sinh bx\,dx = \dfrac{b}{a^2-b^2},\ \ a > 0,\ \ a^2 \neq b^2.$

238. $\int_0^\infty x\,e^{-ax}\sin bx\,dx = \dfrac{2ab}{(a^2+b^2)^2}\ ,\ \ a > 0.$

239. $\displaystyle\int_0^\infty x\, e^{-ax} \cos bx\, dx = \frac{a^2 - b^2}{(a^2 + b^2)^2}$, $a > 0.$

240. $\displaystyle\int_0^\infty x^2\, e^{-ax} \sin bx\, dx = \frac{2b\,(3a^2 - b^2)}{(a^2 + b^2)^3}$, $a > 0.$

241. $\displaystyle\int_0^\infty x^2\, e^{-ax} \cos bx\, dx = \frac{2a(a^2 - 3b^2)}{(a^2 + b^2)^3}$, $a > 0.$

242. $\displaystyle\int_0^\infty x^3\, e^{-ax} \sin bx\, dx = \frac{24ab\,(a^2 - b^2)}{(a^2 + b^2)^4}$, $a > 0.$

243. $\displaystyle\int_0^\infty x^3\, e^{-ax} \cos bx\, dx = \frac{6(a^4 - 6a^2 b^2 + b^4)}{(a^2 + b^2)^4}$, $a > 0.$

244. $\displaystyle\int_0^\infty x^n\, e^{-ax} \sin bx\, dx = \frac{i.n!\,[(a-ib)^{n+1} - (a+ib)^{n+1}]}{2(a^2 + b^2)^{n+1}}$, $a > 0.$

245. $\displaystyle\int_0^\infty x^n\, e^{-ax} \cos bx\, dx = \frac{n!\,[(a-ib)^{n+1} + (a+ib)^{n+1}]}{2(a^2 + b^2)^{n+1}}$, $a > 0.$

246. $\displaystyle\int_0^\infty e^{-x} \log x\, dx = -\gamma = -0.5772157 \ldots .$

247. $\displaystyle\int_0^\infty \left(\frac{1}{1 - e^{-x}} - \frac{1}{x} \right) e^{-x}\, dx = \gamma = 0.5772157 \ldots .$

248. $\displaystyle\int_0^\infty \frac{1}{x} \left(\frac{1}{1 + x} - e^{-x} \right) dx = \gamma = 0.5772157 \ldots .$

249. $\displaystyle\int_0^1 \frac{(1 - e^{-x} - e^{-1/x})}{x}\, dx = \gamma = 0.5772157 \ldots .$

I.9 Miscellaneous Mathematical Tables

(i) Important Constants

N	Log N	N	Log N
π = 3.14159265	0.4971499	π^2 = 9.86960440	0.9942997
2π = 6.28318531	0.7981799	$\dfrac{1}{\pi^2}$ = 0.10132118	9.0057003–10
4π = 12.56637061	1.0992099	$\sqrt{\pi}$ = 1.77245385	0.2485749
$\dfrac{\pi}{2}$ = 1.57079633	0.1961199	$\dfrac{1}{\sqrt{\pi}}$ = 0.56418958	9.7514251–10
$\dfrac{\pi}{3}$ = 1.04719755	0.0200286	$\sqrt{\dfrac{3}{\pi}}$ = 0.97720502	9.9899857–10
$\dfrac{4\pi}{3}$ = 4.18879020	0.6220886	$\sqrt{\dfrac{4}{\pi}}$ = 1.12837917	0.0524551
$\dfrac{\pi}{4}$ = 0.78539816	9.8950899–10	$\sqrt[3]{\pi}$ = 1.46459189	0.1657166
$\dfrac{\pi}{6}$ = 0.52359878	9.7189986–10	$\dfrac{1}{\sqrt[3]{\pi}}$ = 0.68278406	9.8342834–10
$\dfrac{1}{\pi}$ = 0.31830989	9.5028501–10	$\sqrt[3]{\pi^2}$ = 2.14502940	0.3314332
$\dfrac{1}{2\pi}$ = 0.15915494	9.2018201–10	$\sqrt[3]{\dfrac{3}{4\pi}}$ = 0.62035049	9.7926371–10
$\dfrac{3}{\pi}$ = 0.95492966	9.9799714–10	$\sqrt[3]{\dfrac{\pi}{6}}$ = 0.80599598	9.9063329–10
$\dfrac{4}{\pi}$ = 1.27323954	0.1049101		

e = Napierian Base	= 2.71828183	0.43429448
M = $\log_{10} e$	= 0.43429448	9.63778431–10
$1 + M$ = $\log_e 10$	= 2.30258509	0.36221569
$180 \div \pi$ = degrees in 1 radian	= 57.2957795	1.75812263
$\pi \div 180$ = radians in 1°	= 0.01745329	8.24187737—10
$\pi \div 10800$ = radians in 1′	= 0.0002908882	6.46372612—10
$\pi \div 648000$ = radians in 1″	= 0.000004848136811095	4.68557487—10
sin 1″	= 0.000004848136811076	4.68557487—10
tan 1″	= 0.000004848136811152	4.68557487—10
centimeters in 1 ft. (U.S.)	= 30.48006096 (legal)	1.4840158
feet in 1 cm.	= 0.03280833	8.5159842—10
inches in 1 m.	= 39.37 (exact legal value)	1.5951654
pounds in 1 kg.	= 2.204622341	0.3433342
kilograms in 1 lb.	= 0.4535924277	9.6566660—10
cu. in. in 1 (U. S.) gallon	= 231 (exact legal value)	2.3636120
g (average value)	= 32.16 ft./sec./sec.	1.5073
g (legal)	= 980.665 cm./sec.²	2.9915207
weight of 1 cu. ft. of water	= 62.425 lb. (max. density)	1.7953586
weight of 1 cu. ft. of air	= 0.0807 lb. (at 32° F.)	8.907 —10
ft. lb. per sec. in 1 H. P.	= 550 (exact legal value)	2.7403627
kg. m. per sec. in 1 H. P.	= 76.0404	1.8810445
watts in 1 H. P. (legal)	= 745.70	2.8725649

$$\pi = 3.14159\ \ 26535\ \ 89793\ \ 23846$$
$$e = 2.71828\ \ 18284\ \ 59045\ \ 23536$$
$$M = 0.43429\ \ 44819\ \ 03251\ \ 82765$$
$$1 + M = 2.30258\ \ 50929\ \ 94045\ \ 68402$$
$$\log_{10} \pi = 0.49714\ \ 98726\ \ 94133\ \ 85435$$
$$\log_{10} M = 9.63778\ \ 43113\ \ 00536\ \ 78912$$

$$n, \ n^2, \ \sqrt{n}, \ n^3, \ \sqrt[3]{n} \text{ etc.}$$

(ii) **Squares, Cubes, Square Roots and Cube Roots etc.**

Roots of numbers other than those given directly may be found by the following relations: $\sqrt{100n} = 10\sqrt{n}$; $\sqrt{1000n} = 10\sqrt{10n}$; $\sqrt{\frac{1}{10}n} = \frac{1}{10}\sqrt{10n}$; $\sqrt{\frac{1}{100}n} = \frac{1}{10}\sqrt{n}$; $\sqrt{\frac{1}{1000}n} = \frac{1}{100}\sqrt{10n}$; $\sqrt[3]{1000n} = 10\sqrt[3]{n}$; $\sqrt[3]{10,000n} = 10\sqrt[3]{10n}$; $\sqrt[3]{100,000n} = 10\sqrt[3]{100n}$; $\sqrt[3]{\frac{1}{10}n} = \frac{1}{10}\sqrt[3]{100n}$; $\sqrt[3]{\frac{1}{100}n} = 10\sqrt[3]{10n}$; $\sqrt[3]{\frac{1}{1000}n} = \frac{1}{10}\sqrt[3]{n}$.

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
1	1	1.000 000	3.162 278	1	1.000 000	2.154 435	4.641 589
2	4	1.414 214	4.472 136	8	1.259 921	2.714 418	5.848 035
3	9	1.732 051	5 477 226	27	1.442 250	3.107 233	6.694 330
4	16	2.000 000	6.324 555	64	1.587 401	3.419 952	7.368 063
5	25	2 236 068	7.071 068	125	1.709 976	3.684 031	7 937 005
6	36	2.449 490	7.745 967	216	1.817 121	3.914 868	8 434 327
7	49	2.645 751	8.366 600	343	1.912 931	4.121 285	8.879 040
8	64	2.828 427	8.944 272	512	2.000 000	4.308 869	9.283 178
9	81	3.000 000	9 486 833	729	2.080 084	4.481 405	9.654 894
10	100	3.162 278	10 00000	1 000	2.154 435	4 641 589	10.00000
11	121	3.316 625	10.48809	1 331	2.223 980	4.791 420	10.32280
12	144	3.464 102	10.954⁴5	1 728	2.289 428	4.932 424	10.62659
13	169	3 605 551	11.401/5	2 197	2.351 335	5.065 797	10.91393
14	196	3.741 657	11.83216	2 744	2.410 142	5.192 494	11.18689
15	225	3.872 983	12.24745	3 375	2.466 212	5.313 293	11.44714
16	256	4.000 000	12.64911	4 096	2.519 842	5.428 835	11.69607
17	289	4 123 106	13.03840	4 913	2.571 282	5.539 658	11 93483
18	324	4.242 641	13.41641	5 832	2.620 741	5.646 216	12.16440
19	361	4.358 899	13.78405	6 859	2.668 402	5.748 897	12.38562
20	400	4.472 136	14.14214	8 000	2.714 418	5.848 035	12.59921
21	441	4 582 576	14.49138	9 261	2.758 924	5 943 922	12 80579
22	484	4.690 416	14 83240	10 648	2.802 039	6.036 811	13.00591
23	529	4.795 832	15.16575	12 167	2.843 867	o.126 926	13.20006
24	576	4.898 979	15.49193	13 824	2.884 499	6.214 465	13.38866
25	625	5.000 000	15.81139	15 625	2.924 018	6.299 605	13.57209
26	676	5.099 020	16.12452	17 576	2.962 496	6.382 504	13.75069
27	729	5.196 152	16.43168	19 683	3.000 000	6.463 304	13.92477
28	784	5.291 503	16 73320	21 952	3.036 589	6.542 133	14.09460
29	841	5.385 165	17.02939	24 389	3.072 317	6.619 106	14.26043
30	900	5.477 226	17.32051	27 000	3.107 233	6.694 330	14.42250
31	961	5.567 764	17.60682	29 791	3.141 381	6.767 899	14.58100
32	1 024	5.656 854	17.88854	32 768	3.174 802	6.839 904	14.73613
33	1 089	5.744 563	18.16590	35 937	3.207 534	6.910 423	14.88806
34	1 156	5.830 952	18.43909	39 304	3.239 612	6.979 532	15.03695
35	1 225	5.916 080	18.70829	42 875	3.271 066	7.047 299	15.18294
36	1 296	6.000 000	18.97367	46 656	3.301 927	7.113 787	15.32619
37	1 369	6.082 763	19.23538	50 653	3.332 222	7.179 054	15.46680
38	1 444	6.164 414	19.49359	54 872	3.361 975	7.243 156	15.60491
39	1 521	6.244 998	19.74842	59 319	3.391 211	7.306 144	15.74061
40	1 600	6.324 555	20.00000	64 000	3.419 952	7.368 063	15.87401
41	1 681	6.403 124	20.24846	68 921	3.448 217	7.428 959	16.00521
42	1 764	6.480 741	20.49390	74 088	3.476 027	7.488 872	16.13429
43	1 849	6.557 439	20.73644	79 507	3.503 398	7.547 842	16.26133
44	1 936	6.633 250	20.97618	85 184	3.530 348	7.605 905	16.38643
45	2 025	6.708 204	21.21320	91 125	3.556 893	7.663 094	16.50964
46	2 116	6.782 330	21.44761	97 336	3.583 048	7.719 443	16.63103
47	2 209	6.855 655	21.67948	103 823	3.608 826	7.774 980	16.75069
48	2 304	6.928 203	21.90890	110 592	3.634 241	7.829 735	16.86865
49	2 401	7.000 000	22.13594	117 649	3.659 306	7.883 735	16.98499
50	2 500	7.071 068	22.36068	125 000	3.684 031	7.937 005	17.09976

n	n²	$\sqrt{n}$	$\sqrt{10n}$	n³	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
50	2 500	7.071 068	22.36068	125 000	3.684 031	7.937 005	17.09976
51	2 601	7.141 428	22.58318	132 651	3.708 430	7.989 570	17.21301
52	2 704	7.211 103	22.80351	140 608	3.732 511	8.041 452	17.32478
53	2 809	7.280 110	23.02173	148 877	3.756 286	8.092 672	17.43513
54	2 916	7.348 469	23.23790	157 464	3.779 763	8.143 253	17.54411
55	3 025	7.416 198	23.45208	166 375	3.802 952	8.193 213	17.65174
56	3 136	7.483 315	23.66432	175 616	3.825 862	8.242 571	17.75808
57	3 249	7.549 834	23.87467	185 193	3.848 501	8.291 344	17.86316
58	3 364	7.615 773	24.08319	195 112	3.870 877	8.339 551	17.96702
59	3 481	7.681 146	24.28992	205 379	3.892 996	8.387 207	18.06969
60	3 600	7.745 967	24.49490	216 000	3.914 868	8.434 327	18.17121
61	3 721	7.810 250	24.69818	226 981	3.936 497	8.480 926	18.27160
62	3 844	7.874 008	24.89980	238 328	3.957 892	8.527 019	18.37091
63	3 969	7.937 254	25.09980	250 047	3.979 057	8.572 619	18.46915
64	4 096	8.000 000	25.29822	262 144	4.000 000	8.617 739	18.56636
65	4 225	8.062 258	25.49510	274 625	4.020 726	8.662 391	18.66256
66	4 356	8.124 038	25.69047	287 496	4.041 240	8.706 588	18.75777
67	4 489	8.185 353	25.88436	300 763	4.061 548	8.750 340	18.85204
68	4 624	8.246 211	26.07681	314 432	4.081 655	8.793 659	18.94536
69	4 761	8.306 624	26.26785	328 509	4.101 566	8.836 556	19.03778
70	4 900	8.366 600	26.45751	343 000	4.121 285	8.879 040	19.12931
71	5 041	8.426 150	26.64583	357 911	4.140 818	8.921 121	19.21997
72	5 184	8.485 281	26.83282	373 248	4.160 168	8.962 809	19.30979
73	5 329	8.544 004	27.01851	389 017	4.179 339	9.004 113	19.39877
74	5 476	8.602 325	27.20294	405 224	4.198 336	9.045 042	19.48695
75	5 625	8.660 254	27.38613	421 875	4.217 163	9.085 603	19.57434
76	5 776	8.717 798	27.56810	438 976	4.235 824	9.125 805	19.66095
77	5 929	8.774 964	27.74887	456 533	4.254 321	9.165 656	19.74681
78	6 084	8.831 761	27.92848	474 552	4.272 659	9.205 164	19.83192
79	6 241	8.888 194	28.10694	493 039	4.290 840	9.244 335	19.91632
80	6 400	8.944 272	28.28427	512 000	4.308 869	9.283 178	20.00000
81	6 561	9.000 000	28.46050	531 441	4.326 749	9.321 698	20.08299
82	6 724	9.055 385	28.63564	551 368	4.344 481	9.359 902	20.16530
83	6 889	9.110 434	28.80972	571 787	4.362 071	9.397 796	20.24694
84	7 056	9.165 151	28.98275	592 704	4.379 519	9.435 388	20 32793
85	7 225	9.219 544	29.15476	614 125	4.396 830	9.472 682	20.40828
86	7 396	9.273 618	29.32576	636 056	4.414 005	9.509 685	20.48800
87	7 569	9.327 379	29.49576	658 503	4.431 048	9.546 403	20.56710
88	7 744	9.380 832	29.66479	681 472	4.447 960	9.582 840	20.64560
89	7 921	9.433 981	29.83287	704 969	4.464 745	9.619 002	20.72351
90	8 100	9.486 833	30.00000	729 000	4.481 405	9.654 894	20.80084
91	8 281	9.539 392	30.16621	753 571	4.497 941	9.690 521	20.87759
92	8 464	9.591 663	30.33150	778 688	4.514 357	9.725 888	20.95379
93	8 649	9.643 651	30.49590	804 357	4.530 655	9.761 000	21.02944
94	8 836	9.695 360	30.65942	830 584	4.546 836	9.795 861	21.10454
95	9 025	9.746 794	30.82207	857 375	4.562 903	9.830 476	21.17912
96	9 216	9.797 959	30.98387	884 736	4.578 857	9.864 848	21.25317
97	9 409	9.848 858	31.14482	912 673	4.594 701	9.898 983	21.32671
98	9 604	9.899 495	31.30495	941 192	4.610 436	9.932 884	21.39975
99	9 801	9.949 874	31.46427	970 299	4.626 065	9.966 555	21.47229
100	10 000	10.00000	31.62278	1 000 000	4.641 589	10.00000	21.54435

$$n, \; n^2, \; \sqrt{n}, \; n^3, \; \sqrt[3]{n} \; \text{etc.}$$

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
100	10 000	10.00000	31.62278	1 000 000	4.641 589	10.00000	21.54435
101	10 201	10.04988	31.78050	1 030 301	4.657 010	10.03322	21.61592
102	10 404	10.09950	31.93744	1 061 208	4.672 329	10.06623	21.68703
103	10 609	10.14889	32.09361	1 092 727	4.687 548	10.09902	21.75767
104	10 816	10.19804	32.24903	1 124 864	4.702 669	10.13159	21.82786
105	11 025	10.24695	32.40370	1 157 625	4.717 694	10.16396	21.89760
106	11 236	10.29563	32.55764	1 191 016	4.732 623	10.19613	21.96689
107	11 449	10.34408	32.71085	1 225 043	4.747 459	10.22809	22.03575
108	11 664	10.39230	32.86335	1 259 712	4.762 203	10.25986	22.10419
109	11 881	10.44031	33.01515	1 295 029	4.776 856	10.29142	22.17220
110	12 100	10.48809	33.16625	1 331 000	4.791 420	10.32280	22.23980
111	12 321	10.53565	33.31666	1 367 631	4.805 896	10.35399	22.30699
112	12 544	10.58301	33.46640	1 404 928	4.820 285	10.38499	22.37378
113	12 769	10.63015	33.61547	1 442 897	4.834 588	10.41580	22.44017
114	12 996	10.67708	33.76389	1 481 544	4.848 808	10.44644	22.50617
115	13 225	10.72381	33.91165	1 520 875	4.862 944	10.47690	22.57179
116	13 456	10.77033	34.05877	1 560 896	4.876 999	10.50718	22.63702
117	13 689	10.81665	34.20526	1 601 613	4.890 973	10.53728	22.70189
118	13 924	10.86278	34.35113	1 643 032	4.904 868	10.56722	22.76638
119	14 161	10.90871	34.49638	1 685 159	4.918 685	10.59699	22.83051
120	14 400	10.95445	34.64102	1 728 000	4.932 424	10.62659	22.89428
121	14 641	11.00000	34.78505	1 771 561	4.946 087	10.65602	22.95770
122	14 884	11.04536	34.92850	1 815 848	4.959 676	10.68530	23.02078
123	15 129	11.09054	35 07136	1 860 867	4.973 190	10.71441	23.08350
124	15 376	11.13553	35 21363	1 906 624	4.986 631	10.74337	23.14589
125	15 625	11.18034	35.35534	1 953 125	5.000 000	10.77217	23.20794
126	15 876	11.22497	35.49648	2 000 376	5.013 298	10.80082	23.26967
127	16 129	11.26943	35.63706	2 048 383	5.026 526	10.82932	23.33107
128	16 384	11.31371	35.77709	2 097 152	5.039 684	10.85767	23.39214
129	16 641	11.35782	35.91657	2 146 689	5.052 774	10.88587	23.45290
130	16 900	11.40175	36.05551	2 197 000	5.065 797	10.91393	23.51335
131	17 161	11.44552	36.19392	2 248 091	5.078 753	10.94184	23.57348
132	17 424	11.48913	36.33180	2 299 968	5.091 643	10.96961	23 63332
133	17 689	11.53256	36.46917	2 352 637	5.104 469	10.99724	23.69285
134	17 956	11.57584	36.60601	2 406 104	5.117 230	11.02474	23.75208
135	18 225	11.61895	36.74235	2 460 375	5.129 928	11.05209	23 81102
136	18 496	11.66190	36.87818	2 515 456	5.142 563	11.07932	23.86966
137	18 769	11.70470	37.01351	2 571 353	5.155 137	11.10641	23.92803
138	19 044	11.74734	37.14835	2 628 072	5.167 649	11.13336	23 98610
139	19 321	11.78983	37.28270	2 685 619	5.180 101	11.16019	24.04390
140	19 600	11.83216	37.41657	2 744 000	5.192 494	11.18689	24.10142
141	19 881	11.87434	37.54997	2 803 221	5.204 828	11.21346	24.15867
142	20 164	11.91638	37.68289	2 863 288	5.217 103	11.23991	24.21565
143	20 449	11.95826	37.81534	2 924 207	5.229 322	11.26623	24.27236
144	20 736	12.00000	37.94733	2 985 984	5.241 483	11.29243	24.32881
145	21 025	12.04159	38.07887	3 048 625	5.253 588	11.31851	24.38499
146	21 316	12.08305	38.20995	3 112 136	5.265 637	11.34447	24.44092
147	21 609	12.12436	38.34058	3 176 523	5.277 632	11.37031	24.49660
148	21 904	12.16553	38.47077	3 241 792	5.289 572	11.39604	24.55202
149	22 201	12.20656	38.60052	3 307 949	5.301 459	11.42165	24.60719
150	22 500	12.24745	38.72983	3 375 000	5.313 293	11.44714	24.66212

n	n²	$\sqrt{n}$	$\sqrt{10n}$	n³	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
150	22 500	12.24745	38.72983	3 375 000	5.313 293	11.44714	24.66212
151	22 801	12.28821	38.85872	3 442 951	5.325 074	11.47252	24.71680
152	23 104	12.32883	38.98718	3 511 808	5.336 803	11.49779	24.77125
153	23 409	12.36932	39.11521	3 581 577	5.348 481	11.52295	24.82545
154	23 716	12.40967	39.24283	3 652 264	5.360 108	11.54800	24.87942
155	24 025	12.44990	39.37004	3 723 875	5.371 685	11.57295	24.93315
156	24 336	12.49000	39.49684	3 796 416	5.383 213	11.59778	24.98666
157	24 649	12.52996	39.62323	3 869 893	5.394 691	11.62251	25.03994
158	24 964	12.56981	39.74921	3 944 312	5.406 120	11.64713	25.09299
159	25 281	12.60952	39.87480	4 019 679	5.417 502	11.67165	25.14581
160	25 600	12 64911	40.00000	4 096 000	5.428 835	11.69607	25.19842
161	25 921	12.68858	40.12481	4 173 281	5.440 122	11.72039	25.25081
162	26 244	12.72792	40.24922	4 251 528	5.451 362	11.74460	25.30298
163	26 569	12.76715	40.37326	4 330 747	5.462 556	11.76872	25.35494
164	26 896	12.80625	40.49691	4 410 944	5.473 704	11.79274	25.40668
165	27 225	12.84523	40.62019	4 492 125	5.484 807	11.81666	25.45822
166	27 556	12.88410	40.74310	4 574 296	5.495 865	11.84048	25.50954
167	27 889	12.92285	40.86563	4 657 463	5.506 878	11.86421	25.56067
168	28 224	12.96148	40.98780	4 741 632	5.517 848	11.88784	25.61158
169	28 561	13.00000	41.10961	4 826 809	5.528 775	11.91138	25.66230
170	28 900	13.03840	41.23106	4 913 000	5.539 658	11.93483	25.71282
171	29 241	13.07670	41.35215	5 000 211	5 550 499	11.95819	25.76313
172	29 584	13.11488	41.47288	5 088 448	5.561 298	11.98145	25.81326
173	29 929	13.15295	41.59327	5 177 717	5.572 055	12.00463	25.86319
174	30 276	13.19091	41.71331	5 268 024	5.582 770	12.02771	25.91292
175	30 625	13.22876	41.83300	5 359 375	5.593 445	12.05071	25.96247
176	30 976	13.26650	41.95235	5 451 776	5.604 079	12.07362	26.01183
177	31 329	13.30413	42.07137	5 545 233	5.614 672	12.09645	26.06100
178	31 684	13 34166	42.19005	5 639 752	5.625 226	12.11918	26.10999
179	32 041	13.37909	42.30839	5 735 339	5.635 741	12.14184	26.15879
180	32 400	13.41641	42.42641	5 832 000	5.646 216	12.16440	26.20741
181	32 761	13.45362	42.54409	5 929 741	5.656 653	12.18689	26.25586
182	33 124	13.49074	42.66146	6 028 568	5.667 051	12.20929	26.30412
183	33 489	13 52775	42.77850	6 128 487	5.677 411	12.23161	26.35221
184	33 856	13.56466	42.89522	6 229 504	5.687 734	12.25385	26.40012
185	34 225	13.60147	43.01163	6 331 625	5.698 019	12.27601	26.44786
186	34 596	13.63818	43.12772	6 434 856	5.708 267	12.29809	26.49543
187	34 969	13.67479	43.24350	6 539 203	5.718 479	12.32009	26.54283
188	35 344	13.71131	43.35897	6 644 672	5.728 654	12.34201	26.59006
189	35 721	13.74773	43.47413	6 751 269	5.738 794	12.36386	26.63712
190	36 100	13.78405	43.58899	6 859 000	5.748 897	12.38562	26.68402
191	36 481	13.82027	43.70355	6 967 871	5.758 965	12.40731	26.73075
192	36 864	13.85641	43.81780	7 077 888	5.768 998	12.42893	26.77732
193	37 249	13.89244	43.93177	7 189 057	5.778 997	12.45047	26.82373
194	37 636	13.92839	44.04543	7 301 384	5.788 960	12.47194	26.86997
195	38 025	13.96424	44.15880	7 414 875	5.798 890	12.49333	26.91606
196	38 416	14.00000	44.27189	7 529 536	5.808 786	12.51465	26.96199
197	38 809	14.03567	44.38468	7 645 373	5.818 648	12.53590	27.00777
198	39 204	14.07125	44.49719	7 762 392	5.828 477	12.55707	27.05339
199	39 601	14.10674	44.60942	7 880 599	5.838 272	12.57818	27.09886
200	40 000	14.14214	44.72136	8 000 000	5.848 035	12.59921	27.14418

$$n, \quad n^2, \quad \sqrt{n}, \quad n^3, \quad \sqrt[3]{n} \quad \text{etc.}$$

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
200	40 000	14.14214	44.72136	8 000 000	5.848 035	12.59921	27.14418
201	40 401	14.17745	44.83302	8 120 601	5.857 766	12.62017	27.18934
202	40 804	14.21267	44.94441	8 242 408	5.867 464	12.64107	27.23436
203	41 209	14.24781	45.05552	8 365 427	5.877 131	12.66189	27.27922
204	41 616	14.28286	45.16636	8 489 664	5.886 765	12.68265	27.32394
205	42 025	14.31782	45.27693	8 615 125	5.896 369	12.70334	27.36852
206	42 436	14.35270	45.38722	8 741 816	5.905 941	12.72396	27.41295
207	42 849	14.38749	45.49725	8 869 743	5.915 482	12.74452	27.45723
208	43 264	14.42221	45.60702	8 998 912	5.924 992	12.76501	27.50138
209	43 681	14.45683	45.71652	9 129 329	5.934 472	12.78543	27.54538
210	44 100	14.49138	45.82576	9 261 000	5.943 922	12.80579	27.58924
211	44 521	14 52584	45.93474	9 393 931	5.953 342	12.82609	27.63296
212	44 944	14 56022	46.04346	9 528 128	5.962 732	12.84632	27.67655
213	45 369	14.59452	46.15192	9 663 597	5.972 093	12.86648	27.72000
214	45 796	14.62874	46.26013	9 800 344	5.981 424	12.88659	27.76331
215	46 225	14.66288	46.36809	9 938 375	5.990 726	12.90663	27.80649
216	46 656	14.69694	46.47580	10 077 696	6.000 000	12.92661	27.84953
217	47 089	14.73092	46.58326	10 218 313	6.009 245	12.94653	27.89244
218	47 524	14.76482	46.69047	10 360 232	6.018 462	12.96638	27.93522
219	47 961	14.79865	46.79744	10 503 459	6.027 650	12.98618	27.97787
220	48 400	14.83240	46.90416	10 648 000	6.036 811	13.00591	28.02039
221	48 841	14.86607	47.01064	10 793 861	6.045 944	13.02559	28.06278
222	49 284	14.89966	47.11688	10 941 048	6.055 049	13.04521	28.10505
223	49 729	14.93318	47.22288	11 089 567	6.064 127	13.06477	28 14718
224	50 176	14.96663	47.32864	11 239 424	6.073 178	13.08427	28.18919
225	50 625	15.00000	47.43416	11 390 625	6.082 202	13.10371	28 23108
226	51 076	15.03330	47.53946	11 543 176	6.091 199	13.12309	28.27284
227	51 529	15 06652	47.64452	11 697 083	6.100 170	13.14242	28 31448
228	51 984	15.09967	47.74935	11 852 352	6.109 115	13.16169	28 35600
229	52 441	15.13275	47.85394	12 008 989	6.118 033	13.18090	28.39739
230	52 900	15.16575	47.95832	12 167 000	6 126 926	13.20006	28.43867
231	53 361	15.19868	48.06246	12 326 391	6.135 792	13.21916	28 47983
232	53 824	15.23155	48 16638	12 487 168	6.144 634	13 23821	28.52086
233	54 289	15.26434	48.27007	12 649 337	6.153 449	13 25721	28 56178
234	54 756	15.29706	48.37355	12 812 904	6.162 240	13.27614	28.60259
235	55 225	15.32971	48.47680	12 977 875	6.171 006	13.29003	28 64327
236	55 696	15.36229	48.57983	13 144 256	6.179 747	13.31386	28.68384
237	56 169	15.39480	48.68265	13 312 053	6.188 463	13.33264	28 72430
238	56 644	15.42725	48.78524	13 481 272	6.197 154	13.35136	28.76464
239	57 121	15.45962	48.88763	13 651 919	6.205 822	13.37004	28.80487
240	57 600	15.49193	48.98979	13 824 000	6.214 465	13 38866	28.84499
241	58 081	15.52417	49.09175	13 997 521	6.223 084	13.40723	28.88500
242	58 564	15.55635	49.19350	14 172 488	6.231 680	13 42575	28.92489
243	59 049	15.58846	49.29503	14 348 907	6.240 251	13.44421	28.96468
244	59 536	15.62050	49.39636	14 526 784	6.248 800	13.46263	29.00436
245	60 025	15.65248	49 49747	14 706 125	6.257 325	13.48100	29.04393
246	60 516	15.68439	49.59839	14 886 936	6.265 827	13.49931	29.08339
247	61 009	15.71623	49.69909	15 069 223	6.274 305	13.51758	29.12275
248	61 504	15.74802	49.79960	15 252 992	6.282 761	13.53580	29.16196
249	62 001	15.77973	49.89990	15 438 249	6.291 195	13.55397	29.20114
250	62 500	15.81139	50.00000	15 625 000	6.299 605	13.57209	29.24018

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
250	62 500	15.81139	50.00000	15 625 000	6.299 605	13.57209	29.24018
251	63 001	15.84298	50.09990	15 813 251	6.307 994	13.59016	29.27911
252	63 504	15.87451	50.19960	16 003 008	6.316 360	13.60818	29.31794
253	64 009	15.90597	50.29911	16 194 277	6.324 704	13 62616	29.35667
254	64 516	15.93738	50.39841	16 387 064	6.333 026	13.64409	29.39530
255	65 025	15.96872	50.49752	16 581 375	6.341 326	13.66197	29.43383
256	65 536	16.00000	50.59644	16 777 216	6.349 604	13 67981	29.47225
257	66 049	16.03122	50.69517	16 974 593	6.357 861	13 69760	29.51058
258	66 564	16.06238	50.79370	17 173 512	6.366 097	13.71534	29.54880
259	67 081	16.09348	50.89204	17 373 979	6.374 311	13.73304	29.58693
260	67 600	16 12452	50.99020	17 576 000	6.382 504	13 75069	29.62496
261	68 121	16.15549	51.08816	17 779 581	6.390 677	13.76830	29.66289
262	68 644	16.18641	51.18594	17 984 728	6.398 828	13.78586	29.70073
263	69 169	16 21727	51.28353	18 191 447	6.406 959	13.80337	29.73847
264	69 696	16.24808	51.38093	18 399 744	6.415 069	13.82085	29.77611
265	70 225	16 27882	51.47815	18 609 625	6.423 158	13.83828	29.81366
266	70 756	16 30951	51.57519	18 821 096	6.431 228	13.85566	29.85111
267	71 289	16 34013	51.67204	19 034 163	6.439 277	13.87300	29.88847
268	71 824	16.37071	51.76872	19 248 832	6.447 306	13.89030	29.92574
269	72 361	16.40122	51.86521	19 465 109	6.455 315	13.90755	29.96292
270	72 900	16.43168	51.96152	19 683 000	6.463 304	13.92477	30.00000
271	73 441	16.46208	52 05766	19 902 511	6.471 274	13.94194	30.03699
272	73 984	16.49242	52.15362	20 123 648	6.479 224	13.95906	30.07389
273	74 529	16.52271	52.24940	20 346 417	6.487 154	13.97615	30.11070
274	75 076	16.55295	52.34501	20 570 824	6.495 065	13.99319	30.14742
275	75 625	16.58312	52.44044	20 796 875	6.502 957	14.01020	30.18405
276	76 176	16.61325	52.53570	21 024 576	6.510 830	14.02716	30.22060
277	76 729	16.64332	52.63079	21 253 933	6.518 684	14.04408	30.25705
278	77 284	16.67333	52.72571	21 484 952	6.526 519	14.06096	30.29342
279	77 841	16.70329	52.82045	21 717 639	6.534 335	14.07780	30.32970
280	78 400	16.73320	52.91503	21 952 000	6.542 133	14.09460	30.36589
281	78 961	16.76305	53.00943	22 188 041	6.549 912	14.11136	30.40200
282	79 524	16.79286	53.10367	22 425 768	6.557 672	14.12808	30.43802
283	80 089	16.82260	53.19774	22 665 187	6.565 414	14.14476	30.47395
284	80 656	16.85230	53.29165	22 906 304	6.573 138	14.16140	30.50981
285	81 225	16.88194	53.38539	23 149 125	6.580 844	14.17800	30.54557
286	81 796	16.91153	53.47897	23 393 656	6.588 532	14.19456	30.58126
287	82 369	16.94107	53.57238	23 639 903	6.596 202	14.21109	30.61686
288	82 944	16.97056	53.66563	23 887 872	6.603 854	14.22757	30.65238
289	83 521	17.00000	53.75872	24 137 569	6.611 489	14.24402	30.68781
290	84 100	17.02939	53.85165	24 389 000	6.619 106	14.26043	30.72317
291	84 681	17.05872	53.94442	24 642 171	6.626 705	14.27680	30.75844
292	85 264	17.08801	54.03702	24 897 088	6.634 287	14.29314	30.79363
293	85 849	17.11724	54.12947	25 153 757	6.641 852	14.30944	30.82875
294	86 436	17.14643	54.22177	25 412 184	6.649 400	14.32570	30.86378
295	87 025	17.17556	54.31390	25 672 375	6.656 930	14.34192	30.89873
296	87 616	17.20465	54.40588	25 934 336	6.664 444	14.35811	30.93361
297	88 209	17.23369	54.49771	26 198 073	6.671 940	14.37426	30.96840
298	88 804	17.26268	54.58938	26 463 592	6.679 420	14.39037	31.00312
299	89 401	17.29162	54.68089	26 730 899	6.686 883	14.40645	31.03776
300	90 000	17.32051	54.77226	27 000 000	6.694 330	14.42250	31.07233

$n, n^2, \sqrt{n}, n^3, \sqrt[3]{n}$ etc.

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
300	90 000	17.32051	54.77226	27 000 000	6.694 330	14.42250	31.07233
301	90 601	17.34935	54.86347	27 270 901	6.701 759	14.43850	31.10681
302	91 204	17.37815	54.95453	27 543 608	6.709 173	14.45447	31.14122
303	91 809	17.40690	55.04544	27 818 127	6.716 570	14.47041	31.17556
304	92 416	17.43560	55.13620	28 094 464	6.723 951	14.48631	31.20982
305	93 025	17.46425	55.22681	28 372 625	6.731 315	14.50218	31.24400
306	93 636	17.49286	55.31727	28 652 616	6.738 664	14.51801	31.27811
307	94 249	17.52142	55.40758	28 934 443	6.745 997	14.53381	31.31214
308	94 864	17.54993	55.49775	29 218 112	6.753 313	14.54957	31.34610
309	95 481	17.57840	55.58777	29 503 629	6.760 614	14.56530	31.37999
310	96 100	17.60682	55.67764	29 791 000	6.767 899	14.58100	31.41381
311	96 721	17.63519	55.76737	30 080 231	6.775 169	14.59666	31.44755
312	97 344	17.66352	55.85696	30 371 328	6.782 423	14.61229	31.48122
313	97 969	17.69181	55.94640	30 664 297	6.789 661	14.62788	31.51482
314	98 596	17.72005	56.03570	30 959 144	6.796 884	14.64344	31.54834
315	99 225	17.74824	56.12486	31 255 875	6.804 092	14.65897	31.58180
316	99 856	17.77639	56.21388	31 554 496	6.811 285	14.67447	31.61518
317	100 489	17.80449	56.30275	31 855 013	6.818 462	14.68993	31.64850
318	101 124	17.83255	56.39149	32 157 432	6.825 624	14.70536	31.68174
319	101 761	17.86057	56.48008	32 461 759	6.832 771	14.72076	31.71492
320	102 400	17.88854	56.56854	32 768 000	6.839 904	14.73613	31.74802
321	103 041	17.91647	56.65686	33 076 161	6.847 021	14.75146	31.78106
322	103 684	17.94436	56.74504	33 386 248	6.854 124	14.76676	31.81403
323	104 329	17.97220	56.83309	33 698 267	6.861 212	14.78203	31.84693
324	104 976	18.00000	56.92100	34 012 224	6.868 285	14.79727	31.87976
325	105 625	18.02776	57.00877	34 328 125	6.875 344	14.81248	31.91252
326	106 276	18.05547	57.09641	34 645 976	6.882 389	14.82766	31.94522
327	106 929	18.08314	57.18391	34 965 783	6.889 419	14.84280	31.97785
328	107 584	18.11077	57.27128	35 287 552	6.896 434	14.85792	32.01041
329	108 241	18.13836	57.35852	35 611 289	6.903 436	14.87300	32.04291
330	108 900	18.16590	57.44563	35 937 000	6.910 423	14.88806	32.07534
331	109 561	18.19341	57.53260	36 264 691	6.917 396	14.90308	32.10771
332	110 224	18.22087	57.61944	36 594 368	6.924 356	14.91807	32.14001
333	110 889	18.24829	57.70615	36 926 037	6.931 301	14.93303	32.17225
334	111 556	18.27567	57.79273	37 259 704	6.938 232	14.94797	32.20442
335	112 225	18.30301	57.87918	37 595 375	6.945 150	14.96287	32.23653
336	112 896	18.33030	57.96551	37 933 056	6.952 053	14.97774	32.26857
337	113 569	18.35756	58.05170	38 272 753	6.958 943	14.99259	32.30055
338	114 244	18.38478	58.13777	38 614 472	6.965 820	15.00740	32.33247
339	114 921	18.41195	58.22371	38 958 219	6.972 683	15.02219	32.36433
340	115 600	18.43909	58.30952	39 304 000	6.979 532	15.03695	32.39612
341	116 281	18.46619	58.39521	39 651 821	6.986 368	15.05167	32.42785
342	116 964	18.49324	58.48077	40 001 688	6.993 191	15.06637	32.45952
343	117 649	18.52026	58.56620	40 353 607	7.000 000	15.08104	32.49112
344	118 336	18.54724	58.65151	40 707 584	7.006 796	15.09568	32.52267
345	119 025	18.57418	58.73670	41 063 625	7.013 579	15.11030	32.55415
346	119 716	18.60108	58.82176	41 421 736	7.020 349	15.12488	32.58557
347	120 409	18.62794	58.90671	41 781 923	7.027 106	15.13944	32.61694
348	121 104	18.65476	58.99152	42 144 192	7.033 850	15.15397	32.64824
349	121 801	18.68154	59.07622	42 508 549	7.040 581	15.16847	32.67948
350	122 500	18.70829	59.16080	42 875 000	7.047 299	15.18294	32.71066

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
350	122 500	18.70829	59.16080	42 875 000	7.047 209	15.18294	32.71066
351	123 201	18.73499	59.24525	43 243 551	7.054 004	15.19739	32.74179
352	123 904	18.76166	59.32959	43 614 208	7.060 697	15.21181	32 77285
353	124 609	18.78829	59.41380	43 986 977	7.067 377	15.22620	32.80386
354	125 316	18.81489	59.49790	44 361 864	7.074 044	15.24057	32.83480
355	126 025	18.84144	59.58188	44 738 875	7.080 699	15.25490	32.86569
356	126 736	18.86796	59.66574	45 118 016	7.087 341	15.26921	32.89652
357	127 449	18.89444	59.74948	45 499 293	7.093 971	15.28350	32.92730
358	128 164	18.92089	59.83310	45 882 712	7.100 588	15.29775	32.95801
359	128 881	18.94730	59.91661	46 268 279	7.107 194	15.31198	32.98867
360	129 600	18.97367	60.00000	46 656 000	7.113 787	15.32619	33.01927
361	130 321	19.00000	60.08328	47 045 881	7.120 367	15.34037	33 04982
362	131 044	19.02630	60.16644	47 437 928	7.126 936	15.35452	33.08031
363	131 769	19.05256	60.24948	47 832 147	7.133 492	15.36864	33.11074
364	132 496	19.07878	60.33241	48 228 544	7.140 037	15.38274	33.14112
365	133 225	19.10497	60.41523	48 627 125	7.146 569	15.39682	33.17144
366	133 956	19.13113	60.49793	49 027 896	7.153 090	15.41087	33.20170
367	134 689	19.15724	60.58052	49 430 863	7.159 599	15.42489	33.23191
368	135 424	19.18333	60.66300	49 836 032	7.166 096	15.43889	33.26207
369	136 161	19.20937	60.74537	50 243 409	7.172 581	15.45286	33.29217
370	136 900	19.23538	60.82763	50 653 000	7.179 054	15.46680	33.32222
371	137 641	19.26136	60.90977	51 064 811	7.185 516	15.48073	33.35221
372	138 384	19.28730	60.99180	51 478 848	7.191 966	15.49462	33.38215
373	139 129	19.31321	61.07373	51 895 117	7.198 405	15.50849	33.41204
374	139 876	19.33908	61.15554	52 313 624	7.204 832	15.52234	33.44187
375	140 625	19.36492	61.23724	52 734 375	7.211 248	15.53616	33.47165
376	141 376	19.39072	61.31884	53 157 376	7.217 652	15.54996	33.50137
377	142 129	19 41649	61.40033	53 582 633	7.224 045	15.56373	33.53105
378	142 884	19.44222	61.48170	54 010 152	7.230 427	15.57748	33.56067
379	143 641	19.46792	61.56298	54 439 939	7.236 797	15.59121	33.59024
380	144 400	19.49359	61.64414	54 872 000	7.243 156	15.60491	33.61975
381	145 161	19.51922	61.72520	55 306 341	7.249 505	15.61858	33.64922
382	145 924	19.54482	61.80615	55 742 968	7.255 842	15.63224	33.67863
383	146 689	19.57039	61.88699	56 181 887	7.262 167	15.64587	33.70800
384	147 456	19.59592	61.96773	56 623 104	7.268 482	15.65947	33.73731
385	148 225	19.62142	62.04837	57 066 625	7.274 786	15.67305	33.76657
386	148 996	19 64688	62.12890	57 512 456	7.281 079	15.68661	33 79578
387	149 769	19.67232	62.20932	57 960 603	7.287 362	15.70014	33 82494
388	150 544	19.69772	62.28965	58 411 072	7.293 633	15.71366	33.85405
389	151 321	19.72308	62.36986	58 863 869	7.299 894	15.72714	33.88310
390	152 100	19.74842	62.44998	59 319 000	7.306 144	15.74061	33.91211
391	152 881	19.77372	62.52999	59 776 471	7.312 383	15.75405	33.94107
392	153 664	19.79899	62.60990	60 236 288	7.318 611	15.76747	33.96999
393	154 449	19.82423	62.68971	60 698 457	7.324 829	15.78087	33 99885
394	155 236	19.84943	62.76942	61 162 984	7.331 037	15.79424	34.02766
395	156 025	19.87461	62.84903	61 629 875	7.337 234	15.80759	34.05642
396	156 816	19.89975	62.92853	62 099 136	7.343 420	15.82092	34.08514
397	157 609	19.92486	63.00794	62 570 773	7.349 597	15.83423	34.11381
398	158 404	19.94994	63.08724	63 044 792	7.355 762	15.84751	34.14242
399	159 201	19.97498	63.16645	63 521 199	7.361 918	15.86077	34.17100
400	160 000	20.00000	63.24555	64 000 000	7.368 063	15.87401	34.19952

$$n, \ n^2, \sqrt{n}, \ n^3, \sqrt[3]{n} \ \text{etc.}$$

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
400	160 000	20.00000	63.24555	64 000 000	7.368 063	15.87401	34.19952
401	160 801	20.02498	63.32456	64 481 201	7.374 198	15.88723	34.22799
402	161 604	20.04994	63.40347	64 964 808	7.380 323	15.90042	34.25642
403	162 409	20.07486	63.48228	65 450 827	7.386 437	15.91360	34.28480
404	163 216	20.09975	63.56099	65 939 264	7.392 542	15.92675	34.31314
405	164 025	20.12461	63.63961	66 430 125	7.398 636	15.93988	34.34143
406	164 836	20.14944	63.71813	66 923 416	7.404 721	15.95299	34.36967
407	165 649	20.17424	63.79655	67 419 143	7.410 795	15.96607	34.39786
408	166 464	20.19901	63.87488	67 917 312	7.416 860	15.97914	34.42601
409	167 281	20.22375	63.95311	68 417 929	7.422 914	15.99218	34.45412
410	168 100	20.24846	64.03124	68 921 000	7.428 959	16.00521	34.48217
411	168 921	20.27313	64.10928	69 426 531	7.434 994	16.01821	34.51018
412	169 744	20.29778	64.18723	69 934 528	7.441 019	16.03119	34.53815
413	170 569	20.32240	64.26508	70 444 997	7.447 034	16.04415	34.56607
414	171 396	20.34699	64.34283	70 957 944	7.453 040	16.05709	34.59395
415	172 225	20.37155	64.42049	71 473 375	7.459 036	16.07001	34.62178
416	173 056	20.39608	64.49806	71 991 296	7.465 022	16.08290	34.64956
417	173 889	20.42058	64.57554	72 511 713	7.470 999	16.09578	34.67731
418	174 724	20.44505	64.65292	73 034 632	7.476 966	16.10864	34.70500
419	175 561	20.46949	64.73021	73 560 059	7.482 924	16.12147	34.73266
420	176 400	20.49390	64.80741	74 088 000	7.488 872	16.13429	34.76027
421	177 241	20.51828	64.88451	74 618 461	7.494 811	16.14708	34.78783
422	178 084	20.54264	64.96153	75 151 448	7.500 741	16.15986	34.81535
423	178 929	20.56696	65.03845	75 686 967	7.506 661	16.17261	34.84283
424	179 776	20.59126	65.11528	76 225 024	7.512 572	16.18534	34.87027
425	180 625	20.61553	65.19202	76 765 625	7.518 473	16.19806	34.89766
426	181 476	20.63977	65.26868	77 308 776	7.524 365	16.21075	34.92501
427	182 329	20.66398	65.34524	77 854 483	7.530 248	16.22343	34.95232
428	183 184	20.68816	65.42171	78 402 752	7.536 122	16.23608	34.97958
429	184 041	20.71232	65.49809	78 953 589	7.541 937	16.24872	35.00680
430	184 900	20.73644	65.57439	79 507 000	7.547 842	16.26133	35.03398
431	185 761	20.76054	65.65059	80 062 991	7.553 689	16.27393	35.06112
432	186 624	20.78461	65.72671	80 621 568	7.559 526	16.28651	35.08821
433	187 489	20.80865	65.80274	81 182 737	7.565 355	16.29906	35.11527
434	188 356	20.83267	65.87868	81 746 504	7.571 174	16.31160	35.14228
435	189 225	20.85665	65.95453	82 312 875	7.576 985	16.32412	35.16925
436	190 096	20.88061	66.03030	82 881 856	7.582 787	16.33662	35.19618
437	190 969	20.90454	66.10598	83 453 453	7.588 579	16.34910	35.22307
438	191 844	20.92845	66.18157	84 027 672	7.594 363	16.36156	35.24991
439	192 721	20.95233	66.25708	84 604 519	7.600 139	16.37400	35.27672
440	193 600	20.97618	66.33250	85 184 000	7.605 905	16.38643	35.30348
441	194 481	21.00000	66.40783	85 766 121	7.611 663	16.39883	35.33021
442	195 364	21.02380	66.48308	86 350 888	7.617 412	16.41122	35.35689
443	196 249	21.04757	66.55825	86 938 307	7.623 152	16.42358	35.38354
444	197 136	21.07131	66.63332	87 528 384	7.628 884	16.43593	35.41014
445	198 025	21.09502	66.70832	88 121 125	7.634 607	16.44826	35.43671
446	198 916	21.11871	66.78323	88 716 536	7.640 321	16.46057	35.46323
447	199 809	21.14237	66.85806	89 314 623	7.646 027	16.47287	35.48971
448	200 704	21.16601	66.93280	89 915 392	7.651 725	16.48514	35.51616
449	201 601	21.18962	67.00746	90 518 849	7.657 414	16.49740	35.54257
450	202 500	21.21320	67.08204	91 125 000	7.663 094	16.50964	35.56893

n	n^2	$\sqrt{n}$	$\sqrt{10n}$	n^3	$\sqrt[3]{n}$	$\sqrt[3]{10n}$	$\sqrt[3]{100n}$
450	202 500	21.21320	67.08204	91 125 000	7.663 094	16.50964	35.56893
451	203 401	21.23676	67.15653	91 733 851	7.668 766	16.52186	35.59526
452	204 304	21.26029	67.23095	92 345 408	7.674 430	16.53406	35.62155
453	205 209	21.28380	67.30527	92 959 677	7.680 086	16.54624	35.64780
454	206 116	21.30728	67.37952	93 576 664	7.685 733	16.55841	35.67401
455	207 025	21.33073	67.45369	94 196 375	7.691 372	16.57056	35.70018
456	207 936	21.35416	67.52777	94 818 816	7.697 002	16.58269	35.72632
457	208 849	21.37756	67.60178	95 443 993	7.702 625	16.59480	35.75242
458	209 764	21.40093	67.67570	96 071 912	7.708 239	16.60690	35.77848
459	210 681	21.42429	67.74954	96 702 579	7.713 845	16.61897	35.80450
460	211 600	21.44761	67.82330	97 336 000	7.719 443	16.63103	35.83048
461	212 521	21.47091	67.89698	97 972 181	7.725 032	16.64308	35.85642
462	213 444	21.49419	67.97058	98 611 128	7.730 614	16.65510	35.88233
463	214 369	21.51743	68.04410	99 252 847	7.736 188	16.66711	35.90820
464	215 296	21.54066	68.11755	99 897 344	7.741 753	16.67910	35.93404
465	216 225	21.56386	68.19091	100 544 625	7.747 311	16.69108	35.95983
466	217 156	21.58703	68.26419	101 194 696	7.752 861	16.70303	35.98559
467	218 089	21.61018	68.33740	101 847 563	7.758 402	16.71497	36.01131
4t8	219 024	21.63331	68.41053	102 503 232	7.763 936	16.72689	36.03700
4d9	219 961	21.65641	68.48357	103 161 709	7.769 462	16.73880	36.06265
470	220 900	21.67948	68.55655	103 823 000	7.774 980	16.75069	36.08826
471	221 841	21.70253	68.62944	104 487 111	7.780 490	16.76256	36.11384
472	222 784	21.72556	68.70226	105 154 048	7.785 993	16.77441	36.13938
473	223 729	21.74856	68.77500	105 823 817	7.791 488	16.78625	36.16488
474	224 676	21.77154	68.84766	106 496 424	7.796 975	16.79807	36.19035
475	225 625	21.79449	68.92024	107 171 875	7.802 454	16.80988	36.21578
476	226 576	21.81742	68.99275	107 850 176	7.807 925	16.82167	36.24118
477	227 529	21.84033	69.06519	108 531 333	7.813 389	16.83344	36.26654
478	228 484	21.86321	69.13754	109 215 352	7.818 846	16.84519	36.29187
479	229 441	21.88607	69.20983	109 902 239	7.824 294	16.85693	36.31716
480	230 400	21.90890	69.28203	110 592 000	7.829 735	16.86865	36.34241
481	231 361	21.93171	69.35416	111 284 641	7.835 169	16.88036	36.36763
482	232 324	21.95450	69.42622	111 980 168	7.840 595	16.89205	36.39282
483	233 289	21.97726	69.49820	112 678 587	7.846 013	16.90372	36.41797
484	234 256	22.00000	69.57011	113 379 904	7.851 424	16.91538	36.44308
485	235 225	22.02272	69.64194	114 084 125	7.856 828	16.92702	36.46817
486	236 196	22.04541	69.71370	114 791 256	7.862 224	16.93865	36.49321
487	237 169	22.06808	69.78539	115 501 303	7.867 613	16.95026	36.51822
488	238 144	22.09072	69.85700	116 214 272	7.872 994	16.96185	36.54320
489	239 121	22.11334	69.92853	116 930 169	7.878 368	16.97343	36.56815
490	240 100	22.13594	70.00000	117 649 000	7.883 735	16.98499	36.59306
491	241 081	22.15852	70.07139	118 370 771	7.889 095	16.99654	36.61793
492	242 064	22.18107	70.14271	119 095 488	7.894 447	17.00807	36.64278
493	243 049	22.20360	70.21396	119 823 157	7.899 792	17.01959	36.66758
494	244 036	22.22611	70.28513	120 553 784	7.905 129	17.03108	36.69236
495	245 025	22.24860	70.35624	121 287 375	7.910 460	17.04257	36.71710
496	246 016	22.27106	70.42727	122 023 936	7.915 783	17.05404	36.74181
497	247 009	22.29350	70.49823	122 763 473	7.921 099	17.06549	36.76649
498	248 004	22.31591	70.56912	123 505 992	7.926 408	17.07693	36.79113
499	249 001	22.33831	70.63993	124 251 499	7.931 710	17.08835	36.81574
500	250 000	22.36068	70.71068	125 000 000	7.937 005	17.09976	36.84031

(iii) a. <u>**Degrees, Minutes, and Seconds to Radians**</u>

Units in degrees, minutes *or* seconds	Degrees to Radians	Minutes to Radians	Seconds to Radians
10	0.174 5329	0.002 9089	0.000 0485
20	0.349 0659	0.005 8178	0.000 0970
30	0.523 5988	0.008 7266	0.000 1454
40	0.698 1317	0.011 6355	0.000 1939
50	0.872 6646	0.014 5444	0.000 2424
60	1.047 1976	0.017 4533	0.000 2909
70	1.221 7305	(0.020 3622)	(0.000 3394)
80	1.396 2634	(0.023 2711)	(0.000 3879)
90	1.570 7963	(0.026 1800)	(0.000 4364)
100	1.745 3293	. . . .	. . . .
200	3.490 6585	. . . .	. . . .
300	5.235 9878	. . . .	. . . .

where n = 1, 2, 3, 4, etc.   n(100) = n(1.745 3293)

(iii) b. <u>**Radians to Degrees, Minutes and Seconds**</u>

Radians	1.0	0.1	0.01	0.001	0.0001
1	57° 17′ 44.8″	5° 43′ 46.5″	0° 34′ 22.6″	0° 03′ 26.3″	0° 00′ 20.6″
2	114° 35′ 29.6″	11° 27′ 33.0″	1° 08′ 45.3″	0° 06′ 52.5″	0° 00′ 41.3″
3	171° 53′ 14.4″	17° 11′ 19.4″	1° 43′ 07.9″	0° 10′ 18.8″	0° 01′ 01.9″
4	229° 10′ 59.2″	22° 55′ 05.9″	2° 17′ 30.6″	0° 13′ 45.1″	0° 01′ 22.5″
5	286° 28′ 44.0″	28° 38′ 52.4″	2° 51′ 53.2″	0° 17′ 11.3″	0° 01′ 43.1″
6	343° 46′ 28.8″	34° 22′ 38.9″	3° 26′ 15.9″	0° 20′ 37.6″	0° 02′ 03.8″
7	401° 04′ 13.6″	40° 06′ 25.4″	4° 00′ 38.5″	0° 24′ 03.9″	0° 02′ 24.4″
8	458° 21′ 58.4″	45° 50′ 11.8″	4° 35′ 01.2″	0° 27′ 30.1″	0° 02′ 45.0″
9	515° 39′ 43.3″	51° 33′ 58.3″	5° 09′ 23.8″	0° 30′ 56.4″	0° 03′ 05.6″

(iv) Natural Trigonometric Functions

For degrees shown in the left hand column use the column headings at the top. For degrees shown in the right hand column use the column headings at the bottom.

Deg.	Rad	Sin	Cos	Tan	Ctn	Sec	Csc		
0	0.0000	0.0000	1.0000	0.0000	------	1.0000	------	1.5708	90
1	0.0175	0.0175	0.9998	0.0175	57.290	1.0002	57.299	1.5533	89
2	0.0349	0.0349	0.9994	0.0349	28.636	1.0006	28.654	1.5359	88
3	0.0524	0.0523	0.9986	0.0524	19.081	1.0014	19.107	1.5184	87
4	0.0698	0.0698	0.9976	0.0699	14.301	1.0024	14.336	1.5010	86
5	0.0873	0.0872	0.9962	0.0875	11.430	1.0038	11.474	1.4835	85
6	0.1047	0.1045	0.9945	0.1051	9.5144	1.0055	9.5668	1.4661	84
7	0.1222	0.1219	0.9925	0.1228	8.1443	1.0075	8.2055	1.4486	83
8	0.1396	0.1392	0.9903	0.1405	7.1154	1.0098	7.1853	1.4312	82
9	0.1571	0.1564	0.9877	0.1584	6.3138	1.0125	6.3925	1.4137	81
10	0.1745	0.1736	0.9848	0.1763	5.6713	1.0154	5.7588	1.3963	80
11	0.1920	0.1908	0.9816	0.1944	5.1446	1.0187	5.2408	1.3788	79
12	0.2094	0.2079	0.9781	0.2126	4.7046	1.0223	4.8097	1.3614	78
13	0.2269	0.2250	0.9744	0.2309	4.3315	1.0263	4.4454	1.3439	77
14	0.2443	0.2419	0.9703	0.2493	4.0108	1.0306	4.1336	1.3265	76
15	0.2618	0.2588	0.9659	0.2679	3.7321	1.0353	3.8637	1.3090	75
16	0.2793	0.2756	0.9613	0.2867	3.4874	1.0403	3.6280	1.2915	74
17	0.2967	0.2924	0.9563	0.3057	3.2709	1.0457	3.4203	1.2741	73
18	0.3142	0.3090	0.9511	0.3249	3.0777	1.0515	3.2361	1.2566	72
19	0.3316	0.3256	0.9455	0.3443	2.9042	1.0576	3.0716	1.2392	71
20	0.3491	0.3420	0.9397	0.3640	2.7475	1.0642	2.9238	1.2217	70
21	0.3665	0.3584	0.9336	0.3839	2.6051	1.0711	2.7904	1.2043	69
22	0.3840	0.3746	0.9272	0.4040	2.4751	1.0785	2.6695	1.1868	68
23	0.4014	0.3907	0.9205	0.4245	2.3559	1.0864	2.5593	1.1694	67
24	0.4189	0.4067	0.9135	0.4452	2.2460	1.0946	2.4586	1.1519	66
25	0.4363	0.4226	0.9063	0.4663	2.1445	1.1034	2.3662	1.1345	65
26	0.4538	0.4384	0.8988	0.4877	2.0503	1.1126	2.2812	1.1170	64
27	0.4712	0.4540	0.8910	0.5095	1.9626	1.1223	2.2027	1.0996	63
28	0.4887	0.4695	0.8829	0.5317	1.8807	1.1326	2.1301	1.0821	62
29	0.5061	0.4848	0.8746	0.5543	1.8040	1.1434	2.0627	1.0647	61
30	0.5236	0.5000	0.8660	0.5774	1.7321	1.1547	2.0000	1.0472	60
31	0.5411	0.5150	0.8572	0.6009	1.6643	1.1666	1.9416	1.0297	59
32	0.5585	0.5299	0.8480	0.6249	1.6003	1.1792	1.8871	1.0123	58
33	0.5760	0.5446	0.8387	0.6494	1.5399	1.1924	1.8361	0.9948	57
34	0.5934	0.5592	0.8290	0.6745	1.4826	1.2062	1.7883	0.9774	56
35	0.6109	0.5736	0.8192	0.7002	1.4281	1.2208	1.7434	0.9599	55
36	0.6283	0.5878	0.8090	0.7265	1.3764	1.2361	1.7013	0.9425	54
37	0.6458	0.6018	0.7986	0.7536	1.3270	1.2521	1.6616	0.9250	53
38	0.6632	0.6157	0.7880	0.7813	1.2799	1.2690	1.6243	0.9076	52
39	0.6807	0.6293	0.7771	0.8098	1.2349	1.2868	1.5890	0.8901	51
40	0.6981	0.6428	0.7660	0.8391	1.1918	1.3054	1.5557	0.8727	50
41	0.7156	0.6561	0.7547	0.8693	1.1504	1.3250	1.5243	0.8552	49
42	0.7330	0.6691	0.7431	0.9004	1.1106	1.3456	1.4945	0.8378	48
43	0.7505	0.6820	0.7314	0.9325	1.0724	1.3673	1.4663	0.8203	47
44	0.7679	0.6947	0.7193	0.9657	1.0355	1.3902	1.4396	0.8029	46
45	0.7854	0.7071	0.7071	1.0000	1.0000	1.4142	1.4142	0.7854	45
		Cos	Sin	Ctn	Tan	Csc	Sec	Rad	Deg.

(v) Exponential and Hyperbolic Functions
(Values and Common Logarithms)

x	e^x Value	e^x Log$_{10}$	e^{-x} Value	Sinh x Value	Sinh x Log$_{10}$	Cosh x Value	Cosh x Log$_{10}$	Tanh x Value
0.00	1.0000	.00000	1.00000	0.0000	—∞	1.0000	.00000	.00000
0.01	1.0101	.00434	0.99005	0.0100	$\bar{2}$.00001	1.0001	.00002	.01000
0.02	1.0202	.00869	.98020	0.0200	$\bar{2}$.30106	1.0002	.00009	.02000
0.03	1.0305	.01303	.97045	0.0300	$\bar{2}$.47719	1.0005	.00020	.02999
0.04	1.0408	.01737	.96079	0.0400	$\bar{2}$.60218	1.0008	.00035	.03998
0.05	1.0513	.02171	.95123	0.0500	$\bar{2}$.69915	1.0013	.00054	.04996
0.06	1.0618	.02606	.94176	0.0600	$\bar{2}$.77841	1.0018	.00078	.05993
0.07	1.0725	.03040	.93239	0.0701	$\bar{2}$.84545	1.0025	.00106	.06989
0.08	1.0833	.03474	.92312	0.0801	$\bar{2}$.90355	1.0032	.00139	.07983
0.09	1.0942	.03909	.91393	0.0901	$\bar{2}$.95483	1.0041	.00176	.08976
0.10	1.1052	.04343	.90484	0.1002	$\bar{1}$.00072	1.0050	.00217	.09967
0.11	1.1163	.04777	.89583	0.1102	$\bar{1}$.04227	1.0061	.00262	.10956
0.12	1.1275	.05212	.88692	0.1203	$\bar{1}$.08022	1.0072	.00312	.11943
0.13	1.1388	.05646	.87809	0.1304	$\bar{1}$.11517	1.0085	.00366	.12927
0.14	1.1503	.06080	.86936	0.1405	$\bar{1}$.14755	1.0098	.00424	.13909
0.15	1.1618	.06514	.86071	0.1506	$\bar{1}$.17772	1.0113	.00487	.14889
0.16	1.1735	.06949	.85214	0.1607	$\bar{1}$.20597	1.0128	.00554	.15865
0.17	1.1853	.07383	.84366	0.1708	$\bar{1}$.23254	1.0145	.00625	.16838
0.18	1.1972	.07817	.83527	0.1810	$\bar{1}$.25762	1.0162	.00700	.17808
0.19	1.2092	.08252	.82696	0.1911	$\bar{1}$.28136	1.0181	.00779	.18775
0.20	1.2214	.08686	.81873	0.2013	$\bar{1}$.30392	1.0201	.00863	.19738
0.21	1.2337	.09120	.81058	0.2115	$\bar{1}$.32541	1.0221	.00951	.20697
0.22	1.2461	.09554	.80252	0.2218	$\bar{1}$.34592	1.0243	.01043	.21652
0.23	1.2586	.09989	.79453	0.2320	$\bar{1}$.36555	1.0266	.01139	.22603
0.24	1.2712	.10423	.78663	0.2423	$\bar{1}$.38437	1.0289	.01239	.23550
0.25	1.2840	.10857	.77880	0.2526	$\bar{1}$.40245	1.0314	.01343	.24492
0.26	1.2969	.11292	.77105	0.2629	$\bar{1}$.41986	1.0340	.01452	.25430
0.27	1.3100	.11726	.76338	0.2733	$\bar{1}$.43663	1.0367	.01564	.26362
0.28	1.3231	.12160	.75578	0.2837	$\bar{1}$.45282	1.0395	.01681	.27291
0.29	1.3364	.12595	.74826	0.2941	$\bar{1}$.46847	1.0423	.01801	.28213
0.30	1.3499	.13029	.74082	0.3045	$\bar{1}$.48362	1.0453	.01926	.29131
0.31	1.3634	.13463	.73345	0.3150	$\bar{1}$.49830	1.0484	.02054	.30044
0.32	1.3771	.13897	.72615	0.3255	$\bar{1}$.51254	1.0516	.02187	.30951
0.33	1.3910	.14332	.71892	0.3360	$\bar{1}$.52637	1.0549	.02323	.31852
0.34	1.4049	.14766	.71177	0.3466	$\bar{1}$.53981	1.0584	.02463	.32748
0.35	1.4191	.15200	.70469	0.3572	$\bar{1}$.55290	1.0619	.02607	.33638
0.36	1.4333	.15635	.69768	0.3678	$\bar{1}$.56564	1.0655	.02755	.34521
0.37	1.4477	.16069	.69073	0.3785	$\bar{1}$.57807	1.0692	.02907	.35399
0.38	1.4623	.16503	.68386	0.3892	$\bar{1}$.59019	1.0731	.03063	.36271
0.39	1.4770	.16937	.67706	0.4000	$\bar{1}$.60202	1.0770	.03222	.37136
0.40	1.4918	.17372	.67032	0.4108	$\bar{1}$.61358	1.0811	.03385	.37995
0.41	1.5068	.17806	.66365	0.4216	$\bar{1}$.62488	1.0852	.03552	.38847
0.42	1.5220	.18240	.65705	0.4325	$\bar{1}$.63594	1.0895	.03723	.39693
0.43	1.5373	.18675	.65051	0.4434	$\bar{1}$.64677	1.0939	.03897	.40532
0.44	1.5527	.19109	.64404	0.4543	$\bar{1}$.65738	1.0984	.04075	.41364
0.45	1.5683	.19543	.63763	0.4653	$\bar{1}$.66777	1.1030	.04256	.42190
0.46	1.5841	.19978	.63128	0.4764	$\bar{1}$.67797	1.1077	.04441	.43008
0.47	1.6000	.20412	.62500	0.4875	$\bar{1}$.68797	1.1125	.04630	.43820
0.48	1.6161	.20846	.61878	0.4986	$\bar{1}$.69779	1.1174	.04822	.44624
0.49	1.6323	.21280	.61263	0.5098	$\bar{1}$.70744	1.1225	.05018	.45422
0.50	1.6487	.21715	.60653	0.5211	$\bar{1}$.71692	1.1276	.05217	.46212

x	e^x		e^{-x}	Sinh x		Cosh x		Tanh x
	Value	Log$_{10}$	Value	Value	Log$_{10}$	Value	Log$_{10}$	Value
0.50	1.6487	.21715	.60653	0.5211	$\overline{1}$.71692	1.1276	.05217	.46212
0.51	1.6653	.22149	.60050	0.5324	$\overline{1}$.72624	1.1329	.05419	.46995
0.52	1.6820	.22583	.59452	0.5438	$\overline{1}$.73540	1.1383	.05625	.47770
0.53	1.6989	.23018	.58860	0.5552	$\overline{1}$.74442	1.1438	.05834	.48538
0.54	1.7160	.23452	.58275	0.5666	$\overline{1}$.75330	1.1494	.06046	.49299
0.55	1.7333	.23886	.57695	0.5782	$\overline{1}$.76204	1.1551	.06262	.50052
0.56	1.7507	.24320	.57121	0.5897	$\overline{1}$.77065	1.1609	.06481	.50798
0.57	1.7683	.24755	.56553	0.6014	$\overline{1}$.77914	1.1669	.06703	.51536
0.58	1.7860	.25189	.55990	0.6131	$\overline{1}$.78751	1.1730	.06929	.52267
0.59	1.8040	.25623	.55433	0.6248	$\overline{1}$.79576	1.1792	.07157	.52990
0.60	1.8221	.26058	.54881	0.6367	$\overline{1}$.80390	1.1855	.07389	.53705
0.61	1.8404	.26492	.54335	0.6485	$\overline{1}$.81194	1.1919	.07624	.54413
0.62	1.8589	.26926	.53794	0.6605	$\overline{1}$.81987	1.1984	.07861	.55113
0.63	1.8776	.27361	.53259	0.6725	$\overline{1}$.82770	1.2051	.08102	.55805
0.64	1.8965	.27795	.52729	0.6846	$\overline{1}$.83543	1.2119	.08346	.56490
0.65	1.9155	.28229	.52205	0.6967	$\overline{1}$.84308	1.2188	.08593	.57167
0.66	1.9348	.28664	.51685	0.7090	$\overline{1}$.85063	1.2258	.08843	.57836
0.67	1.9542	.29098	.51171	0.7213	$\overline{1}$.85809	1.2330	.09095	.58498
0.68	1.9739	.29532	.50662	0.7336	$\overline{1}$.86548	1.2402	.09351	.59152
0.69	1.9937	.29966	.50158	0.7461	$\overline{1}$.87278	1.2476	.09609	.59798
0.70	2.0138	.30401	.49659	0.7586	$\overline{1}$.88000	1.2552	.09870	.60437
0.71	2.0340	.30835	.49164	0.7712	$\overline{1}$.88715	1.2628	.10134	.61068
0.72	2.0544	.31269	.48675	0.7838	$\overline{1}$.89423	1.2706	.10401	.61691
0.73	2.0751	.31703	.48191	0.7966	$\overline{1}$.90123	1.2785	.10670	.62307
0.74	2.0959	.32138	.47711	0.8094	$\overline{1}$.90817	1.2865	.10942	.62915
0.75	2.1170	.32572	.47237	0.8223	$\overline{1}$.91504	1.2947	.11216	.63515
0.76	2.1383	.33006	.46767	0.8353	$\overline{1}$.92185	1.3030	.11493	.64108
0.77	2.1598	.33441	.46301	0.8484	$\overline{1}$.92859	1.3114	.11773	.64693
0.78	2.1815	.33875	.45841	0.8615	$\overline{1}$.93527	1.3199	.12055	.65271
0.79	2.2034	.34309	.45384	0.8748	$\overline{1}$.94190	1.3286	.12340	.65841
0.80	2.2255	.34744	.44933	0.8881	$\overline{1}$.94846	1.3374	.12627	.66404
0.81	2.2479	.35178	.44486	0.9015	$\overline{1}$.95498	1.3464	.12917	.66959
0.82	2.2705	.35612	.44043	0.9150	$\overline{1}$.96144	1.3555	.13209	.67507
0.83	2.2933	.36046	.43605	0.9286	$\overline{1}$.96784	1.3647	.13503	.68048
0.84	2.3164	.36481	.43171	0.9423	$\overline{1}$.97420	1.3740	.13800	.68581
0.85	2.3396	.36915	.42741	0.9561	$\overline{1}$.98051	1.3835	.14099	.69107
0.86	2.3632	.37349	.42316	0.9700	$\overline{1}$.98677	1.3932	.14400	.69626
0.87	2.3869	.37784	.41895	0.9840	$\overline{1}$.99299	1.4029	.14704	.70137
0.88	2.4109	.38218	.41478	0.9981	$\overline{1}$.99916	1.4128	.15009	.70642
0.89	2.4351	.38652	.41066	1.0122	0.00528	1.4229	.15317	.71139
0.90	2.4596	.39087	.40657	1.0265	0.01137	1.4331	.15627	.71630
0.91	2.4843	.39521	.40252	1.0409	.01741	1.4434	.15939	.72113
0.92	2.5093	.39955	.39852	1.0554	.02341	1.4539	.16254	.72590
0.93	2.5345	.40389	.39455	1.0700	.02937	1.4645	.16570	.73059
0.94	2.5600	.40824	.39063	1.0847	.03530	1.4753	.16888	.73522
0.95	2.5857	.41258	.38674	1.0995	.04119	1.4862	.17208	.73978
0.96	2.6117	.41692	.38289	1.1144	.04704	1.4973	.17531	.74428
0.97	2.6379	.42127	.37908	1.1294	.05286	1.5085	.17855	.74870
0.98	2.6645	.42561	.37531	1.1446	.05864	1.5199	.18181	.75307
0.99	2.6912	.42995	.37158	1.1598	.06439	1.5314	.18509	.75736
1.00	2.7183	.43429	.36788	1.1752	.07011	1.5431	.18839	.76159

x	e^x		e^{-x}	Sinh x		Cosh x		Tanh x
	Value	Log_{10}	Value	Value	Log_{10}	Value	Log_{10}	Value
1.00	2.7183	.43429	.36788	1.1752	.07011	1.5431	.18839	.76159
1.01	2.7456	.43864	.36422	1.1907	.07580	1.5549	.19171	.76576
1.02	2.7732	.44298	.36060	1.2063	.08146	1.5669	.19504	.76987
1.03	2.8011	.44732	.35701	1.2220	.08708	1.5790	.19839	.77391
1.04	2.8292	.45167	.35345	1.2379	.09268	1.5913	.20176	.77789
1.05	2.8577	.45601	.34994	1.2539	.09825	1.6038	.20515	.78181
1.06	2.8864	.46035	.34646	1.2700	.10379	1.6164	.20855	.78566
1.07	2.9154	.46470	.34301	1.2862	.10930	1.6292	.21197	.78946
1.08	2.9447	.46904	.33960	1.3025	.11479	1.6421	.21541	.79320
1.09	2.9743	.47338	.33622	1.3190	.12025	1.6552	.21886	.79688
1.10	3.0042	.47772	.33287	1.3356	.12569	1.6685	.22233	.80050
1.11	3.0344	.48207	.32956	1.3524	.13111	1.6820	.22582	.80406
1.12	3.0649	.48641	.32628	1.3693	.13649	1.6956	.22931	.80757
1.13	3.0957	.49075	.32303	1.3863	.14186	1.7093	.23283	.81102
1.14	3.1268	.49510	.31982	1.4035	.14720	1.7233	.23636	.81441
1.15	3.1582	.49944	.31664	1.4208	.15253	1.7374	.23990	.81775
1.16	3.1899	.50378	.31349	1.4382	.15783	1.7517	.24346	.82104
1.17	3.2220	.50812	.31037	1.4558	.16311	1.7662	.24703	.82427
1.18	3.2544	.51247	.30728	1.4735	.16836	1.7808	.25062	.82745
1.19	3.2871	.51681	.30422	1.4914	.17360	1.7957	.25422	.83058
1.20	3.3201	.52115	.30119	1.5095	.17882	1.8107	.25784	.83365
1.21	3.3535	.52550	.29820	1.5276	.18402	1.8258	.26146	.83668
1.22	3.3872	.52984	.29523	1.5460	.18920	1.8412	.26510	.83965
1.23	3.4212	.53418	.29229	1.5645	.19437	1.8568	.26876	.84258
1.24	3.4556	.53853	.28938	1.5831	.19951	1.8725	.27242	.84546
1.25	3.4903	.54287	.28650	1.6019	.20464	1.8884	.27610	.84828
1.26	3.5254	.54721	.28365	1.6209	.20975	1.9045	.27979	.85106
1.27	3.5609	.55155	.28083	1.6400	.21485	1.9208	.28349	.85380
1.28	3.5966	.55590	.27804	1.6593	.21993	1.9373	.28721	.85648
1.29	3.6328	.56024	.27527	1.6788	.22499	1.9540	.29093	.85913
1.30	3.6693	.56458	.27253	1.6984	.23004	1.9709	.29467	.86172
1.31	3.7062	.56893	.26982	1.7182	.23507	1.9880	.29842	.86428
1.32	3.7434	.57327	.26714	1.7381	.24009	2.0053	.30217	.86678
1.33	3.7810	.57761	.26448	1.7583	.24509	2.0228	.30594	.86925
1.34	3.8190	.58195	.26185	1.7786	.25008	2.0404	.30972	.87167
1.35	3.8574	.58630	.25924	1.7991	.25505	2.0583	.31352	.87405
1.36	3.8962	.59064	.25666	1.8198	.26002	2.0764	.31732	.87639
1.37	3.9354	.59498	.25411	1.8406	.26496	2.0947	.32113	.87869
1.38	3.9749	.59933	.25158	1.8617	.26990	2.1132	.32495	.88095
1.39	4.0149	.60367	.24908	1.8829	.27482	2.1320	.32878	.88317
1.40	4.0552	.60801	.24660	1.9043	.27974	2.1509	.33262	.88535
1.41	4.0960	.61236	.24414	1.9259	.28464	2.1700	.33647	.88749
1.42	4.1371	.61670	.24171	1.9477	.28952	2.1894	.34033	.88960
1.43	4.1787	.62104	.23931	1.9697	.29440	2.2090	.34420	.89167
1.44	4.2207	.62538	.23693	1.9919	.29926	2.2288	.34807	.89370
1.45	4.2631	.62973	.23457	2.0143	.30412	2.2488	.35196	.89569
1.46	4.3060	.63407	.23224	2.0369	.30896	2.2691	.35585	.89765
1.47	4.3492	.63841	.22993	2.0597	.31379	2.2896	.35976	.89958
1.48	4.3929	.64276	.22764	2.0827	.31862	2.3103	.36367	.90147
1.49	4.4371	.64710	.22537	2.1059	.32343	2.3312	.36759	.90332
1.50	4.4817	.65144	.22313	2.1293	.32823	2.3524	.37151	.90515

x	e^x		e^{-x}	Sinh x		Cosh x		Tanh x
	Value	Log$_{10}$	Value	Value	Log$_{10}$	Value	Log$_{10}$	Value
1.50	4.4817	.65144	.22313	2.1293	.32823	2.3524	.37151	.90515
1.51	4.5267	.65578	.22091	2.1529	.33303	2.3738	.37545	.90694
1.52	4.5722	.66013	.21871	2.1768	.33781	2.3955	.37939	.90870
1.53	4.6182	.66447	.21654	2.2008	.34258	2.4174	.38334	.91042
1.54	4.6646	.66881	.21438	2.2251	.34735	2.4395	.38730	.91212
1.55	4.7115	.67316	.21225	2.2496	.35211	2.4619	.39126	.91379
1.56	4.7588	.67750	.21014	2.2743	.35686	2.4845	.39524	.91542
1.57	4.8066	.68184	.20805	2.2993	.36160	2.5073	.39921	.91703
1.58	4.8550	.68619	.20598	2.3245	.36633	2.5305	.40320	.91860
1.59	4.9037	.69053	.20393	2.3499	.37105	2.5538	.40719	.92015
1.60	4.9530	.69487	.20190	2.3756	.37577	2.5775	.41119	.92167
1.61	5.0028	.69921	.19989	2.4015	.38048	2.6013	.41520	.92316
1.62	5.0531	.70356	.19790	2.4276	.38518	2.6255	.41921	.92462
1.63	5.1039	.70790	.19593	2.4540	.38987	2.6499	.42323	.92606
1.64	5.1552	.71224	.19398	2.4806	.39456	2.6746	.42725	.92747
1.65	5.2070	.71659	.19205	2.5075	.39923	2.6995	.43129	.92886
1.66	5.2593	.72093	.19014	2.5346	.40391	2.7247	.43532	.93022
1.67	5.3122	.72527	.18825	2.5620	.40857	2.7502	.43937	.93155
1.68	5.3656	.72961	.18637	2.5896	.41323	2.7760	.44341	.93286
1.69	5.4195	.73396	.18452	2.6175	.41788	2.8020	.44747	.93415
1.70	5.4739	.73830	.18268	2.6456	.42253	2.8283	.45153	.93541
1.71	5.5290	.74264	.18087	2.6740	.42717	2.8549	.45559	.93665
1.72	5.5845	.74699	.17907	2.7027	.43180	2.8818	.45966	.93786
1.73	5.6407	.75133	.17728	2.7317	.43643	2.9090	.46374	.93906
1.74	5.6973	.75567	.17552	2.7609	.44105	2.9364	.46782	.94023
1.75	5.7546	.76002	.17377	2.7904	.44567	2.9642	.47191	.94138
1.76	5.8124	.76436	.17204	2.8202	.45028	2.9922	.47600	.94250
1.77	5.8709	.76870	.17033	2.8503	.45488	3.0206	.48009	.94361
1.78	5.9299	.77304	.16864	2.8806	.45948	3.0492	.48419	.94470
1.79	5.9895	.77739	.16696	2.9112	.46408	3.0782	.48830	.94576
1.80	6.0496	.78173	.16530	2.9422	.46867	3.1075	.49241	.94681
1.81	6.1104	.78607	.16365	2.9734	.47325	3.1371	.49652	.94783
1.82	6.1719	.79042	.16203	3.0049	.47783	3.1669	.50064	.94884
1.83	6.2339	.79476	.16041	3.0367	.48241	3.1972	.50476	.94983
1.84	6.2965	.79910	.15882	3.0689	.48698	3.2277	.50889	.95080
1.85	6.3598	.80344	.15724	3.1013	.49154	3.2585	.51302	.95175
1.86	6.4237	.80779	.15567	3.1340	.49610	3.2897	.51716	.95268
1.87	6.4883	.81213	.15412	3.1671	.50066	3.3212	.52130	.95359
1.88	6.5535	.81647	.15259	3.2005	.50521	3.3530	.52544	.95449
1.89	6.6194	.82082	.15107	3.2341	.50976	3.3852	.52959	.95537
1.90	6.6859	.82516	.14957	3.2682	.51430	3.4177	.53374	.95624
1.91	6.7531	.82950	.14808	3.3025	.51884	3.4506	.53789	.95709
1.92	6.8210	.83385	.14661	3.3372	.52338	3.4838	.54205	.95792
1.93	6.8895	.83819	.14515	3.3722	.52791	3.5173	.54621	.95873
1.94	6.9588	.84253	.14370	3.4075	.53244	3.5512	.55038	.95953
1.95	7.0287	.84687	.14227	3.4432	.53696	3.5855	.55455	.96032
1.96	7.0993	.85122	.14086	3.4792	.54148	3.6201	.55872	.96109
1.97	7.1707	.85556	.13946	3.5156	.54600	3.6551	.56290	.96185
1.98	7.2427	.85990	.13807	3.5523	.55051	3.6904	.56707	.96259
1.99	7.3155	.86425	.13670	3.5894	.55502	3.7261	.57126	.96331
2.00	7.3891	.86859	.13534	3.6269	.55953	3.7622	.57544	.96403

(vi) Complete Elliptic Integrals for Different Values of k

$$K = \int_0^{\pi/2} dx / \sqrt{1-k^2 \sin^2 x} \; ; \quad E = \int_0^{\pi/2} \sqrt{1-k^2 \sin^2 x} \; dx$$

$\sin^{-1}k$	K	E
0°	1.5708	1.5708
1	1.5709	1.5707
2	1.5713	1.5703
3	1.5719	1.5697
4	1.5727	1.5689
5	1.5738	1.5678
6	1.5751	1.5665
7	1.5767	1.5649
8	1.5785	1.5632
9	1.5805	1.5611
10	1.5828	1.5589
11	1.5854	1.5564
12	1.5882	1.5537
13	1.5913	1.5507
14	1.5946	1.5476
15	1.5981	1.5442
16	1.6020	1.5405
17	1.6061	1.5367
18	1.6105	1.5326
19	1.6151	1.5283
20	1.6200	1.5238
21	1.6252	1.5191
22	1.6307	1.5141
23	1.6365	1.5090
24	1.6426	1.5037
25	1.6490	1.4981
26	1.6557	1.4924
27	1.6627	1.4864
28	1.6701	1.4803
29	1.6777	1.4740
30	1.6858	1.4675
31	1.6941	1.4608
32	1.7028	1.4539
33	1.7119	1.4469
34	1.7214	1.4397
35	1.7312	1.4323
36	1.7415	1.4248
37	1.7522	1.4171
38	1.7633	1.4092
39	1.7748	1.4013
40	1.7868	1.3931
41	1.7992	1.3849
42	1.8122	1.3765
43	1.8256	1.3680
44	1.8396	1.3594
45	1.8541	1.3506
46	1.8691	1.3418
47	1.8848	1.3329
48	1.9011	1.3238
49	1.9180	1.3147

$\sin^{-1}k$	K	E
50°	1.9356	1.3055
51	1.9539	1.2963
52	1.9729	1.2870
53	1.9927	1.2776
54	2.0133	1.2681
55	2.0347	1.2587
56	2.0571	1.2492
57	2.0804	1.2397
58	2.1047	1.2301
59	2.1300	1.2206
60	2.1565	1.2111
61	2.1842	1.2015
62	2.2132	1.1920
63	2.2435	1.1826
64	2.2754	1.1732
65	2.3088	1.1638
65.5	2.3261	1.1592
66.0	2.3439	1.1545
66.5	2.3622	1.1499
67.0	2.3809	1.1453
67.5	2.4001	1.1408
68.0	2.4198	1.1362
68.5	2.4401	1.1317
69.0	2.4610	1.1272
69.5	2.4825	1.1228
70.0	2.5046	1.1184
70.5	2.5273	1.1140
71.0	2.5507	1.1096
71.5	2.5749	1.1053
72.0	2.5998	1.1011
72.5	2.6256	1.0968
73.0	2.6521	1.0927
73.5	2.6796	1.0885
74.0	2.7081	1.0844
74.5	2.7375	1.0804
75.0	2.7681	1.0764
75.5	2.7998	1.0725
76.0	2.8327	1.0686
76.5	2.8669	1.0648
77.0	2.9026	1.0611
77.5	2.9397	1.0574
78.0	2.9786	1.0538
78.5	3.0192	1.0502
79.0	3.0617	1.0468
79.5	3.1064	1.0434
80.0	3.1534	1.0401
80.2	3.1729	1.0388
80.4	3.1928	1.0375
80.6	3.2132	1.0363
80.8	3.2340	1.0350

$\sin^{-1}k$	K	E
81°.0	3.2553	1.0338
81.2	3.2771	1.0326
81.4	3.2995	1.0314
81.6	3.3223	1.0302
81.8	3.3458	1.0290
82.0	3.3699	1.0278
82.2	3.3946	1.0267
82.4	3.4199	1.0256
82.6	3.4460	1.0245
82.8	3.4728	1.0234
83.0	3.5004	1.0223
83.2	3.5288	1.0213
83.4	3.5581	1.0202
83.6	3.5884	1.0192
83.8	3.6196	1.0182
84.0	3.6519	1.0172
84.2	3.6852	1.0163
84.4	3.7198	1.0153
84.6	3.7557	1.0144
84.8	3.7930	1.0135
85.0	3.8317	1.0127
85.2	3.8721	1.0118
85.4	3.9142	1.0110
85.6	3.9583	1.0102
85.8	4.0044	1.0094
86.0	4.0528	1.0086
86.2	4.1037	1.0079
86.4	4.1574	1.0072
86.6	4.2142	1.0065
86.8	4.2744	1.0059
87.0	4.3387	1.0053
87.2	4.4073	1.0047
87.4	4.4811	1.0041
87.6	4.5609	1.0036
87.8	4.6477	1.0031
88.0	4.7427	1.0026
88.2	4.8478	1.0021
88.4	4.9654	1.0017
88.6	5.0988	1.0014
88.8	5.2527	1.0010
89.0	5.4349	1.0008
89.1	5.5402	1.0006
89.2	5.6579	1.0005
89.3	5.7914	1.0004
89.4	5.9455	1.0003
89.5	6.1278	1.0002
89.6	6.3509	1.0001
89.7	6.6385	1.0001
89.8	7.0440	1.0000
89.9	7.7371	1.0000

(vii) Bessel Functions $J_0(x)$ and $J_1(x)$

$$J_0(x) = 1 - \left(\tfrac{x}{2}\right)^2 + \frac{\left(\tfrac{x}{2}\right)^4}{1^2 \cdot 2^2} - \frac{\left(\tfrac{x}{2}\right)^6}{1^2 \cdot 2^2 \cdot 3^2} + - \cdots$$

$$J_1(x) = -J_0'(x) = \frac{x}{2} - \frac{\left(\tfrac{x}{2}\right)^3}{1^2 \cdot 2} + \frac{\left(\tfrac{x}{2}\right)^5}{1^2 \cdot 2^2 \cdot 3} - + \cdots$$

$$J_n(x) = \sum_{k=0}^{\infty} \frac{(-1)^k x^{n+2k}}{2^{n+2k} k!(n+k)!} \quad (n = 0, 1, 2, 3, \ldots)$$

$J_0(x) = 0 : x = 2.405,\ 5.520,\ 8.654,\ 11.792,\ 14.931,\ 18.071,\ 21.212,\ 24.352.$

$J_1(x) = 0 : x = 3.832,\ 7.016,\ 10.173,\ 13.324,\ 16.471,\ 19.616$

x	$J_0(x)$	$J_1(x)$	x	$J_0(x)$	$J_1(x)$	x	$J_0(x)$	$J_1(x)$
0.0	1.0000	.0000	5.0	−.1776	−.3276	10.0	−.2459	.0435
0.1	.9975	.0499	5.1	−.1443	−.3371	10.1	−.2490	.0184
0.2	.9900	.0995	5.2	−.1103	−.3432	10.2	−.2496	−.0066
0.3	.9776	.1483	5.3	−.0758	−.3460	10.3	−.2477	−.0313
0.4	.9604	.1960	5.4	−.0412	−.3453	10.4	−.2434	−.0555
0.5	.9385	.2423	5.5	−.0068	−.3414	10.5	−.2366	−.0789
0.6	.9120	.2867	5.6	.0270	−.3343	10.6	−.2276	−.1012
0.7	.8812	.3290	5.7	.0599	−.3241	10.7	−.2161	−.1224
0.8	.8463	.3688	5.8	.0917	−.3110	10.8	−.2032	−.1422
0.9	.8075	.4059	5.9	.1220	−.2951	10.9	−.1881	−.1603
1.0	.7652	.4401	6.0	.1506	−.2767	11.0	−.1712	−.1768
1.1	.7196	.4709	6.1	.1773	−.2559	11.1	−.1528	−.1913
1.2	.6711	.4983	6.2	.2017	−.2329	11.2	−.1330	−.2039
1.3	.6201	.5220	6.3	.2238	−.2081	11.3	−.1121	−.2143
1.4	.5669	.5419	6.4	.2433	−.1816	11.4	−.0902	−.2225
1.5	.5118	.5579	6.5	.2601	−.1538	11.5	−.0677	−.2284
1.6	.4554	.5699	6.6	.2740	−.1250	11.6	−.0446	−.2320
1.7	.3980	.5778	6.7	.2851	−.0953	11.7	−.0213	−.2333
1.8	.3400	.5815	6.8	.2931	−.0652	11.8	.0020	−.2323
1.9	.2818	.5812	6.9	.2981	−.0349	11.9	.0250	−.2290
2.0	.2239	.5767	7.0	.3001	−.0047	12.0	.0177	−.2234
2.1	.1666	.5683	7.1	.2991	.0252	12.1	.0697	−.2157
2.2	.1104	.5560	7.2	.2951	.0543	12.2	.0908	−.2060
2.3	.0555	.5399	7.3	.2882	.0826	12.3	.1108	−.1943
2.4	.0025	.5202	7.4	.2786	.1096	12.4	.1296	−.1807
2.5	−.0484	.4971	7.5	.2663	.1352	12.5	.1469	−.1655
2.6	−.0968	.4708	7.6	.2516	.1592	12.6	.1626	−.1487
2.7	−.1424	.4416	7.7	.2346	.1813	12.7	.1766	−.1307
2.8	−.1850	.4097	7.8	.2154	.2014	12.8	.1887	−.1114
2.9	−.2243	.3754	7.9	.1944	.2192	12.9	.1988	−.0912
3.0	−.2601	.3391	8.0	.1717	.2346	13.0	.2069	−.0703
3.1	−.2921	.3009	8.1	.1475	.2476	13.1	.2129	−.0489
3.2	−.3202	.2613	8.2	.1222	.2580	13.2	.2167	−.0271
3.3	−.3443	.2207	8.3	.0960	.2657	13.3	.2183	−.0052
3.4	−.3643	.1792	8.4	.0692	.2708	13.4	.2177	.0166
3.5	−.3801	.1374	8.5	.0419	.2731	13.5	.2150	.0380
3.6	−.3918	.0955	8.6	.0146	.2728	13.6	.2101	.0590
3.7	−.3992	.0538	8.7	−.0125	.2697	13.7	.2032	.0791
3.8	−.4026	.0128	8.8	−.0392	.2641	13.8	.1943	.0984
3.9	−.4018	−.0272	8.9	−.0653	.2559	13.9	.1836	.1165
4.0	−.3971	−.0660	9.0	−.0903	.2453	14.0	.1711	.1334
4.1	−.3887	−.1033	9.1	−.1142	.2324	14.1	.1570	.1488
4.2	−.3766	−.1386	9.2	−.1367	.2174	14.2	.1414	.1626
4.3	−.3610	−.1719	9.3	−.1577	.2004	14.3	.1245	.1747
4.4	−.3423	−.2028	9.4	−.1768	.1816	14.4	.1065	.1850
4.5	−.3205	−.2311	9.5	−.1939	.1613	14.5	.0875	.1934
4.6	−.2961	−.2566	9.6	−.2090	.1395	14.6	.0679	.1999
4.7	−.2693	−.2791	9.7	−.2218	.1166	14.7	.0476	.2043
4.8	−.2404	−.2985	9.8	−.2323	.0928	14.8	.0271	.2066
4.9	−.2097	−.3147	9.9	−.2403	.0684	14.9	.0064	.2069

(viii) <u>Probability Functions</u>

$$\tfrac{1}{2}(1+\alpha) = \int_{-\infty}^{x} \phi(x)\,dx = \text{Area under } \phi(x) \text{ from } -\infty \text{ to } x,$$

$$\alpha = \int_{-x}^{x} \phi(x)\,dx, \quad \phi(x) = \frac{1}{\sqrt{2\pi}}\, e^{-\frac{x^2}{2}} = \text{Normal function}$$

$$\phi^{(2)}(x) = (x^2 - 1)\,\phi(x) \qquad = \text{Second derivative of } \phi(x).$$

$$\phi^{(3)}(x) = (3x - x^3)\,\phi(x) \qquad = \text{Third derivative of } \phi(x).$$

$$\phi^{(4)}(x) = (x^4 - 6x^2 + 3)\,\phi(x) \qquad = \text{Fourth derivative of } \phi(x).$$

x	$\tfrac{1}{2}(1+a)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$	x	$\tfrac{1}{2}(1+a)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$
0.00	.5000	.3989	−.3989	.0000	1.1968	0.50	.6915	.3521	−.2641	.4841	.5501
0.01	.5040	.3989	−.3989	.0120	1.1965	0.51	.6950	.3503	−.2592	.4895	.5279
0.02	.5080	.3989	−.3987	.0239	1.1956	0.52	.6985	.3485	−.2543	.4947	.5056
0.03	.5120	.3988	−.3984	.0359	1.1941	0.53	.7019	.3467	−.2493	.4996	.4831
0.04	.5160	.3986	−.3980	.0478	1.1920	0.54	.7054	.3448	−.2443	.5043	.4605
0.05	.5199	.3984	−.3975	.0597	1.1894	0.55	.7088	.3429	−.2392	.5088	.4378
0.06	.5239	.3982	−.3968	.0716	1.1861	0.56	.7123	.3410	−.2341	.5131	.4150
0.07	.5279	.3980	−.3960	.0834	1.1822	0.57	.7157	.3391	−.2289	.5171	.3921
0.08	.5319	.3977	−.3951	.0952	1.1778	0.58	.7190	.3372	−.2238	.5209	.3691
0.09	.5359	.3973	−.3941	.1070	1.1727	0.59	.7224	.3352	−.2185	.5245	.3461
0.10	.5398	.3970	−.3930	.1187	1.1671	0.60	.7257	.3332	−.2133	.5278	.3231
0.11	.5438	.3965	−.3917	.1303	1.1609	0.61	.7291	.3312	−.2080	.5309	.3000
0.12	.5478	.3961	−.3904	.1419	1.1541	0.62	.7324	.3292	−.2027	.5338	.2770
0.13	.5517	.3956	−.3889	.1534	1.1468	0.63	.7357	.3271	−.1973	.5365	.2539
0.14	.5557	.3951	−.3873	.1648	1.1389	0.64	.7389	.3251	−.1919	.5389	.2309
0.15	.5596	.3945	−.3856	.1762	1.1304	0.65	.7422	.3230	−.1865	.5411	.2078
0.16	.5636	.3939	−.3838	.1874	1.1214	0.66	.7454	.3209	−.1811	.5431	.1849
0.17	.5675	.3932	−.3819	.1986	1.1118	0.67	.7486	.3187	−.1757	.5448	.1620
0.18	.5714	.3925	−.3798	.2097	1.1017	0.68	.7517	.3166	−.1702	.5463	.1391
0.19	.5753	.3918	−.3777	.2206	1.0911	0.69	.7549	.3144	−.1647	.5476	.1164
0.20	.5793	.3910	−.3754	.2315	1.0799	0.70	.7580	.3123	−.1593	.5486	.0937
0.21	.5832	.3902	−.3730	.2422	1.0682	0.71	.7611	.3101	−.1538	.5495	.0712
0.22	.5871	.3894	−.3706	.2529	1.0560	0.72	.7642	.3079	−.1483	.5501	.0487
0.23	.5910	.3885	−.3680	.2634	1.0434	0.73	.7673	.3056	−.1428	.5504	.0265
0.24	.5948	.3876	−.3653	.2737	1.0302	0.74	.7704	.3034	−.1373	.5506	.0043
0.25	.5987	.3867	−.3625	.2840	1.0165	0.75	.7734	.3011	−.1318	.5505	−.0176
0.26	.6026	.3857	−.3596	.2941	1.0024	0.76	.7764	.2989	−.1262	.5502	−.0394
0.27	.6064	.3847	−.3566	.3040	0.9878	0.77	.7794	.2966	−.1207	.5497	−.0611
0.28	.6103	.3836	−.3535	.3138	0.9727	0.78	.7823	.2943	−.1153	.5490	−.0825
0.29	.6141	.3825	−.3504	.3235	0.9572	0.79	.7852	.2920	−.1098	.5481	−.1037
0.30	.6179	.3814	−.3471	.3330	0.9413	0.80	.7881	.2897	−.1043	.5469	−.1247
0.31	.6217	.3802	−.3437	.3423	0.9250	0.81	.7910	.2874	−.0988	.5456	−.1455
0.32	.6255	.3790	−.3402	.3515	0.9082	0.82	.7939	.2850	−.0933	.5440	−.1660
0.33	.6293	.3778	−.3367	.3605	0.8910	0.83	.7967	.2827	−.0880	.5423	−.1862
0.34	.6331	.3765	−.3330	.3693	0.8735	0.84	.7995	.2803	−.0825	.5403	−.2063
0.35	.6368	.3752	−.3293	.3779	0.8556	0.85	.8023	.2780	−.0771	.5381	−.2260
0.36	.6406	.3739	−.3255	.3864	0.8373	0.86	.8051	.2756	−.0718	.5358	−.2455
0.37	.6443	.3725	−.3216	.3947	0.8186	0.87	.8078	.2732	−.0664	.5332	−.2646
0.38	.6480	.3712	−.3176	.4028	0.7996	0.88	.8106	.2709	−.0611	.5305	−.2835
0.39	.6517	.3697	−.3135	.4107	0.7803	0.89	.8133	.2685	−.0558	.5276	−.3021
0.40	.6554	.3683	−.3094	.4184	0.7607	0.90	.8159	.2661	−.0506	.5245	−.3203
0.41	.6591	.3668	−.3059	.4259	0.7408	0.91	.8186	.2637	−.0453	.5212	−.3383
0.42	.6628	.3653	−.3008	.4332	0.7206	0.92	.8212	.2613	−.0401	.5177	−.3559
0.43	.6664	.3637	−.2965	.4403	0.7001	0.93	.8238	.2589	−.0350	.5140	−.3731
0.44	.6700	.3621	−.2920	.4472	0.6793	0.94	.8264	.2565	−.0299	.5102	−.3901
0.45	.6736	.3605	−.2875	.4539	0.6583	0.95	.8289	.2541	−.0248	.5062	−.4066
0.46	.6772	.3589	−.2830	.4603	0.6371	0.96	.8315	.2516	−.0197	.5021	−.4228
0.47	.6808	.3572	−.2783	.4666	0.6156	0.97	.8340	.2492	−.0147	.4978	−.4387
0.48	.6844	.3555	−.2736	.4727	0.5940	0.98	.8365	.2468	−.0098	.4933	−.4541
0.49	.6879	.3538	−.2689	.4785	0.5721	0.99	.8389	.2444	−.0049	.4887	−.4692

The sum of those terms of $(p+q)^n \equiv \sum\limits_{t=0}^{n} \binom{n}{t} p^{n-t} q^t$, $p+q=1$,

in which t ranges from a to b, inclusive, a and b being integers, $(a \leq t \leq b)$, is (if n is large enough) approximately

$$\int_{x_1}^{x_2} \Phi(x)\,dx + \left[\frac{q-p}{6\sigma} \Phi^{(2)}(x) + \frac{1}{24}\left(\frac{1}{\sigma^2} - \frac{6}{n} \right)\Phi^{(3)}(x) \right]_{x_1}^{x_2},$$

where $x_1 = (a - \tfrac{1}{2} - nq)/\sigma$, $x_2 = (b + \tfrac{1}{2} - nq)/\sigma$, $\sigma = \sqrt{npq}$.

x	$\frac{1}{2}(1+a)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$	x	$\frac{1}{2}(1+a)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$
1.00	.8413	.2420	.0000	.4839	−.4839	1.50	.9332	.1295	.1619	.1457	−.7043
1.01	.8438	.2396	.0048	.4790	−.4983	1.51	.9345	.1276	.1633	.1387	−.6994
1.02	.8461	.2371	.0096	.4740	−.5122	1.52	.9357	.1257	.1647	.1317	−.6942
1.03	.8485	.2347	.0143	.4688	−.5257	1.53	.9370	.1238	.1660	.1248	−.6888
1.04	.8508	.2323	.0190	.4635	−.5389	1.54	.9382	.1219	.1672	.1180	−.6831
1.05	.8531	.2299	.0236	.4580	−.5516	1.55	.9394	.1200	.1683	.1111	−.6772
1.06	.8554	.2275	.0281	.4524	−.5639	1.56	.9406	.1182	.1694	.1044	−.6710
1.07	.8577	.2251	.0326	.4467	−.5758	1.57	.9418	.1163	.1704	.0977	−.6646
1.08	.8599	.2227	.0371	.4409	−.5873	1.58	.9429	.1145	.1714	.0911	−.6580
1.09	.8621	.2203	.0414	.4350	−.5984	1.59	.9441	.1127	.1722	.0846	−.6511
1.10	.8643	.2179	.0458	.4290	−.6091	1.60	.9452	.1109	.1730	.0781	−.6441
1.11	.8665	.2155	.0500	.4228	−.6193	1.61	.9463	.1092	.1738	.0717	−.6368
1.12	.8686	.2131	.0542	.4166	−.6292	1.62	.9474	.1074	.1745	.0654	−.6293
1.13	.8708	.2107	.0583	.4102	−.6386	1.63	.9484	.1057	.1751	.0591	−.6216
1.14	.8729	.2083	.0624	.4038	−.6476	1.64	.9495	.1040	.1757	.0529	−.6138
1.15	.8749	.2059	.0664	.3973	−.6561	1.65	.9505	.1023	.1762	.0468	−.6057
1.16	.8770	.2036	.0704	.3907	−.6643	1.66	.9515	.1006	.1766	.0408	−.5975
1.17	.8790	.2012	.0742	.3840	−.6720	1.67	.9525	.0989	.1770	.0349	−.5891
1.18	.8810	.1989	.0780	.3772	−.6792	1.68	.9535	.0973	.1773	.0290	−.5806
1.19	.8830	.1965	.0818	.3704	−.6861	1.69	.9545	.0957	.1776	.0233	−.5720
1.20	.8849	.1942	.0854	.3635	−.6926	1.70	.9554	.0940	.1778	.0176	−.5632
1.21	.8869	.1919	.0890	.3566	−.6986	1.71	.9564	.0925	.1779	.0120	−.5542
1.22	.8888	.1895	.0926	.3496	−.7042	1.72	.9573	.0909	.1780	.0065	−.5452
1.23	.8907	.1872	.0960	.3425	−.7094	1.73	.9582	.0893	.1780	.0011	−.5360
1.24	.8925	.1849	.0994	.3354	−.7141	1.74	.9591	.0878	.1780	−.0042	−.5267
1.25	.8944	.1826	.1027	.3282	−.7185	1.75	.9599	.0863	.1780	−.0094	−.5173
1.26	.8962	.1804	.1060	.3210	−.7224	1.76	.9608	.0848	.1778	−.0146	−.5079
1.27	.8980	.1781	.1092	.3138	−.7259	1.77	.9616	.0833	.1777	−.0196	−.4983
1.28	.8997	.1758	.1123	.3065	−.7291	1.78	.9625	.0818	.1774	−.0245	−.4887
1.29	.9015	.1736	.1153	.2992	−.7318	1.79	.9633	.0804	.1772	−.0294	−.4789
1.30	.9032	.1714	.1182	.2918	−.7341	1.80	.9641	.0790	.1769	−.0341	−.4692
1.31	.9049	.1691	.1211	.2845	−.7361	1.81	.9649	.0775	.1765	−.0388	−.4593
1.32	.9066	.1669	.1239	.2771	−.7376	1.82	.9656	.0761	.1761	−.0433	−.4494
1.33	.9082	.1647	.1267	.2697	−.7388	1.83	.9664	.0748	.1756	−.0477	−.4395
1.34	.9099	.1626	.1293	.2624	−.7395	1.84	.9671	.0734	.1751	−.0521	−.4295
1.35	.9115	.1604	.1319	.2550	−.7399	1.85	.9678	.0721	.1746	−.0563	−.4195
1.36	.9131	.1582	.1344	.2476	−.7400	1.86	.9686	.0707	.1740	−.0605	−.4095
1.37	.9147	.1561	.1369	.2402	−.7396	1.87	.9693	.0694	.1734	−.0645	−.3995
1.38	.9162	.1539	.1392	.2328	−.7389	1.88	.9699	.0681	.1727	−.0685	−.3894
1.39	.9177	.1518	.1415	.2254	−.7378	1.89	.9706	.0669	.1720	−.0723	−.3793
1.40	.9192	.1497	.1437	.2180	−.7364	1.90	.9713	.0656	.1713	−.0761	−.3693
1.41	.9207	.1476	.1459	.2107	−.7347	1.91	.9719	.0644	.1705	−.0797	−.3592
1.42	.9222	.1456	.1480	.2033	−.7326	1.92	.9726	.0632	.1697	−.0832	−.3492
1.43	.9236	.1435	.1500	.1960	−.7301	1.93	.9732	.0620	.1688	−.0867	−.3392
1.44	.9251	.1415	.1519	.1887	−.7274	1.94	.9738	.0608	.1679	−.0900	−.3292
1.45	.9265	.1394	.1537	.1815	−.7243	1.95	.9744	.0596	.1670	−.0933	−.3192
1.46	.9279	.1374	.1555	.1742	−.7209	1.96	.9750	.0584	.1661	−.0964	−.3093
1.47	.9292	.1354	.1572	.1670	−.7172	1.97	.9756	.0573	.1651	−.0994	−.2994
1.48	.9306	.1334	.1588	.1599	−.7132	1.98	.9761	.0562	.1641	−.1024	−.2895
1.49	.9319	.1315	.1604	.1528	−.7089	1.99	.9767	.0551	.1630	−.1052	−.2797

The sum of the first $(t + 1)$ terms of

$$(p + q)^n \equiv \sum_{t=0}^{n} \binom{n}{t} p^{n-t} q^{t}, \quad p + q = 1, \text{ is approximately,}$$

$$\int_{x}^{\infty} \Phi(x) \, dx + \frac{q - p}{6\sigma} \Phi^{(2)}(x) - \frac{1}{24} \left(\frac{1}{\sigma^2} - \frac{6}{n} \right) \Phi^{(3)}(x).$$

where $x = (s - \frac{1}{2} - np)/\sigma$, $s = n - t$. The sum of the last $(s + 1)$ terms is approximately

$$\int_{x}^{\infty} \Phi(x) \, dx - \frac{q - p}{6\sigma} \Phi^{(2)}(x) - \frac{1}{24} \left(\frac{1}{\sigma^2} - \frac{6}{n} \right) \Phi^{(3)}(x),$$

where $x = (t - \frac{1}{2} - nq)/\sigma$, $t = n - s$, $\sigma = \sqrt{npq}$.

x	$\frac{1}{2}(1+\alpha)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$	x	$\frac{1}{2}(1+\alpha)$	$\Phi(x)$	$\Phi^{(2)}(x)$	$\Phi^{(3)}(x)$	$\Phi^{(4)}(x)$
2.00	.9772	.0540	.1620	−.1080	−.2700	2.50	.9938	.0175	.0920	−.1424	.0800
2.01	.9778	.0529	.1609	−.1106	−.2603	2.51	.9940	.0171	.0906	−.1416	.0836
2.02	.9783	.0519	.1598	−.1132	−.2506	2.52	.9941	.0167	.0892	−.1408	.0871
2.03	.9788	.0508	.1586	−.1157	−.2411	2.53	.9943	.0163	.0878	−.1399	.0905
2.04	.9793	.0498	.1575	−.1180	−.2316	2.54	.9945	.0158	.0864	−.1389	.0937
2.05	.9798	.0488	.1563	−.1203	−.2222	2.55	.9946	.0154	.0850	−.1380	.0968
2.06	.9803	.0478	.1550	−.1225	−.2129	2.56	.9948	.0151	.0836	−.1370	.0998
2.07	.9808	.0468	.1538	−.1245	−.2036	2.57	.9949	.0147	.0823	−.1360	.1027
2.08	.9812	.0459	.1526	−.1265	−.1945	2.58	.9951	.0143	.0809	−.1350	.1054
2.09	.9817	.0449	.1513	−.1284	−.1854	2.59	.9952	.0139	.0796	−.1339	.1080
2.10	.9821	.0440	.1500	−.1302	−.1765	2.60	.9953	.0136	.0782	−.1328	.1105
2.11	.9826	.0431	.1487	−.1320	−.1676	2.61	.9955	.0132	.0769	−.1317	.1129
2.12	.9830	.0422	.1474	−.1336	−.1588	2.62	.9956	.0129	.0756	−.1305	.1152
2.13	.9834	.0413	.1460	−.1351	−.1502	2.63	.9957	.0126	.0743	−.1294	.1173
2.14	.9838	.0404	.1446	−.1366	−.1416	2.64	.9959	.0122	.0730	−.1282	.1194
2.15	.9842	.0395	.1433	−.1380	−.1332	2.65	.9960	.0119	.0717	−.1270	.1213
2.16	.9846	.0387	.1419	−.1393	−.1249	2.66	.9961	.0116	.0705	−.1258	.1231
2.17	.9850	.0379	.1405	−.1405	−.1167	2.67	.9962	.0113	.0692	−.1245	.1248
2.18	.9854	.0371	.1391	−.1416	−.1086	2.68	.9963	.0110	.0680	−.1233	.1264
2.19	.9857	.0363	.1377	−.1426	−.1006	2.69	.9964	.0107	.0668	−.1220	.1279
2.20	.9861	.0355	.1362	−.1436	−.0927	2.70	.9965	.0104	.0656	−.1207	.1293
2.21	.9864	.0347	.1348	−.1445	−.0850	2.71	.9966	.0101	.0644	−.1194	.1306
2.22	.9868	.0339	.1333	−.1453	−.0774	2.72	.9967	.0099	.0632	−.1181	.1317
2.23	.9871	.0332	.1319	−.1460	−.0700	2.73	.9968	.0096	.0620	−.1168	.1328
2.24	.9875	.0325	.1304	−.1467	−.0626	2.74	.9969	.0093	.0608	−.1154	.1338
2.25	.9878	.0317	.1289	−.1473	−.0554	2.75	.9970	.0091	.0597	−.1141	.1347
2.26	.9881	.0310	.1275	−.1478	−.0484	2.76	.9971	.0088	.0585	−.1127	.1356
2.27	.9884	.0303	.1260	−.1483	−.0414	2.77	.9972	.0086	.0574	−.1114	.1363
2.28	.9887	.0297	.1245	−.1486	−.0346	2.78	.9973	.0084	.0563	−.1100	.1369
2.29	.9890	.0290	.1230	−.1490	−.0279	2.79	.9974	.0081	.0552	−.1087	.1375
2.30	.9893	.0283	.1215	−.1492	−.0214	2.80	.9974	.0079	.0541	−.1073	.1379
2.31	.9896	.0277	.1200	−.1494	−.0150	2.81	.9975	.0077	.0531	−.1059	.1383
2.32	.9898	.0270	.1185	−.1495	−.0088	2.82	.9976	.0075	.0520	−.1045	.1386
2.33	.9901	.0264	.1170	−.1496	−.0027	2.83	.9977	.0073	.0510	−.1031	.1389
2.34	.9904	.0258	.1155	−.1496	.0033	2.84	.9977	.0071	.0500	−.1017	.1390
2.35	.9906	.0252	.1141	−.1495	.0092	2.85	.9978	.0069	.0490	−.1003	.1391
2.36	.9909	.0246	.1126	−.1494	.0149	2.86	.9979	.0067	.0480	−.0990	.1391
2.37	.9911	.0241	.1111	−.1492	.0204	2.87	.9979	.0065	.0470	−.0976	.1391
2.38	.9913	.0235	.1096	−.1490	.0258	2.88	.9980	.0063	.0460	−.0962	.1389
2.39	.9916	.0229	.1081	−.1487	.0311	2.89	.9981	.0061	.0451	−.0948	.1388
2.40	.9918	.0224	.1066	−.1483	.0362	2.90	.9981	.0060	.0441	−.0934	.1385
2.41	.9920	.0219	.1051	−.1480	.0412	2.91	.9982	.0058	.0432	−.0920	.1382
2.42	.9922	.0213	.1036	−.1475	.0461	2.92	.9982	.0056	.0423	−.0906	.1378
2.43	.9925	.0208	.1022	−.1470	.0508	2.93	.9983	.0055	.0414	−.0893	.1374
2.44	.9927	.0203	.1007	−.1465	.0554	2.94	.9984	.0053	.0405	−.0879	.1369
2.45	.9929	.0198	.0992	−.1459	.0598	2.95	.9984	.0051	.0396	−.0865	.1364
2.46	.9931	.0194	.0978	−.1453	.0641	2.96	.9985	.0050	.0388	−.0852	.1358
2.47	.9932	.0189	.0963	−.1446	.0683	2.97	.9985	.0048	.0379	−.0838	.1352
2.48	.9934	.0184	.0949	−.1439	.0723	2.98	.9986	.0047	.0371	−.0825	.1345
2.49	.9936	.0180	.0935	−.1432	.0762	2.99	.9986	.0046	.0363	−.0811	.1337

PROBABILITY FUNCTIONS

x	½(1+α)	Φ(x)	Φ⁽²⁾(x)	Φ⁽³⁾(x)	Φ⁽⁴⁾(x)	x	½(1+α)	Φ(x)	Φ⁽²⁾(x)	Φ⁽³⁾(x)	Φ⁽⁴⁾(x)
3.00	.9987	.0044	.0355	−.0798	.1330	3.50	.9998	.0009	.0098	−.0283	.0694
3.01	.9987	.0043	.0347	−.0785	.1321	3.51	.9998	.0008	.0095	−.0276	.0681
3.02	.9987	.0042	.0339	−.0771	.1313	3.52	.9998	.0008	.0093	−.0269	.0669
3.03	.9988	.0040	.0331	−.0758	.1304	3.53	.9998	.0008	.0090	−.0262	.0656
3.04	.9988	.0039	.0324	−.0745	.1294	3.54	.9998	.0008	.0087	−.0256	.0643
3.05	.9989	.0038	.0316	−.0732	.1285	3.55	.9998	.0007	.0085	−.0249	.0631
3.06	.9989	.0037	.0309	−.0720	.1275	3.56	.9998	.0007	.0082	−.0243	.0618
3.07	.9989	.0036	.0302	−.0707	.1264	3.57	.9998	.0007	.0080	−.0237	.0606
3.08	.9990	.0035	.0295	−.0694	.1254	3.58	.9998	.0007	.0078	−.0231	.0594
3.09	.9990	.0034	.0288	−.0682	.1243	3.59	.9998	.0006	.0075	−.0225	.0582
3.10	.9990	.0033	.0281	−.0669	.1231	3.60	.9998	.0006	.0073	−.0219	.0570
3.11	.9991	.0032	.0275	−.0657	.1220	3.61	.9998	.0006	.0071	−.0214	.0559
3.12	.9991	.0031	.0268	−.0645	.1208	3.62	.9999	.0006	.0069	−.0208	.0547
3.13	.9991	.0030	.0262	−.0633	.1196	3.63	.9999	.0005	.0067	−.0203	.0536
3.14	.9992	.0029	.0256	−.0621	.1184	3.64	.9999	.0005	.0065	−.0198	.0524
3.15	.9992	.0028	.0249	−.0609	.1171	3.65	.9999	.0005	.0063	−.0192	.0513
3.16	.9992	.0027	.0243	−.0598	.1159	3.66	.9999	.0005	.0061	−.0187	.0502
3.17	.9992	.0026	.0237	−.0586	.1146	3.67	.9999	.0005	.0059	−.0182	.0492
3.18	.9993	.0025	.0232	−.0575	.1133	3.68	.9999	.0005	.0057	−.0177	.0481
3.19	.9993	.0025	.0226	−.0564	.1120	3.69	.9999	.0004	.0056	−.0173	.0470
3.20	.9993	.0024	.0220	−.0552	.1107	3.70	.9999	.0004	.0054	−.0168	.0460
3.21	.9993	.0023	.0215	−.0541	.1093	3.71	.9999	.0004	.0052	−.0164	.0450
3.22	.9994	.0022	.0210	−.0531	.1080	3.72	.9999	.0004	.0051	−.0159	.0440
3.23	.9994	.0022	.0204	−.0520	.1066	3.73	.9999	.0004	.0049	−.0155	.0430
3.24	.9994	.0021	.0199	−.0509	.1053	3.74	.9999	.0004	.0048	−.0150	.0420
3.25	.9994	.0020	.0194	−.0499	.1039	3.75	.9999	.0004	.0046	−.0146	.0410
3.26	.9994	.0020	.0189	−.0488	.1025	3.76	.9999	.0003	.0045	−.0142	.0401
3.27	.9995	.0019	.0184	−.0478	.1011	3.77	.9999	.0003	.0043	−.0138	.0392
3.28	.9995	.0018	.0180	−.0468	.0997	3.78	.9999	.0003	.0042	−.0134	.0382
3.29	.9995	.0018	.0175	−.0458	.0983	3.79	.9999	.0003	.0041	−.0131	.0373
3.30	.9995	.0017	.0170	−.0449	.0969	3.80	.9999	.0003	.0039	−.0127	.0365
3.31	.9995	.0017	.0166	−.0439	.0955	3.81	.9999	.0003	.0038	−.0123	.0356
3.32	.9995	.0016	.0162	−.0429	.0941	3.82	.9999	.0003	.0037	−.0120	.0347
3.33	.9996	.0016	.0157	−.0420	.0927	3.83	.9999	.0003	.0036	−.0116	.0339
3.34	.9996	.0015	.0153	−.0411	.0913	3.84	.9999	.0003	.0034	−.0113	.0331
3.35	.9996	.0015	.0149	−.0402	.0899	3.85	.9999	.0002	.0033	−.0110	.0323
3.36	.9996	.0014	.0145	−.0393	.0885	3.86	.9999	.0002	.0032	−.0107	.0315
3.37	.9996	.0014	.0141	−.0384	.0871	3.87	.9999	.0002	.0031	−.0104	.0307
3.38	.9996	.0013	.0138	−.0376	.0857	3.88	.9999	.0002	.0030	−.0100	.0299
3.39	.9997	.0013	.0134	−.0367	.0843	3.89	.9999	.0002	.0029	−.0098	.0292
3.40	.9997	.0012	.0130	−.0359	.0829	3.90	1.0000	.0002	.0028	−.0095	.0284
3.41	.9997	.0012	.0127	−.0350	.0815	3.91	1.0000	.0002	.0027	−.0092	.0277
3.42	.9997	.0012	.0123	−.0342	.0801	3.92	1.0000	.0002	.0026	−.0089	.0270
3.43	.9997	.0011	.0120	−.0334	.0788	3.93	1.0000	.0002	.0026	−.0086	.0263
3.44	.9997	.0011	.0116	−.0327	.0774	3.94	1.0000	.0002	.0025	−.0084	.0256
3.45	.9997	.0010	.0113	−.0319	.0761	3.95	1.0000	.0002	.0024	−.0081	.0250
3.46	.9997	.0010	.0110	−.0311	.0747	3.96	1.0000	.0002	.0023	−.0079	.0243
3.47	.9997	.0010	.0107	−.0304	.0734	3.97	1.0000	.0002	.0022	−.0076	.0237
3.48	.9997	.0009	.0104	−.0297	.0721	3.98	1.0000	.0001	.0022	−.0074	.0230
3.49	.9998	.0009	.0101	−.0290	.0707	3.99	1.0000	.0001	.0021	−.0072	.0224

x	½(1+α)	Φ(x)	Φ⁽²⁾(x)	Φ⁽³⁾(x)	Φ⁽⁴⁾(x)	x	½(1+α)	Φ(x)	Φ⁽²⁾(x)	Φ⁽³⁾(x)	Φ⁽⁴⁾(x)
4.00	1.0000	.0001	.0020	−.0070	.0218	4.50	1.0000	.0000	.0003	−.0012	.0047
4.05	1.0000	.0001	.0017	−.0059	.0190	4.55	1.0000	.0000	.0003	−.0010	.0039
4.10	1.0000	.0001	.0014	−.0051	.0165	4.60	1.0000	.0000	.0002	−.0009	.0033
4.15	1.0000	.0001	.0012	−.0043	.0143	4.65	1.0000	.0000	.0002	−.0007	.0027
4.20	1.0000	.0001	.0010	−.0036	.0123	4.70	1.0000	.0000	.0001	−.0006	.0023
4.25	1.0000	.0000	.0008	−.0031	.0105	4.75	1.0000	.0000	.0001	−.0005	.0019
4.30	1.0000	.0000	.0007	−.0026	.0090	4.80	1.0000	.0000	.0001	−.0004	.0016
4.35	1.0000	.0000	.0006	−.0022	.0077	4.85	1.0000	.0000	.0001	−.0003	.0013
4.40	1.0000	.0000	.0005	−.0018	.0065	4.90	1.0000	.0000	.0001	−.0003	.0011
4.45	1.0000	.0000	.0004	−.0015	.0055	4.95	1.0000	.0000	.0000	−.0002	.0009

II BASIC CONCEPTS OF GENERAL PHYSICS AND CHEMISTRY

II.1, Units, Dimensions and Conversion Factors

* Standards and Units

  Length (l), Mass (m) and time (t) are the three fundamental
  quantities used to express other physical quantities. Standards
  for their measurement are fixed by convention and units of their
  measurement are chosen by convenience with reference to the
  standards.

* Table of commonly used systems of units and standards

	Length		Mass		Time	
	Standard	Unit	Standard	Unit	Standard	Unit
FPS system	Yard	Foot =1/3(Yard)	Pound	Pound	Mean Solar Day (Time between two transits of sun averaged over a year)	Second= 1/86400
CGS system	Metre	c.m. =1/100 (metre)	Kilogram	gram =1/1000 (kilogram)	Mean Solar Day	Second
MKS system	Metre	Metre	Kilogram	Kilogram	Mean Solar Day	Second

* Conversion Factors

  (a) Length

	Centimeter	Metre	Kilometer	Inch	Foot	Mile
1 Centimeter =	1	10^{-2}	10^{-5}	0.3937	3.28×10^{-2}	6.214×10^{-6}
1 Metre =	10^{-2}	1	10^{-3}	39.37	3.281	6.214×10^{-4}
1 Kilometer =	10^{5}	10^{3}	1	39370	3281	0.6214
1 Inch =	2.540	2.54×10^{-2}	2.54×10^{-5}	1	8.333×10^{-2}	1.578×10^{-5}
1 Foot =	30.48	0.3048	3.048×10^{-4}	12	1	1.894×10^{-4}
1 Mile =	1.609×10^{5}	1609	1.609	6.336×10^{4}	5280	1

Some other useful units of length are –

1 angstrom (A) $= 10^{-10}$ meter

1 X-unit $= 10^{-13}$ meter

1 Fermi $= 10^{-15}$ meter

1 Micron $= 10^{-6}$ meter

1 Millimicron $= 10^{-9}$ meter

1 light – year $= 9.46 \times 10^{15}$ meters

(b) Mass

	Gramme	Kilogram	Pound	Quintal	Tonne (Metric ton)	Milligram	Microgram	Ounce	AMU Atomic Mass Unit
1 Gramme =	1	10^{-3}	2.205×10^{-3}	10^{-5}	10^{-6}	10^3	10^6	3.527×10^{-2}	6.024×10^{23}
1 Kilogram =	10^3	1	2.205	1/100	10^{-3}	10^6	10^9	35.27	6.024×10^{26}
1 Pound =	453.6	0.4536	1	4.536×10^{-3}	4.536×10^{-4}	453.6×10^3	453.6×10^6	16	2.732×10^{26}
1 Quintal =	10^5	100	2.205×10^2	1	1/10	10^8	10^{11}	3527	6.024×10^{28}
1 Tonne (Metric Ton) =	10^6	1000	2.205×10^3	10	1	10^9	10^{12}	35270	6.024×10^{29}
1 Milligram =	10^{-3}	10^{-6}	2.205×10^{-6}	10^{-8}	10^{-9}	1	10^3	3.527×10^{-5}	6.024×10^{20}
1 Microgram =	10^{-6}	10^{-9}	2.205×10^{-9}	10^{-11}	10^{-12}	10^{-3}	1	3.527×10^{-8}	6.024×10^{17}
1 Ounce =	28.35	2.835×10^{-2}	6.250×10^{-2}	2.835×10^{-4}	2.835×10^{-5}	2.835×10^4	2.835×10^7	1	1.708×10^{25}
1 AMU (Atomic Mass Unit) =	1.660×10^{-24}	1.660×10^{-27}	3.660×10^{-27}	1.660×10^{-29}	1.660×10^{-30}	1.660×10^{-21}	1.660×10^{-18}	5.855×10^{-26}	1

(c) Time

	Year	Day	Hour	Second	Milli Second	Microsecond	Nanosecond
1 Year =	1	365.2	8.766×10^3	3.156×10^7	3.156×10^{10}	3.156×10^{13}	3.156×10^{16}
1 Day =	2.738×10^{-3}	1	24	8.640×10^4	8.640×10^7	8.640×10^{10}	8.640×10^{13}
1 Hour =	1.141×10^{-4}	1/24	1	3600	3.600×10^6	3.600×10^9	3.600×10^{12}
1 Second =	3.169×10^{-8}	1.157×10^{-5}	1/3600	1	10^3	10^6	10^9
1 Milli second =	3.169×10^{-11}	1.157×10^{-8}	2.778×10^{-7}	10^{-3}	1	10^3	10^6
1 Micro second =	3.169×10^{-14}	1.157×10^{-11}	2.778×10^{-10}	10^{-6}	10^{-3}	1	10^3
1 Nano second =	3.169×10^{-17}	1.157×10^{-14}	2.778×10^{-13}	10^{-9}	10^{-6}	10^{-3}	1

* Derived Units

    Units of physical quantities which are expressible in terms of
    mass, length and time in suitable combinations, are called derived
    units. An example is newton, ($=$Kg x Meter/Sec^2), the unit of force
    in M.K.S. system.

* Dimensions

    The exact combination of l, m and t that occurs in a physical
    quantity is called the Dimension of that quantity. For example,
    velocity has dimension (l t $^{-1}$). Pure numbers, logarithms,
    trigonometric and exponential functions, ratios of physical
    quantities (of the same dimensions) etc. are said to be dimension-
    less.

    All equations relating various physical quantities must be
    dimensionally consistent, i.e., the dimensions of physical quan-
    tities on both sides of the equality sign must match.

II.2 Mechanics

    Mechanics is the study of the motion of material bodies. A suitable
co-ordinate system for specifying positions and a reference event for
setting the origin of the time scale are needed for this study.

* Kinematics

    The velocity ($\vec{v}$) which is the rate of change of position ($\vec{r}$)
    and the acceleration ($\vec{a}$) which is the rate of change of $\vec{v}$ with
    respect to time are given by the following expressions for different
    co-ordinate systems,

$$\vec{v} = \begin{cases} \hat{i}\,\dfrac{dx}{dt} + \hat{j}\,\dfrac{dy}{dt} + \hat{k}\,\dfrac{dz}{dt} \quad \text{(cartesian)} \\[2mm] \hat{e}_r\,\dfrac{dr}{dt} + \hat{e}_\theta\, r\,\dfrac{d\theta}{dt} + \hat{e}_z\,\dfrac{dz}{dt} \quad \text{(cylindrical)} \\[2mm] \hat{e}_r\,\dfrac{dr}{dt} + \hat{e}_\theta\, r\,\dfrac{d}{dt} + \hat{e}_\varphi\, r\,\sin\theta\,\dfrac{d\varphi}{dt} \quad \text{(spherical polar)} \end{cases}$$

$$\vec{a} = \begin{cases} \hat{i}\,\dfrac{d^2x}{dt^2} + \hat{j}\,\dfrac{d^2y}{dt^2} + \hat{k}\,\dfrac{d^2z}{dt^2} \quad \text{(cartesian)} \\[2mm] \hat{e}_r\left[\dfrac{d^2r}{dt^2} - r\left(\dfrac{d\theta}{dt}\right)^2\right] + \hat{e}_\theta\left[r\,\dfrac{d^2\theta}{dt^2} + 2\,\dfrac{dr}{dt}\,\dfrac{d\theta}{dt}\right] + \hat{e}_z\,\dfrac{d^2z}{dt^2} \quad \text{(cylindrical)} \\[2mm] \hat{e}_r\left[\dfrac{d^2r}{dt^2} - r\left(\dfrac{d\theta}{dt}\right)^2 - r\,\sin^2\theta\left(\dfrac{d\varphi}{dt}\right)^2\right] + \hat{e}_\theta\left[r\,\dfrac{d^2\theta}{dt^2} + 2\,\dfrac{dr}{dt}\,\dfrac{d\theta}{dt}\right. \\[2mm] \left. - r\,\sin\theta\,\cos\theta\left(\dfrac{d\varphi}{dt}\right)^2\right] + \hat{e}_\varphi\left[r\,\sin\theta\,\dfrac{d^2\varphi}{dt^2} + 2\,r\,\cos\theta\,\dfrac{d\theta}{dt}\,\dfrac{d\varphi}{dt}\right. \\[2mm] \left. + 2\,\sin\theta\,\dfrac{dr}{dt}\,\dfrac{d\varphi}{dt}\right] \quad \text{(spherical polar)} \end{cases}$$

* **Motion with Uniform Velocity** $(\vec{v})$

$$\vec{r} = \vec{r}_0 + \vec{v}t$$

* **Motion with Uniform Acceleration** $(\vec{a})$

$$\vec{r} = \vec{r}_0 + \vec{v}_0 t + \frac{1}{2}\vec{a}t^2 \; ; \; \vec{v} = \vec{v}_0 + \vec{a}t$$
$$v^2 = v_0^2 + 2\vec{a}(\vec{r} - \vec{r}_0)$$

* **Momentum**

$$\vec{p} = m\vec{v}, \quad \text{(m is the mass)}.$$

* **Newton's Laws of Motion**

    (1) Every body continues in a state of rest or of uniform motion in a straight line unless it is compelled to change that state by forces impressed upon it.

    (2) The rate of change of momentum is proportional to the impressed force and is in the direction in which the force acts.

    (3) To every action, there is always opposed an equal reaction.

* **Inertial Frame**

    The frame of reference in which Newton's first law is valid is called an Inertial frame.

* **Force**

    From Newton's second law, the force is given by,

$$\vec{F} = \frac{d\vec{p}}{dt} = m\frac{d\vec{v}}{dt} = m\frac{d^2\vec{r}}{dt^2} \qquad \text{(Equation of motion)}$$

Unit of force in MKS system is a newton, the force which acting on one kilogram produces an acceleration of one meter per sec^2. In CGS system it is a dyne, which is the force acting on one gram produces acceleration of 1 cm/sec^2.

* **Law of Conservation of Momentum**

    If there is no applied force, the momentum of a particle remains constant.

* **Work Done by a Force**

    Work done on a particle by the action of a force which moves it from r_1 to r_2, is

$$W = \int_{r_1}^{r_2} \vec{F} \cdot d\vec{r}$$

* **Kinetic Energy**

$$E_K = \frac{1}{2}mv^2$$

It follows from the equation of motion that, $W = \frac{1}{2} m(v_2^2 - v_1^2) = E_{K_2} - E_{K_1}$
Thus, work done = change in kinetic energy. The MKS unit of work or energy is a joule which is the work done by a force of one Newton to produce a displacement of one meter. The CGS unit is an erg = 10^{-7} joule.

* **Conservative force and potential**

  If the force $\vec{F}$ is such that

  $$\text{Curl } \vec{F} = \vec{\nabla} \times \vec{F} = 0$$

  then the force is said to be conservative and it can be derived from a potential energy function $V(\vec{r})$ through the relation,

  $$F = -\text{grad } V(\vec{r}) = -\nabla V(\vec{r}).$$

* **Law of Conservation of Mechanical Energy**

  Total Energy $= E = \frac{1}{2} m v^2 + V(\vec{r}) = $ constant   (conservative forces).

* **Condition for Equilibrium for a Particle**

  The vector sum of the forces applied to a particle must be zero to produce equilibrium which at a particular position is stable, unstable or neutral depending upon whether the potential is a minimum, maximum or stationary respectively .

* **Circular Motion of a Particle**

  If the particle is moving with uniform speed v along a circle of radius R, the centripetal acceleration experienced by it is

  $$a_R = \frac{v^2}{R}$$

  corresponding to a centripetal force

  $$F_R = \frac{m v^2}{R}$$

  Centrifugal force is the reaction to this force and is experienced by the agency responsible for the circular motion.

  Angular velocity $\vec{\omega}$ about the centre of the circle is defined through the relation

  $$\vec{v} = \vec{\omega} \times \vec{R} \quad (\vec{v} \text{ is the instantaneous vector velocity of the particle})$$

For uniform motion on the circle, the angular velocity is given by

$$\omega = \frac{v}{R}$$

* Simple Harmonic Motion

When a particle is in uniform circular motion, the projection of this motion on a line in the plane of the circle is called simple harmonic motion. The displacement on the line as a function of time is given by,

$$x = R \cos (\omega t + \varphi)$$

$$= R \cos (2\pi \nu t + \varphi) = R \cos (\frac{2\pi}{T} t + \varphi)$$

R amplitude, ν = frequency, T = time period = $\frac{1}{\nu}$. If the force on a particle is of the form

$$\vec{F} = - k \vec{r}$$

the motion will be simple harmonic, with the frequency

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad .$$

* Centre of Mass

For a system of N particles of masses m_j at positions $\vec{r}_j$, j=1, 2,.,N, the position of the centre of mass is

$$\vec{R} = \frac{\sum_{j=1}^{N} m_j \vec{r}_j}{\sum_{j=1}^{N} m_j}$$

·For a continuous distribution of matter with total mass M

$$\vec{R} = \frac{1}{M} \int \vec{r} \, dm = \frac{1}{M} \int \rho(\vec{r}) d\tau, \; (\rho(\vec{r})=\text{density})$$

Two masses m_1 and m_2 separated by a distance d have their centre of mass at a distance d_1 from m_1 such that

$$d_1 = \frac{m_2}{m_1 + m_2} \, d$$

* Angular Momentum

The angular momentum of a particle of mass m_j moving with velocity $\vec{v}_j$ at the position $\vec{r}_j$ about the origin is

$$\vec{L}_j = \vec{r}_j \times m_j \vec{v}_j$$

The total angular momentum of an assembly of N particles about the origin is

$$= \sum_{j=1}^{N} \vec{L}_j = \sum_{j=1}^{N} m_j (\vec{\delta}_j \times d\vec{r}_j/dt)$$

* Rigid Body

An assembly of particles consitute a rigid body if the distance between any pair of them remains fixed.

* Moment of Inertia

If a rigid body rotates about an aixs with angular velocity then

$$\vec{L} = \mathbb{I} \vec{\omega}$$

where $\mathbb{I}$ is called moment of inertial tensor. Componentwise the above equation becomes

$$\vec{L} = \hat{i} \left[\omega_x I_{xx} - \omega_y I_{xy} - \omega_z I_{xz} \right]$$

$$+ \hat{j} \left[-\omega_x I_{yx} + \omega_y I_{yy} - \omega_z I_{yz} \right]$$

$$+ \hat{k} \left[-\omega_x I_{zx} - \omega_y I_{zy} + \omega_z I_{zz} \right]$$

I_{xx}, I_{yy} and I_{zz} are called the moments of inertia of the body about x, y and z axes respectively and I_{xy}, I_{yz}, I_{zx} etc. are called the products of inertia.

If the coordinate system is so chosen that the products of inertia vanish, the x, y and z axes are called the principal axes, and the corresponding moments of inertia are called principal moments of inertia.

Principal moments of inertia of common objects

Object	Axis	Moment of Inertia
Rod	Normal to length at centre	$m\dfrac{\ell^2}{12}$
	Normal to length at one end	$m\,\ell^{2}/3$
Rectangular Sheet, sides a and b	Through center, parallel to b	$m\,a^{2}/12$
	Through centre normal to the plane	$m\dfrac{a^2 + b^2}{12}$
Circular Sheet radius r	Normal to the plane through the center	$m\,r^{2}/2$
	Along any diameter	$m\,r^{2}/4$
Circular ring radii r_1, and r_2	Normal to the plane through the center	$m(r_1^2 + r_2^2)/2$
	Any diameter	$m(r_1^2 + r_2^2)/4$
Sphere of radius r	Any diameter	$\dfrac{2}{5} mr^2$
Right circular cylinder of radius r and length 1	Transverse diameter	$m\left(\dfrac{r^2}{4} + \dfrac{\ell^2}{12}\right)$

* **Parallel-axis theorem**

   If the moment of inertia of an object of mass M about an axis is I, then its moment of inertia about another axis parallel to the previous one and at a distance R is given by

$$I' = I + MR^2$$

* **Perpendicular-axis theorem**

   In a plane laminar object of negligible thickness the moment of inertia about an axis normal to the plane equals the sum of the moments of inertia about two mutually perpendicular axes which are in the plane of the object and which intersect at the point of intersection of the original axis and the plane of the lamina.

* **Rotational Kinetic energy**

$$K.E = \tfrac{1}{2}\,\vec{\omega} \cdot \vec{L}$$

When the axis of rotation coincides with one of the principal axes,

$$K.E. = \tfrac{1}{2} I\omega^2 \text{ (I the moment of inertia about that axis)}$$

* Torque

    For rotational motion, the role of force is played by Torque, which is defined as

$$\vec{T} = \vec{r} \times \vec{F}$$

The equation of motion of a rigid body about a fixed origin becomes

$$\frac{d}{dt}\vec{L} = \vec{T}$$

and the expression for infinitesimal work is $dW = \vec{T}.\ \vec{\omega}\ dt$.

* Elastic constants

    The various moduli of elasticity are defined as the ratio of stress to the appropriate strain. Stress is force per unit area. Strain is deformation expressed in a dimensionless manner, as defined below.

Young's modulus $\quad$ E or $Y = \dfrac{\text{Tensile Stress}}{\text{Linear Strain}}$

$\quad$ Tensile stress is tensile force per unit cross sectional area; linear strain is the change in length per unit length.

Shear modulus $\quad$ G or $\mu = \dfrac{\text{Shearing stress}}{\text{Shear Strain}}$
(Rigidity Modulus)

$\quad$ Shear strain is the difference between the displacements of two parallel planes in the medium divided by the perpendicular distance between them.

Bulk Modulus $\quad$ K $= \dfrac{\text{Compressional Stress}}{\text{Volume strain}}$

$\quad$ Compressional stress is pressure and volume strain is change of volume per unit volume, i.e., the negative of the change of density divided by the mean density.

    The following relations hold among the moduli in an isotropic medium:

$$Y = 3K(1 - 2\sigma) = 2\mu(1 + \sigma)$$

$$Y = \frac{9K\mu}{\mu + 3K}$$

Here σ is called <u>Poisson's ratio</u> .

Elastic limit is the stress beyond which strain is no longer proportional to stress. Breaking stress is the stress at which the sample will break.

For table of elastic moduli see **page 171**

* <u>Friction</u>

The coefficient of static friction is defined as

$$f_s = \frac{\text{magnitude of maximum frictional force}}{\text{magnitude of normal thrust}}$$

The coefficient of kinetic or sliding friction f_k is the same ratio after motion is established. In general $f_k < f_s$ for the same surface. f_s does not depend on the surface area of contact.

* <u>Miscellaneous Astronomical Constants</u>

Mean solar day	$= 86,400$ sec $= 1.0027379$ side-real day
Sidereal day	$= 86164.09054$ mean solar sec.
	$= 23$ hr 56 min 4.09054 sec. mean solar time
Mass of the earth	$= 5.975 \times 10^{24}$ kg.
Mass of the sun	$= 1.987 \times 10^{30}$ kg.
Mass of the moon	$= 7.343 \times 10^{22}$ kg.
Mean distance of the moon from earth	$= 384,400$ km.
Earth's orbital velocity	$= 18.5$ miles/sec
Gravitational constant G	$= 6.670 \times 10^{-8}$ dyne cm^2/gram^2
Acceleration of gravity g at equator	$= 978.0495$ cm/Sec^2
Sun's radius	$= 6.965 \times 10^{10}$ cm.
Sun's mean density	$= 1.41$ gm/cm^3
Earth's mean density	$= 5.52$ gm/cm^3
Escape velocity from earch	$= 11.3$ km/sec.

II.3 <u>Acoustics</u>

Acoustics deals with the study of sound waves, their production, transmission and effects.

* <u>Velocity of sound waves</u>

Sound waves are longitudinal and transverse elastic waves propagated through matter in all its forms with various degrees of effectiveness. In fluids they are longitudinal and the wave velocity is related to the adiabatic bulk modulus K and density ρ

$$v = \sqrt{\frac{K}{\rho}}$$

It depends upon temperature and usually decreases with rise in temperature.

* **The wave equation**

$$\nabla^2 u = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2}$$

where u is the departure from equilibrium of a local condition in the medium such as density, pressure, displacement etc.

* **Sinusoidal wave**

A sinusoidal (pure) sound wave is described by

$$u(x, t) = u_0 \sin(\omega t - kx)$$
$$= u_0 \sin 2\pi \left(v t - \frac{x}{\lambda}\right)$$
$$= u_0 \sin \frac{2\pi}{\lambda}(v t - x), \text{ etc.}$$

Wavelength λ and frequency ν are related by the equation

$$v = \lambda \nu .$$

* **Vibrating String**

If a uniform string (or wire) of density ρ per unit length is under a tension T, then the velocity of transverse waves on it is given by,

$$v = \sqrt{\frac{T}{\rho}}$$

If the total length is ℓ and it is fixed at both the ends, it can vibrate in several modes.

The frequencies of the various modes are given by

$$\nu_n = \frac{n}{2L} v = \frac{n}{2L}\sqrt{\frac{T}{\rho}} \; ; \; n = 1,2,3..$$

The wave lengths of the various modes are given by

$$\lambda_n = \frac{v}{\nu_n} = \frac{2L}{n} \quad ; \; n = 1,2,3,$$

These modes correspond to standing waves on the string, i.e. super-position of forward and backward travelling waves, and can be represented by

$$u_n(x,t) = u_0 \cos(2\pi \nu_n t) \cdot \cos\left(\frac{2\pi}{\lambda_n} x\right).$$

* **Velocity of Sound in Different Media:**

Medium	v in m/sec at 0°C	Medium	v in m/sec at 0°C
Air	331.45	Fresh water (25°C)	1493.2
CO_2	258.0 (low freq)	Sea water (25°C) (Salinity 3.6%)	1532.8
	268.61 (high freq)	Distilled water (25°C)	1500
Helium	970	Glycerin (22°C)	1986
H_2	1269.5	Methyl Alchohol	1130
N_2	337	Ethyl Alchohol	1207
O_2	317.2	Mercury	1450
Steam (100°C)	404.8	Aluminium	6420 (Longitudinal)
		Pyrex glass	5640 (")

* **Beats**

    The waxing and waning of sound due to superposition of two sound waves of equal amplitides but slightly different frequencies (v and $v+\Delta v$) is known as beats. The number (n) of beats per second is

$$n = 2\Delta v$$

* **Doppler Effect**

    When the source emitting sound waves and the observer are in relative motion (relative speed v_0 , medium stationary) the observed frequency v' is different from the frequency v emitted by the source. This is known as Doppler effect. Let v be the speed of sound in the stationary medium. Then,

$$v' = v\left(\frac{v+v_0}{v}\right) \quad \text{(observer moving toward the source)}$$

$$v' = v\left(\frac{v-v_0}{v}\right) \quad \text{(observer moving away from the source)}$$

$$v' = v\left(\frac{v}{v-v_0}\right) \quad \text{(Source moving toward the observer)}$$

$$v' = v\left(\frac{v}{v+v_0}\right) \quad \text{(Source moving away from the observer)}$$

If v_0 and v_s are the speeds of observer and source respectively with respect to the stationary medium, then

$$v' = v\left(\frac{v+v_0}{v-v_s}\right) \quad \text{(Source and observer moving toward each other)}$$

$$v' = v\left(\frac{v-v_0}{v+v_s}\right) \quad \text{(Source and observer moving away from each other)}$$

II.4 **Heat**

Heat is the energy associated with random motion of atoms and molecules in a substance. Dissipation of other forms of energy (mechanical, electrical etc) results in the appearance of heat in the system.

* **Calorie**

The unit of heat is

1 Calorie = 4.186 Joule = 4.186×10^7 ergs

* **Temperature**

Temperature is an index of the thermal state of a body (see also the thermodynamic definition) and it is measured by a thermometer. Celsius (International Scale) (°C), Fahrenheit (°F) and Kelvin (Absolute thermodynamic scale) (°K) are the three commonly used scales of temperature.

* **Conversion Equations**

$$T°C = \frac{5}{9} (T°F - 32)$$

$$T°K = T°C + 273.16$$

* **Ideal Gas Temperature**

This is measured by a constant volume gas thermometer and is defined by

$$T = 273.16°K \lim_{P_0 \to 0} \left(\frac{P}{P_0} \right)$$

P_0 is the pressure at the triple point of water and P is the measure at the temperature to be measured. The limit signifies that a gas becomes ideal at vanishingly small pressure.

The ideal gas scale and the Kelvin thermodynamic scale are identical in the range of temperatures in which a gas thermometer is used.

* **Thermal Expansion**

Rise of temperature of a substance leads to change in its size, usually an increase. This is called thermal expansion.

* **Coefficient of Linear Expansion**

$$\alpha = \frac{1}{\ell} \frac{\Delta \ell}{\Delta T}$$

where $\Delta \ell$ is the change in length ℓ due to a change ΔT in temperature

* Coefficients of Areal expansion β and Volume Expansion γ

$$\beta = \frac{1}{A}\frac{\Delta A}{\Delta T} \approx 2\alpha \quad , \qquad \gamma = \frac{1}{V}\frac{\Delta V}{\Delta T} \approx 3\alpha \ .$$

The coefficient α , β and γ are slowly varying functions of temperature, and are usually evaluated at room temperatures.

* Heat Capacity

$C_H = \frac{\Delta Q}{\Delta T}$, where temperature rises by ΔT when heat ΔQ is supplied.

* Specific Heat

$C_s = \frac{C_H}{m}$ where m is the mass of the body.

Heat that must be given to a body to raise its temperature from T_1, to T_2 is

$$Q = m \int_{T_i}^{T_2} C_s \, dT$$

Usually the specific heat C_S depends upon temperature.

* Thermal Conduction

When two parts of a body are at different temperatures there is a flow of heat from the hot to the cold region in the body. The heat flow per second across an imaginary surface of area   A is given by

$$Q = -KA \frac{dT}{dx}$$

where $\frac{dT}{dx}$ is the temperature gradient across the surface; and the constant K is called the thermal conductivity of the substance.

The unit of K is kilocalories per sec per meter per °C.

II.5 Electricity and Magnetism

Laws of Electrostatics
  (i) Like charges repel and unlike charges attract each other.
  (ii) Coulomb's law: The force between two charges q_1 and q_2 which
       are separated by the distance r satisfies the relation:
$$F = \gamma \frac{q_1 q_2}{r^2}$$
     γ depends upon the medium and the system of units.
  (iii) In a closed system, the total charge is conserved.

* Unit of Charge

The unit of charge is a coulomb. It is that charge which when

carried by each of two bodies placed at a distance r meters apart in vacuum produces a mutual repulsion of 8.9874 $r^{-2} \times 10^9$ newtons.

In the MKS system $\gamma = \frac{1}{4\pi\epsilon_0}$ in vacuum where $\epsilon_0 = 8.85415 \times 10^{-12}$ coul^2/nt-meter^2

In the CGS system $\gamma = 1$ in vacuum.

* Conductors and Insulators

Substances (like metals and alloys) in which electric charges can move around freely from one point to another are called conductors. Insulators are those in which this does not happen - glass, rubber and plastics etc. are examples of insulators.

* Electric Current

Where charges flow in a conductor, an electric current is said to exist in it. The MKS unit of current is an ampere. It is that current which when carried by each of two long parallel wires placed one meter apart produces a mutual attraction per unit length of 2×10^{-7} newton/meter (operational definition). This corresponds to a flow of one coulomb of charge per second across the cross section of each of the two wires.

* Electric Field

The field of force surrounding a charge or distribution of charges is called the electric field. The electric field strength $\vec{E}(\vec{\gamma})$ at a point $\vec{\gamma}$ is defined through the relation

$$\vec{F}(\vec{\gamma}) = q\vec{E}(\vec{\gamma})$$

where $\vec{F}(\vec{\gamma})$ is the force experienced by a test charge q placed at that point.

The relationship between electric field $\vec{E}(\vec{\gamma})$ and the charge density $\rho(\vec{\gamma})$, is

$$\vec{\nabla} \cdot \vec{E} = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = \frac{\rho}{\epsilon_0} \quad \text{(MKS system)}$$

$$= 4\pi\rho \quad \text{(CGS system)}$$

* Electrostatic Potential

Electrostatic potential $\phi(\vec{\gamma})$ is defined by

$$E = -\nabla\phi(\vec{\gamma}) = -\left(\frac{\partial\phi}{\partial x}\hat{i} + \frac{\partial\phi}{\partial y}\hat{j} + \frac{\partial\phi}{\partial z}\hat{k} \right)$$

$\phi(\vec{\gamma})$ is related to $\rho(\vec{\gamma})$ through

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2} = \nabla^2\phi = -\frac{\rho}{\epsilon_0}$$

(Poisson's equation in MKS system of units)

In charge-free space

$$\nabla^2 \phi = 0 \qquad \text{(Laplace's equation)}$$

* Electric field and potential for certain charge distributions (MKS system)

Nature of charge distribution	$\vec{E}(\vec{r})$	$\phi(\vec{r})$
1. Point Charge q ...	$\dfrac{q}{4\pi\epsilon_o r^2}\hat{e}_r$	$\dfrac{q}{4\pi\epsilon_o r}$
2. Line charge along z axis, charge per unit length n	$\dfrac{n}{2\pi\epsilon_o r}\hat{e}_r$	$-\dfrac{n}{2\pi\epsilon_o}\ln r$
3. Surface charge in xy plane, with charge density σ	$\dfrac{\sigma}{2\epsilon_o}\hat{e}_z$	$-\dfrac{\sigma}{2\epsilon_o}z$
4. Sphere of radius a, charge density ρ	$\begin{cases} \dfrac{\rho r}{3\epsilon_o}\hat{e}_r, & r < a \\[2mm] \dfrac{a^3}{3\epsilon_o r^2}\hat{e}_r, & r > a \end{cases}$	$\begin{cases} -\dfrac{\rho r^2}{6\epsilon_o} \\[2mm] \dfrac{a^3}{3\epsilon_o r} \end{cases}$
5. Solid cylinder of radius a, charge density ρ	$\begin{cases} \dfrac{\rho r}{2\epsilon_o}\hat{e}_r, & r > a \\[2mm] \dfrac{a^2}{2\epsilon_o r}\hat{e}_r, & r < a \end{cases}$	$\begin{cases} -\dfrac{\rho r^2}{4} \\[2mm] -\dfrac{\rho a^2}{2\epsilon_o}\ln r \end{cases}$
6. Inside a charged conductor	zero	The same as at the surface
7. A positive charge e and an equal negative charge −e separated by a small distance d along z axis at the origin (dipole).	$\dfrac{2ed\cos\theta}{r^3}\hat{e}_r$ $+\dfrac{ed\sin\theta}{r^3}\hat{e}_\theta$	$\dfrac{ed\cos\theta}{r^2}$

* ·Potential Difference

Potential difference between two points in an electrical circuit is defined as the work done per unit charge in taking a test charge through the circuit between these two points. It is measured in volts (=joule/coulomb).

* Ohm's Law

If a current I flows in a conductor due to application of a voltage V then, $I = \dfrac{V}{R}$ (Ohm's law).

R is called the resistance of the conductor. The unit of R is ohm (volt/ampere). $G = \dfrac{1}{R}$ is called the conductance of the conductor.

* Joule's law

The heat produced per second due to the passage of an electric current

through a conductor is

$$H = RI^2 = V^2/R$$

* Conductivity Tensor

   In terms of current density $\vec{J}(\vec{r})$ in a medium and the electric
field $\vec{E}(\vec{r})$, the general relationship equivalent to Ohm's Law is

$$\vec{J}(\vec{r}) = \sigma \vec{E}(\vec{r})$$

where σ is called the conductivity tensor.

* Resistances Connected in Series

$$R = R_1 + R_2 + \ldots\ldots + R_n \text{ (n resistors in series)}.$$

* Resistances Connected in Parallel

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} + \ldots\ldots + \frac{1}{R_n}$$

* Capacitance

   When a body acquires charge, its electrostatic potential changes.
The relationship between the potential V and charge Q is given by,

$$C = \frac{Q}{V}$$

where C is called the capacitance (or capacity) of the body. Usual
capacitors are parallel plate condensers, electrolytic condensers
etc.
Unit of capacity is a Farad (=coulomb/volt)

* Capacitors Connected in Series

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} + \ldots\ldots + \frac{1}{C_n}$$

* Capacitors Connected in Parallel

$$C = C_1 + C_2 + \ldots + C_n$$

* Dielectric Constant

   The introduction of an insulating medium between two bodies form-
ing a capacitor increases the capacity by a factor K, called the
dielectric constant of the insulator (also called dielectric medium).

$$K = \frac{\text{Capacitance of a parallel plate condenser with the medium between the plates}}{\text{Capacitance in vacuum}}$$

   The electric field strength (and also the potential) due to a
point charge q in a dielectric medium is different from that in

vacuum and is given by

$$\vec{E}(\vec{r}) = \frac{1}{4\pi\epsilon_o K} \; \frac{q}{r^2} \; \hat{e}_r$$

Dielectric constants of insulators

Insulator	K	Insulator	K
Vacuum	1.00000	Polyethelene	2.3
Air (Dry)	1.00054	Polystyrene	2.6
Water (pure)	78.0	Teflon	2.1
Mica	5.4	Neoprene	6.9
Amber	2.7	Paper	3.5
Fused Quartz	3.8	Titanium Dioxide	100.0

* **Energy stored in a capacitor**

     Electrical energy stored in a capacitor is

$$U_c = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2$$

* **Table of capacity of some capacitors (MKS system).**

Description	C
Sphere of radius a	$4\pi\epsilon_o \times Ka$
Circular Disc of radius a	$8\epsilon_o \times Ka$
Two spheres of radius a in contact	$4\pi\epsilon_o \times Ka \ln 2$
Parallel plate capacitor (plates of area A each placed at a distance d apart)	$\epsilon A/d$
Two coaxial cylinders of length l and radius a and b (b > a)	$2\pi\epsilon_o \, l/\left(\ln\frac{b}{a}\right)$
Concentric spherical shell (Radii a and b, a < b)	$4\pi\epsilon_o \dfrac{ab}{a-b}$

* **Field of magnetic induction (Magnetic field)**

     A field of magnetic induction (magnetic field) of strength $\vec{B}(\vec{r})$ is said to be present at $\vec{r}$ if a charge q moving with velocity $\vec{v}$ experiences a sidewise force $\vec{F}(\vec{r})$ at that point at right angles to $\vec{v}$, given by the relation

$$\vec{F}(\vec{r}) = q \; \vec{v} \times \vec{B}(\vec{r})$$

* **Ampere's law**

$\oint B.dl = \mu_o I$, for any closed path enclosing current I

* **Flux of magnetic induction**

     The flux of magnetic induction (or magnetic flux) ϕ_B through

a surface S is given by

$$\phi_B = \int \vec{B} \cdot \vec{dS} \qquad (\vec{dS} \text{ is an element of area}).$$

* Faraday's Law of Electromagnetic Induction

   When the flux of magnetic induction changes through a closed circuit, EMF is induced in it. The induced EMF $\mathcal{E}$ satisfies the relation

$$\mathcal{E} = - \frac{d\phi_B}{dt}$$

   Equivalently, if $\vec{E}$ is the electric field induced due to the change of flux,

$$\oint \vec{E} \cdot \vec{dl} = - \frac{d\phi_B}{dt}$$

   where the integral is over the closed loop.

* Lenz's Law

   The current due to the induced EMF flows in a direction such that it opposes the change that produced it. (The minus sign in Faraday's law arises from this).

* Inductance

   If the current I changes in a circuit, ϕ_B changes and hence an induced EMF ($\mathcal{E}$) appears in the circuit according to the relation

$$\mathcal{E} = -\frac{dI}{dt} L$$

L is called the inductance of the circuit and its unit is a henry (= volt. sec/amp.). The mutual inductance M between two conductors 1 and 2 is defined through the relation

$$\mathcal{E}_2 = - M \frac{dI_1}{dt}$$

* Energy Stored in an Inductor

$$U_L = \tfrac{1}{2} L I^2$$

* L-C-R Circuit

   If an alternating EMF of the form $E = E_0 (\sin \omega t)$ is applied to a circuit consisting of a resistance R, capacitance C and inductance L in series, the current in the circuit is given by

$$I = \frac{E_0}{\sqrt{R^2 + (L\omega - \frac{1}{c\omega})^2}} \sin(\omega t + \phi); \quad \tan\phi = \frac{L\omega - \frac{1}{c\omega}}{R}.$$

* Kirchhoff's Laws

   (1) The algebraic sum of currents flowing into any point in a network is zero. (2) The algebraic sum of the products of currents and resistances around any closed path in a network equals the algebraic sum of the EMFs present in that path.

* Lorentz Force (MKS system)

    The force experienced by a charge q moving in a combined electric field $\vec{E}$ and magnetic field $\vec{B}$ with a velocity $\vec{v}$ is given by

$$F = q \ (\vec{E} + \ \vec{v} \times \vec{B})$$

* Maxwell's Equations (MKS system)

$$\vec{\nabla} \times \vec{E} = - \frac{\partial \vec{B}}{\partial t}$$

$$\vec{\nabla} \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}$$

$$\vec{\nabla} \cdot \vec{D} = \rho$$

$$\vec{\nabla} \cdot \vec{B} = 0$$

For isotropic media, $D = \epsilon E$, $B = \mu H$. Here $\vec{J}$ and ρ are current and charge densities respectively.

* Boundary Conditions

    If $\hat{n}$ is unit normal to the boundary between media 1 and 2, then

1. $\hat{n} \times (\vec{E_2} - \vec{E_1}) = 0$
2. $\hat{n} \cdot (\vec{D_2} - \vec{D_1}) = \rho s$, ρs equals surface charge density at the Boundary.
3. $\hat{n} \times (\vec{H_2} - \vec{H_1}) = 0$
4. $\hat{n} \cdot (\vec{B_2} - \vec{B_1}) = 0$

* Energy Density of Electromagnetic Field (MKS system)

$$U = \tfrac{1}{2} \ (\vec{E} \cdot \vec{D} + \vec{H} \cdot \vec{B})$$

*. Scalar and Vector Potentials

    . Scalar potential is the electrostatic potential defined earlier. Vector potential is denoted by the symbol '$\vec{A}$'. They are related to electric and magnetic field through the equations

$$\vec{E} = - \frac{\partial \vec{A}}{\partial t} - \vec{\nabla} \phi$$

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

* Gauges

    A and ϕ defined above are not unique. If $\chi(\vec{r})$ is any arbitrary function of co-ordinates then $\vec{A}' = \vec{A} - \vec{\nabla} \chi$ and $\phi' = \phi + \frac{\partial}{\partial t} \chi$ lead to the same $\vec{E}$ and $\vec{B}$ as $\vec{A}$ and ϕ . This arbitrary parameter χ is called the gauge parameter and a specific choice of χ leads to a specific gauge.

* Lorentz Gauge

    Here is χ is chosen such that $\qquad \vec{\nabla} \cdot \vec{A} + \sqrt{\mu \epsilon}\ \dfrac{\partial \phi}{\partial t} = 0$

    The Maxwell's equations give (in the Lorentz gauge)

    $$\nabla^2 \vec{A} - \mu \epsilon \frac{\partial^2 \vec{A}}{\partial t^2} = -\mu \vec{J} \; ; \nabla^2 \phi - \mu \epsilon \frac{\partial^2 \phi}{\partial t^2} = -\rho/\epsilon.$$

* Electromagnetic Waves

    In a charge free, non-conducting medium,

    $$\nabla^2 \vec{E} = \mu \epsilon \frac{\partial^2 \vec{E}}{\partial t^2}$$

    $$\nabla^2 \vec{H} = \mu \epsilon \frac{\partial^2 \vec{H}}{\partial t^2}$$

    These refer to propagating electromagnetic waves whose velocity is $\dfrac{1}{\sqrt{\mu \epsilon}}$. For vacuum this velocity is $\dfrac{1}{\sqrt{\mu_0 \epsilon_0}}$ · c, the speed of light.

* Poynting Vector

    $$\vec{S} = \frac{1}{\mu_0} \quad (\vec{E} \times \vec{B})$$

    gives the flow of energy per unit time per unit area normal to the direction of propagation of waves.

* Poynting's Theorem

    $$\vec{\nabla} \cdot \vec{S} + \frac{\partial U}{\partial t} = 0$$

    Where the energy density $U = \frac{1}{2} (\vec{E} \cdot \vec{D} + \vec{H} \cdot \vec{B})$

* Magnetic Properties of Matter

    Magnetic properties of matter arise from the fact that the constituent charged particles have orbital and spin angular momenta. The major contribution comes from orbital motion and spin of the electrons. Both these motions result in magnetic dipole moments $\vec{\mu}$ which when placed in a field $\vec{B}$ experience a torque

    $$\vec{\tau} = \vec{\mu} \times \vec{B}$$

    and acquires the potential energy

    $$u = -\vec{\mu} \cdot \vec{B}$$

    The macroscopic magnetism in all its forms is a purely quantum effect, requiring use of quantum mechanics for explanation.

* Magnetization

    The magnetic moment per unit volume ($\vec{M}$) is called magnetization.

* Paramagnetic Substances

    When placed in an inhomogeneous magnetic field, these substances tend to move toward its stronger regions.

* Paramagnetic Susceptibility

The magnetization ($\vec{M}$) in a paramagnetic substance is related to applied field ($\vec{H}$) by the paramagnetic susceptibility χ_m

$$\vec{M} = \chi_m \vec{H} \text{ (Isotropic Medium)}$$

* Langevin's Formula for $\vec{M}$ (Paramagnetism)

$$\vec{M} = N \vec{\mu} \, \mathcal{L}\left(\frac{\mu H}{kT}\right)$$

Where N = number of atoms per unit volume,

μ = dipole moment of each atom,

k = Boltzman's constant

and Langevin's function $\mathcal{L}(x)$ is given by

$$\mathcal{L}(x) = \coth x - \frac{1}{x}$$

* Curie Law

For $H\mu \ll kT$, Langevin's formula leads to

$$\chi_m = \frac{N\mu^2}{3kT} = \frac{C}{T} \, , \quad C = \frac{N\mu^2}{3k}$$

* Quantum Mechanical Formula for M (Paramagnetism)

$$M = N\mu_B g J \, B_J\left(\frac{gJ\mu_B H}{kT}\right)$$

where μ_B = Bohr magneton   g = Lande' g factor, J is the total angular momentum quantum number and the Brillouin function

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

For x $\ll$ 1

$$\chi_m = NJ(J+1)\frac{g^2\mu_B^2}{3kT}$$

* Diamagnetic Substances

When placed in an inhomogenous magnetic field, these substances tend to move toward its weaker regions. This effect is present in all substances but it is so weak that it is often masked in paramagnetic and other substances. Microscopically, this effect arises due to the orbital motion of the electron.

* Langevin-Pauli Formula for Diamagnetic Susceptibility

$$\vec{M} = \vec{H}\chi$$

$$\chi = -\frac{Ne^2}{6mc^2} \sum \overline{r^2}$$

Where $\overline{r^2}$ is the mean square distance of the electron of charge e and mass m from the nucleus. The summation is over all the electrons.

* **Ferromagnetic Materials**

In these materials, magnetization is produced by cooperative action between groups or domains of collectively oriented molecules. These are characterized by the onset of spontaneous magnetization (in zero applied field) at temperatures $T < T_c$ where T_c is called Curie temperature.

* **Weiss Molecular Field**

Weiss assumed the existence of an internal field proportional to the magnetization in Ferromagnetic materials.

Then
$$M = \mu N \mathcal{L}\left(\frac{H_a + qM}{kT}\right)$$

where H_a is the applied field and q is a constant. $\mathcal{L}(x)$ is again the Langevin function.

For $T \leqslant T_c$ where $T_c = \frac{N\mu^2 q}{3k}$ one gets a non-vanishing solution for M.

* **Curie-Weiss Law**

If $T > T_c$, the susceptibility in the above case becomes

$$\chi = \frac{N\mu^2}{3k(T-T_c)} = \frac{C}{T-T_c}$$

* **Heisenberg Exchange Coupling**

Heisenberg replaces the molecular field assumption by the exchange coupling between pairs of atoms, a purely quantum mechanical concept. The problem is solved under approximations to yield

$$M = gNS\mu_B \, B_S(x)$$

where S is the spin, $x = \frac{gS\mu_B}{kT}(H + qM)$,

$$q = \frac{2zj}{Ng^2\mu_B^2}, \quad j = \text{exchange energy}, \quad z = \text{no of nearest neighbors}.$$

Also $B_S(x)$ is Brillouin function (see paramagnetism) and

$$T_c = \frac{2zjS(S+1)}{3k}, \quad \chi = \frac{4N\,B^2S(S+1)}{3k(T-T_c)} \text{ for } T > T_c.$$

* **Curie Temperature of Ferromagnetic Elements (in °C)**

Fe, 770; CO, 1131; Ni, 358; Gd, 16; and Dy, -168.

* **Antiferromagnetic Substances for Antiferromagnetic Susceptibility**

In these substances the magnetic ions can be divided into equivalent sublattices which become spontaneously magnetized in an antiparallel arrangement below some temperature T_c.

* **Van-Vleck's Result**

$$\chi = \frac{g^2 N \mu_B^2 \, S(S+1)}{3k(T+T_c)} = \frac{C}{(T+T_c)}$$

II.6 Optics

The study of the physical phenomena concerning light and the physical concepts that underlie their interpretation constitute the subject matter of optics.

* Laws of Geometrical Optics

  (i) Light travels in straight lines in a homogeneous medium, (Law of rectilinear propagation)

  (ii) Angle of incidence = Angle of reflection (Law of reflection)

  (iii) $\frac{\text{Sin } i}{\text{Sin } r} = n_{12}$ (Snell's law)

  (iv) The incident, reflected and refracted rays and the normal to the surface lie in one plane.

* Refractive Index

  The refractive index n_{12} of medium 2 with respect to that of medium 1 is the ratio of the velocity of light in medium 1 to that in medium 2. Generally the medium 1 is assumed to be vacuum and then the refractive index is denoted by n. It depends upon changes in the medium due to changes in pressure, temperature etc. and also on the wavelength (see later) of the light used.

Table of refractive indices (sodium light, temp.=20°C)

	Fused Quartz	1.458	Solutions	10%		1.348
	High-dispersion crown	1.520	of	20%		1.364
Glass	Light flint	1.575	sucrose	40%		1.400
	Heavy flint	1.650	in	60%		1.442
	Heaviest flint	1.890	water	85%		1.503
Water		1.333	Air (NTP)			1.0002926
Ethyl Alcohol		1.361	Carbon dioxide (NTP)			1.00045

* Fermat's Principle

  $$\delta \int n ds = 0$$

  for the actual path traversed by light. Thus the optical path (defined as the product of the refractive index and the distance traveled by light) can be minimum, stationary or maximum and it is reversible. An equivalent formulation is in terms of the time taken by light to traverse the path. This time should be an extremum.

* Image

  If a bundle of rays diverging (or appearing to diverge) from a point S is somehow changed into another bundle of rays which converge to or diverge from a different point S', then S' is said to be the image of S. It is real (or virtual) if the rays converge to (or

diverge from) it.

* Optical System

    A system of optical accessories like lenses, mirrors, prisms etc.
    can form images constitute an optical system.

* Axis of an Optical System

    This is defined as that line around which the system can be rotated
    arbitrarily without altering the object and the image.

* Focal Points

    Incident rays parallel to the axis converge to (or appear to diverge
    from) a point F_2 called secondary principal focus. Rays diverging from
    F_1, the primary focal point on the axis, emerge parallel to the axis.

* Conjugate Points

    Object and image points are interchangeable (reversibility of light)
    and they are called conjugate points.

* Principal Points

    These are the conjugate points for which the object size equals
    image size (i.e., unit lateral) magnification.

* Thin Optical Systems and the Optical Centre

    These are the systems for which the principal points coincide and
    this point is called the optical centre of the thin system.

* Magnifications

    Ratio of the size of the image to that of the object is called
    magnification. Lateral magnification (m) is the ratio of dimensions
    of image and the object measured perpendicular to the axis. Transverse
    magnification (β) is the ratio of the dimensions parallel to the axis
    and angular magnification (γ) is the ratio of angles subtended by
    the image and the object at the optical centre.

* Nodal Points

    These are conjugate points of unit angular magnification. They
    coincide with the optical centre for thin systems.

* Focal Lengths

    Distances of the foci from optical centres are called focal lengths.

* Gaussian Convention

    All distances are measured from the optical centre.

* Newtonian Convention

    All distances are measured from the focal points.

* Sign Convention

    In the formulae for conjugate points it is necessary to fix up the
    convention for the signs of various distances measured. For example
    focal lengths are considered positive for converging system and
    negative for diverging system, convex surfaces are taken to have a
    positive radius and so on.

* <u>Paraxial Rays</u>

    Rays which make small angles (u) (so that $\cos u \simeq 1$ and $\sin u \simeq u$) with the axis are called paraxial rays.

* <u>Paraxial Ray Theory</u>

    The theory of image formation which treats the paraxial rays as adequate description is called paraxial ray theory (First order theory). For the third order theory one must use $\cos u \simeq 1 - \dfrac{u^2}{2}$ and $\sin u \simeq u - \dfrac{u^3}{6}$ and this is usually used to describe the aberrations (defects) of the images.

* <u>Table of relations between conjugate points for some simple optical systems (paraxial ray theory).</u>

Description of the optical system	Focal length	Conjugate relations (Gaussian convention) s =object distance, s '=image distance	Lateral magnifi- cation m
Plane Mirror	∞	$s' = s$	1
Plane refracting surface of index n, viewed from a medium of index n'.	∞	$s' = \dfrac{n'}{n} s$	1
Spherical refracting surface (n), viewed from (n'). Radius of curvature r.	$\dfrac{n}{f} - \dfrac{n'}{f'} = \dfrac{n-n'}{r}$	$\dfrac{n}{s} + \dfrac{n'}{s'} = \dfrac{n-n'}{r} = \dfrac{n}{f}$	$\dfrac{r-s}{r+s'}$
Thin spherical mirror of radius r	$f = f' = -\dfrac{r}{2}$	$\dfrac{1}{s} + \dfrac{1}{s'} = -\dfrac{2}{r} = \dfrac{1}{f}$	$-\dfrac{s'}{s}$
Thin lens of refractive index n (placed in air) with r_1 and r_2 as radii of curvature	$\dfrac{1}{f} = (n-1)(\dfrac{1}{r_1} - \dfrac{1}{r_2}) = \dfrac{1}{f'}$ (Note that $f \neq f'$ if the media on both sides of the lens are not the same).	$\dfrac{1}{s} + \dfrac{1}{s'} = \dfrac{1}{f}$ (xx'=ff' in Newtonian convention)	$-\dfrac{s'}{s}$
Thick lens of refractive index n' with medium of index n to the left and that of index n" to the right. r_1 and r_2 are the two radii of curvature and 'd' is the distance between the points where the axis cuts the surfaces	$\dfrac{n}{f} = \dfrac{n}{f'} - \dfrac{n'}{f_1'} + \dfrac{n''}{f_2''} - \dfrac{n''d}{f_1'f_2''}$ where f_1, f_1' are focal lengths of the first surface and f_2, f_2'' are for the second surface and $\dfrac{n}{f_1} = \dfrac{n'}{f_1'}$, $\dfrac{n'}{f_2} = \dfrac{n''}{f_2''}$	$\dfrac{n}{s_1} + \dfrac{n'}{s_1'} = \dfrac{n'-n}{r_1}$ (first surface) $\dfrac{n'}{s_2'} + \dfrac{n''}{s_2''} = \dfrac{n''-n'}{r_2}$ (second surface) $\dfrac{n}{s} + \dfrac{n''}{s''} = \dfrac{n}{f} = \dfrac{n''}{f''}$ (over all)	$\dfrac{p-s''}{p+s}$ where $p = \dfrac{f''(n''-n)}{n''}$

* <u>Combination of thin lenses</u>

    The focal length f of a system having two thin lenses separated

by a distance d in air is

$$f = \frac{f_1 f_2}{f_1 + f_2 - d}$$

* Defects in Optical Systems

If an optical system is constructed by using the results of paraxial ray theory of image formation then it shows many defects out of which the following ones are important.

(1) Spherical Aberration: This arises due to the fact that all rays from the object point do not focus at a single point and the result is a blurred image.

(2) Coma: This defect gives rise to a comet like appearance for an object point located off the axis. The comet like image is formed on a plane perpendicular to the axis.

(3) Astigmatism: This defect is like coma except that the blurring of image is parallel to the axis. An optical system corrected for spherical aberration and coma shows this effect in a pronounced way. However all the three defects can be eliminated simultaneously and then a point object forms a point image.

(4) Curvature of the field: An optical system corrected for the above three defects may form a curved image for a plane extended object because the image points may not necessarily be in one plane.

(5) Chromatic Aberration: All the above defects may be corrected for light of a single colour but the optical system still shows the defects for other colours because the refractive index varies with colour. This gives rise to chromatic aberrations.

* Wave Optics

Light is a part of the electromagnetic radiation that can be studied through the use of Maxwell's equations. The study of light waves (with wavelengths λ, frequence ν and velocity $\lambda\nu$) constitutes the subject matter of wave optics.

* Approximate Ranges of Wavelengths of Various Radiations

Gamma rays	0.005-0.1 $\mathring{A}$
X-Rays	0.1-1000 $\mathring{A}$
Ultraviolet, Vacuum	1700$\mathring{A}$
Ultraviolet, far	1700-2200 $\mathring{A}$
Ultraviolet, near	2200-4000 $\mathring{A}$
Visible	4000-7500 $\mathring{A}$
Infrared	7500 $\mathring{A}$ - 15μ $\left(\mu = \text{micron}\right)$
Far infrared	15μ - 1mm
Microwave	1 mm - 1C cm

Beyond a wave length 10 cm, the radiation is conventionally termed radio waves.

* Wavelengths

The unit of measurement of λ is usually an Angstrom ($\mathring{A}$)= 10^{-8}cm. For visible light, λ varies from about 3800 $\mathring{A}$ (violet) to about

7200 Å (red). For a given colour λ varies in a certain range.
However for light of some particular colours emitted by certain
specific sources, λ has definite values. Standard wavelengths
are chosen from among some of these wavelengths.

Table of some standard sources with the wavelengths of
spectral lines emitted by them (Entries are in Angstroms).

Helium	Sodium	Hydrogen	Mercury	Calcium (Ionized)	Cadmium	Iron
6678.15		6562.82	5790.65		6438.47	5269.59
5875.62	5895.92	4861.33	5769.59	3968.47	5085.82	4307.91
5047.74	5889.95	4340.46	5460.74	3933.67	4799.92	
5015.67		4101.74	4916.04		4678.16	
4921.93			4358.35			
4713.14			4077.81			
4471.48			4046.56			
4437.55						
4387.93						

* Fraunhofer Lines

It is a basic law of spectroscopy that substances that emit
certain lines (spetral lines) when excited, can absorb strongly
these very lines, Thus absorption lines can also serve as standards
for wavelength and Fraunhofer lines are some standard absorption
lines that appear in the spectrum of the sun.

Table of most intense Frauhofer bands and lines (in Angstroms)

Designation	Wavelength(s)	Designation	Wavelength	Designation	Wavelength
A	7594 to 7621 (Band)	E_2	5269.541	f	4340.465
B	6867 to 6884 (Band)	b_1	5183.618	G	4307.906 (Emitted by Iron)
C	6562.816	b_2	5172.699		
	6276 to 6287	b_3	5168.901		
α	(Band)	b_4	5167.491 (Emitted by Iron)	g	4226.728
D_1	5895.923 (Emitted by Sodium)	c	4957.609	h	4101.735
		F	4861.327	H	3968.468
D_2	5889.953	d	4668.140	K	3933.666
D_3	5875.618	e	4383.547		

* Interference

When waves are superimposed, they produce the phenomenon of
Interference. Interference of light waves has many interesting appli-
cations.

Since wave propagation is a periodic phenomenon, the mathematical technique of Fourier Analysis can be used to decompose the wave in terms of pure sine and cosine waves (plane waves). Therefore it is adequate to study the interference of two sine (plane) waves.

* Interference Between Sine Waves

When two sine waves of same frequency ω, travelling with velocity V from two sources meet at a point which is at distances d_1 and d_2 respectively from the two sources, then the resultant amplitude

$$S = S_1 + S_2 = A_1 \sin\left[\omega\left(t - \frac{d_1}{v}\right) + \epsilon_1\right] + A_2 \sin\left[\omega\left(t - \frac{d_2}{v}\right) + \epsilon_2\right] = A \sin(\omega t - \delta)$$

where ϵ_1 and ϵ_2 are phase constants and

$$A^2 = A_1^2 + A_2^2 + 2 A_1 A_1 \cos\Delta$$

with $\Delta = \frac{2\pi}{\lambda}(d_1 - d_2) + (\epsilon_2 - \epsilon_1)$

The intensity which is proportional to A^2 varies between

$$(A_1 + A_2)^2 \text{ and } (A_1 - A_2)^2$$

* Coherent Sources

If the two sources are different or even different parts of an extended source, then ϵ_1 and ϵ_2 vary rapidly by arbitrary amounts and the time average of Δ is zero. Then the sources are said to be incoherent and there is no change in the intensity pattern. But if $(\epsilon_2 - \epsilon_1)$ is a constant at all times, then the sources and the waves are said to be coherent. Such coherent waves are obtained by the division of a single wave into two parts. This division can be achieved by (a) division of wave front or (b) division of amplitude.

* Interference Pattern

When the waves are coherent, the intensity varies from point to point because Δ is a function of $d_1 - d_2$. If $A_1 = A_2$ then one observes alternate dark and bright patterns called interference fringes.

* Huygen's Principle

This principle states that every point on the wavefront can be regarded as a centre of new disturbance and therefore a source of secondary wavelets. These secondary wavelets travelling with equal velocity are enveloped by a surface identical in its properties with the original wavefront. This is then the new wavefront. It is a simple but adequate approximation to the actual problem of light propagation in the presence of partially obstructing opaque objects.

Table of some arrangements for observing interference patterns

Description of the arrangement	Type of division of wave	Shape of the fringes	Fringe width (separation between two bright or two dark fringes for light of wavelength λ)
1. Fresnel Biprism: A thin double prism of angle α is placed in front of a slit at the distance D_1 along its axis and the pattern is observed at a distance D_2 from the thin biprism of refractive index n.	Division of wavefront	Parallel straight line fringes	$\dfrac{(D_1+D_2)\lambda}{2D_1(n-1)\alpha}$
2. Newton's rings: A plane convex lens of radius of curvature r and refractive index n is placed in contact with a plane glass plate with the plane surface of the lens parallel to the glass plate	Division of Amplitude	Circular·central fringe dark	Fringe width not constant. Separation between successive rings is $\lambda r(\sqrt{m+1}-\sqrt{m})$ Here m is an integer which is zero for the central dark ring
3. Michelson's Interferometer: Two highly polished mirrors M_1 and M_2 mounted on two arms at right angles with two plane parallel glass plates G_1 and G_2 at 45° to the arms placed at the junction are the essential parts of the arrangement. Light from the slit rendered parallel by a lens travels parallel to one arm and fringes are viewed through a lens L_2 in a direction parallel to the other arm. The back of one of	Division of Amplitude	All conic sections (like parabola, ellipse hyperbola, circles, straight lines). Circular and straight line fringes are specially interesting	$\dfrac{\lambda}{2\tan\theta}$ for straight line fringes (Localized fringes) These appear when $t \simeq 0$, $\varphi \neq 0$. For $t \neq 0$, $\varphi = 0$. One gets circular fringes whose radius $\propto \frac{1}{m}$ for large t. These fringes are formed at infinity and not localized.

Table of some arrangements for observing interference patterns (continued)

Description of the arrangement	Type of division of wave	Shape of the fringes	Fringe width (separation between two bright or two dark fringes for light of wavelength
the glass plates G_1 is slightly silvered. The image M_2' of M_2 seen from L_2 by reflection from G_1 makes an angle φ with M_1 and the mean distance of separation of the two is t.			
4. Fabry-Perot Interferometer: This utilizes the transmitted light from plane parallel plates, partially silvered and viewed through a focusing lens	Successive division of amplitude	Circular $2d \cos \varphi = n\lambda$ defines bright fringes	Fringe width varies.

* **Diffraction**

    The phenomenon of spreading of light into the region of geometrical shadow is called diffraction. On the basis of Huygen's principle, this can be looked upon as due to the interference among the secondary wavelets. The phenomena of diffraction can be broadly divided into the following two categories.

* **Fraunhofer Diffraction**

    In this type of diffraction the source of light and the screen on which the diffraction is observed are effectively at infinite distance from the aperture causing diffraction. This can be done, for example by placing the aperture and the screen at the foci of two converging lenses.

* **Fresnel Diffraction**

    In this case the source and the screen are at finite distances from the aperture. This is a mathematically complicated problem to analyse.

* **Table of Fraunhofer diffraction in a few cases**

Description of arrangement	Description of the diffraction pattern	Result for the Intensity at a point P on the screen
Single slit: Width is b. The P on the screen is at a distance x from the slit and the joining line makes an angle $\frac{\pi}{2}-\theta$ at P, with the screen	A central maximum followed by minima and other maxima with decreasing intensity. The pattern is symmetrical about the central maximum.	$I \propto A_o^2 \times \dfrac{\sin^2\beta}{\beta^2}$ where $\beta = \pi\, b\,\sin\theta$ And $A_o = \dfrac{b}{x}$
Double Slit: Each of width b with a distance d between their centres	The central maximum and neighbouring maxima become very intense but narrow. The pattern is again symmetrical.	$I \propto 4A_o^2\ \dfrac{\sin^2\beta}{\beta^2}\cos^2\gamma$ where $\gamma = \dfrac{\pi d}{\lambda}\sin\theta$
Diffraction Grating: N slits of width b each and equal separation d. For usual laboratory gratings $N \sim 1000$ lines/cm.	Well separated very intense and very narrow lines $d\sin\theta = m\lambda$ for these lines, m = 0 or integer	$I \propto A_o^2\ \dfrac{\sin^2\beta}{\beta^2}\ \dfrac{\sin^2 N\gamma}{\sin^2\gamma}$ (Note that this reduces to double slit formula for N = 2)

* **Polarised Light**

    Light which exhibits different properties in different directions at right angles to the line of propagation is called polarized light. Maxwell's equations show that an electromagnetic wave is a transverse wave and when it propagates, the $\vec{E}$ ($\vec{r}$) at different points ($\vec{r}$) are

parallel among themselves ($\vec{H}$ is perpendicular to $\vec{E}$ and both of these are perpendicular to the direction of propagation). The plane containing $\vec{E}$ ($\vec{r}$) and the line of propagation is called the plane of polarization.

Ordinary light, emitted by different atoms, is a mixture of waves whose planes of polarization are randomly oriented and it is said to be unpolarized. However on passing this light through anisotropic media like crystals (calcite for example), the transmitted light gets plane polarized.

* Malus's Law

A second calcite crystal can be placed parallel to the first crystal which transmits plane polarized light. If the intensity of the emergent light (I) is studied as a function of the angle of rotation of the second crystal, then Malus's law is found to hold good.

$$I = I_m \cos^2 \varphi$$

* Polarization by Ordinary Refraction and Brewster's Law

During ordinary refraction, for a specific angle of incidence θ_p (called Brewster's angle) the reflected and refracted rays are at right angles and if the incident ray is unpolarized the refracted ray is polarized in the plane of incidence and the reflected light is polarized perpendicular to this plane. If n is the refractive index, then

$$\tan \theta_p = n. \quad \text{(Brewster's law)}.$$

* Light Propagation in Anisotropic Media

Microscopically, reflection, transmission and absorption of light wave are the results of the scattering of light from elementary electric dipoles in the medium. In anisotropic media like crystals (cubic crystals are exceptions), these dipoles are arranged such that the electrical property of the medium is different in different directions. Thus the dielectric constant and hence the index of refraction are different in different directions. Then

$$\vec{D} = \epsilon \vec{E}$$

where ϵ is the dielectric tensor. It is always possible to find three mutually perpendicular axes called principal axes along which this equation reduces to

$$D_x = \epsilon_1 E_x, \quad D_y = \epsilon_2 E_y, \quad D_z = \epsilon_3 E_z$$

ϵ_1, ϵ_2 and ϵ_3 are principal dielectric constants and n_1, n_2 and n_3 are the corresponding refractive indices corresponding to velocities v_1, v_2 and v_3.

* Optic Axes

   If a wave of velocity v travels in an arbitrary direction with direction cosine $(1_x, 1_y, 1_z)$, then

$$\frac{\ell_x^2}{v_1^2 - v^2} + \frac{\ell_y^2}{v_2^2 - v^2} + \frac{\ell_z^2}{v_3^2 - v^2} = 0$$

and this yields two values of v^2 showing that the wave breaks up into two waves traveling with different velocities and remarkably then can be shown to be polarized at right angles. It also follows from the above equation that for specific directions the two values of v^2 become the same and these directions are called optic axes. Uniaxial crystals have one optic axis while Biaxial crystals have two.

* Double Refraction

   Since $\vec{D}$ and $\vec{E}$ are not in the same direction in anisotropic media, the direction of wave propagation $\vec{D} \times \vec{H}$ is different from that of energy flow $\vec{E} \times \vec{H}$ (Poynting vector direction, ray direction). In an anisotropic medium there will be two different ray directions and the incident ray breaks up into two rays. This is called double refraction. One ray follows Snell's law and is called the ordinary ray while the other one is called extraordinary. The corresponding indices of refraction are denoted by n_o and n_e. The two rays coincide along the optic axes.

* Optical Activity

   Certain materials such as sugar solutions and quartz (along its optic axes) have the property of rotating the plane of polarization while transmitting polarized light through them. This is called optical activity and has many applications.

* Speed of Light

   The speed of light in vacuum (c) appears as a fundamental constant in modern physics and according to Einstein's theory of relativity, no speed can ever exceed c. Some of the more recent measurements of c (in Km sec^{-1}) are given below:

Year	Authors	Method	Value of c
1954	Rank, Shearer and Wiggins	Molecular Spectra	299,789.8 ± 3.0
1957	Bergstrand	Geodimeter	299,792.9 ± 0.16
1958	Froome	Microwave interferometer	299,792.5 ± 0.1

II.6a Special Theory of Relativity

   1. All inertial frames (see Newton's law) are equivalent insofar as the formulation of physical laws is concerned.

   2. Velocity of light in vacuum (c) is the same in all frames of reference.

* Lorentz Transformation

   Let an event occur at time t and position (x,y,z) in an inertial

frame S and let an observer in another inertial frame S' characterize
the same event by t' and (x', y', z'). If S' is moving with uniform
velocity v with respect to S along the x-direction such that at $t=0$
the origins of S and S' coincide, then

$$x = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} (x' + vt) \qquad\qquad x' = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} (x-vt)$$

$$y = y' \qquad\qquad\qquad\qquad\qquad y' = y$$

$$z = z' \qquad\qquad\qquad\qquad\qquad z' = z$$

$$t = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \left(t' + \frac{vx}{c^2}\right) \qquad\qquad t' = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} \left(t - \frac{vx}{c^2}\right)$$

In the limit of $\frac{v}{c} \sim 0$, these transformation equations go over to the
Galilean Transformation equations

$$x' = x-vt$$
$$y' = y$$
$$z' = z$$
$$t' = t$$

* **Transformation of Length, Mass and Time**

    The length l, mass m and time interval t measured in S are
related to the corresponding quantities l', m' and t' measured in
S through the equations

$$l' = \left(\sqrt{1-\frac{v^2}{c^2}}\right) l \quad , \quad m' = \frac{m}{\sqrt{1-\frac{v^2}{c^2}}} \quad , \quad t' = \frac{t}{\sqrt{1-\frac{v^2}{c^2}}}$$

Rest mass (m_0) of a particle is the mass measured in the frame of
reference in which the particle is at rest.

* **Addition of Velocities**

    If an entity is moving with velocity v_1 w.r.t. S in positive
x-direction, then its velocity v_2 measured in S will be given by

$$v_2 = \frac{v_1 + v}{1 + \frac{v_1 v}{c^2}} \quad .$$

* **Energy Momentum Relation**

    The energy E and momentum p of a particle of rest mass m_0 is
given by

$$E^2 = c^2 p^2 + m_0^2 c^4 \quad .$$

II. 7 Gases, Liquids and Solids

(1) Gases

* Boyle's Law : PV = Constant at Constant T

* Charles' Law: V = Constant xT at constant P

* Ideal Gas Law: PV = nRT where n = number of
  moles and R = gas constant

* Gas Constant: R = 0.082054   liter atm/mole deg

          82.055   cc atm/mole deg

          8.314   joule/mole deg

          8.314×10^{7} ergs/mole deg

          1.987   cal/mole deg

* Dalton's Law: $P_{Total} = p_A + p_B + p_C$ .... where p_A,

  p_B and p_C refer to partial pressures
  of components A, B and C.

* Avogadro's Principle: Equal volumes of all gases
  contain equal number of molecules at
  the same P and T.

  $$N = \frac{PV}{kT}$$

  V of 1 mole of gas at STP = 22.413 liters

* PVT Behaviour of Real Gases: PA = ZnRT where
  Z is the compressibility factor

* Van der Waals Equation of State: $(P + a/V^2) (V-b)$ = RT
  for one mole

* Berthelot Equation of State: $(P + A/TV^2)(V-B)$=RT for one mole

* Critical constants: The temperature at which the liquid
  miniscus disappears (while cooling a gas)
  is the critical temperature T_c. The vapour
  pressure at T_c is P_c. The volume at T_c and
  P_c is V_c.

* <u>Reduced Quantities:</u> $P_R = P/P_c$; $V_R = V/V_c$ and $T_R = T/T_c$

* <u>van der Waals constants:</u> $T_c = 8a/27bR$; $P_c = a/27b^2$; $V_c = 3b$

$$P_c V_c / T_c = 3R/8$$

* <u>Kinetic Theory of Gases:</u> $PV = 1/3 (Nmc^2)$

$$E_{kinetic} = 3/2 \, nRT$$

    Root mean square velocity $= c^2 = (3RT/M)^{1/2}$

    Average velocity $= c = (8RT/\pi M)^{1/2}$

* <u>Graham's Law of Effusion:</u> $r_1/r_2 = (M_2/M_1)^{1/2}$

    where r and M stand for the rate of effusion and molecular mass of the gas. 1 and 2 are two different gases.

* <u>Mean Free Path:</u> $\lambda = 1/2^{1/2} \, N' \sigma^2$

    where N' is the number of molecules per cc and σ is the molecular diameter.

* <u>Viscosity of a Gas:</u> $\eta = m \bar{c} /2(2)^{1/2} \pi \sigma^2$

* <u>Boltzmann Distribution Law:</u> $N_i = N_o \exp(-E_i/kT)$

    where N_o is the number of particles in a given state and N_i is the number of particles whose energy E_i is above that of the given state. If several states have the same energy (degeneracy of level E_i), $N_i = g_i N_o \exp(-E_i/kT)$. If N is the total number of particles,

    $$N_i/N = g_i \exp(-E_i/kT) \Big/ \sum g_i \exp(-E_i/kT)$$

(ii) <u>Liquids</u>

* <u>Viscosity</u> $\eta = \pi P r^4 t/8Vl$ where t is the time required for Vml of liquid to flow through a capillary tube of length l and radius r under an applied pressure P(Poiseuille equation).

    $\eta/\eta_o = (t/t_o) \times (\rho_o/\rho)$ where ρ_o and ρ

are densities of a known and an unknown liquid and
t_o and t are the times required for the discharge
of the same volumes of the two liquids through a
capillary.

$$\eta = A \exp \left(\Delta E/RT\right)$$

* Surface Tension   dw $=\gamma$ dA   where dw is the work
        done on the surface in extending its area by dA and
        γ is the surface tension. By the capillary rise
        method

$$\gamma = 1/2 \, \rho ghr$$

where r is the radius of the capillary, h the
capillary rise, ρ the density of the liquid and
g the acceleration due to gravity

* Vapour Pressure and Boiling Point:

        The pressure of the vapour in equilibrium with a
        liquid at a temperature is the vapour pressure.
        At the boiling point, the equilibrium vapour
        pressure is equal to the external pressure. At
        the normal boiling point, the external pressure
        is 1 atm.

(iii) Solids

* Space lattice: A space lattice is an arrangement of points
        in space such that the environment about a point is
        the same as about every other point.

* Unit Cell : A unit cell is the basic structural unit that
        repeats itself infinitely in three dimensions.

* Symmetry: Crystals may have four kinds of symmetry:
        (i) Rotation axes (ii) Mirror planes (iii) Center
        of inversion and (iv) Rotation-inversion axes.

* Miller indices: The intercepts of the plane of a face of
        a crystal on the three axes may be expressed as
        ratios to unit distances a, b, and c along these
        axes. The Miller indices are the reciprocals of
        the intercepts of the axes in terms of these unit
        distances multiplied by a factor to eliminate fractions.

Intercepts on X, Y and Z axes	Miller indices
(1) 2a , b , c/2	(hkl)
or 2 , 1 , 1/2	1 , 2 , 4
(2) a , b , ∞	
or 1 , 1 , ∞	1 , 1 , 0

* The Seven Crystal Systems:

System	Axes	Angles
Cubic	a=b=c	$\alpha = \beta = \gamma = 90°$
Tetragonal	a=b;c	$\alpha = \beta = \gamma = 90°$
Orthorhombic	a;b;c	$\alpha = \beta = \gamma = 90°$
Monoclinic	a;b;c	$\alpha = \gamma = 90°$; β
Rhombohedral	a=b=c	$\alpha = \beta = \gamma$
Hexagonal	a=b;c	$\alpha = \beta = 90°$; $\gamma = 120°$
Triclinic	a;b;c	α ; β ; γ

* The 14 Bravais Lattices:

1. Triclinic 2. Simple monoclinic 3. Side-centered
monoclinic 4. Simple orthorhombic 5. End-centered
orthorhombic 6. Face-centered orthorhombic 7. Body-
centered orthorhombic 8. Hexagonal 9. Rhombohedral
10. Simple tetragonal 11. Body-centered tetragonal
12. Simple cubic 13. Body-centered cubic 14. Face-
centered cubic.
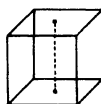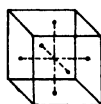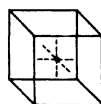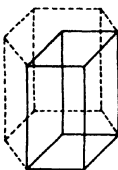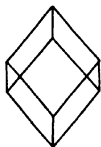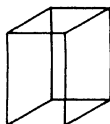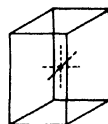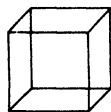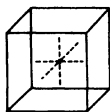
Solids

1. Triclinic.   2 Simple Monoclinic.   3 Side-centered
                                                    Monoclinic.

4. Simple   5. End-centered   6. Face-centered   7. Body-centered
   Orthorhombic   Orthorhombic   Orthorhombic   Orthorhombic

8 Hexagonal   9. Rhombohedral 10. Simple   11 Body-centered
                                        Tetragonal   Tetragonal
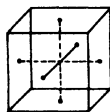
12 Simple   13. Body-centered   14 Face-centered
   Cubic   Cubic   Cubic

* **The Bragg equation:** $n\lambda = 2d \sin\theta$, where n is the
       order of reflection, λ the wavelength of x-rays,
       θ the angle of reflection and d the distance
       between planes.

* **Relation between d and lattice parameters:**

  Cubic $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$

  Tetragonal $d_{hkl} = 1 / (h^2/a^2 + k^2/a^2 + l^2/c^2)^{1/2}$

Orthorhombic $d_{hkl} = 1/(h^2/a^2 + k^2/b^2 + l^2/c^2)^{1/2}$

Hexagonal $d_{hkl} = 1/[4/3a^2(h^2+hk+k^2)+l^2/c^2]^{1/2}$

For cubic lattices:

$d_{100} : d_{110} : d_{111} = a:(1/\sqrt{2})a : (1/\sqrt{3})a$ (simple cubic)

$d_{200} : d_{110} : d_{222} = a/2 : (1/\sqrt{2})a : (1/2\sqrt{3})a$ (Bcc)

$d_{200} : d_{220} : d_{111} = a/2 : (1/2\sqrt{2})a : (1/\sqrt{3})a$ (Fcc)

* Amplitude of x-rays scattered from the hkl planes of all the atoms in a unit cell (structure factor):

$F(hkl) = \sum_j f_j \exp 2\pi i(hx/a+ky/b+lz/c)$ where

x, y and z are the coordinates of the atom and f_j is the atomic scattering factor

* Point Defects

```
+ - + - +      + - + - +      + - + - +
· + - · -      - + - ⊞ -      - ⊞ - + -
+ - + - +      + - + - +      + - + ⊟ +
```

Interstitials   Frenkel   Schottky
   defects   defects

Entropy due to n imperfections distributed among a total of N crystal sites,

$$S = k\ln N! / (N-n)! \, n!$$

* Band Model

Conductors or metals offer low resistance to the flow of electrons. The resistivities of metals are in the range 10^{-4} to 10^{-6} ohm cm at 25°C and increase with increase in temperature Insulators have high resistivities in the range 10^{10} to 10^{22} ohm cm at room temperature. Semiconductors show resistivities in between those of metals and insulators and the resistivities decrease with increasing temperatures (proportional to $\exp(\epsilon/kT)$

The schematic band representation of an insulator,
a metal, an intrinsic semiconductor and an impurity
semiconductor is shown below:
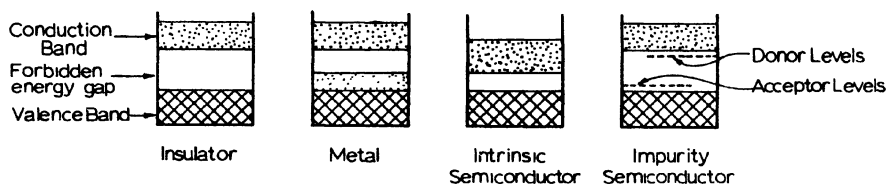
In impurity semiconductors (eg. germanium
doped with Group V or III impurities) the
impurity may produce electrons (eg. As, n-
type semiconduction) or positive holes
(eg., In, p-type semiconduction)

* Dislocations: Crystals contain defects similar to rucks
            in carpets. These are called dislocations. These
            occur when the periodicity in the lattice is in-
            terrupted along certain directions.

    There can be edge dislocations as well as screw
    dislocations. Dislocations provide mechanisms
    for many of the processes occuring in the solid state,
    particularly the mechanical properties of crystals.

* Ionic Crystals[1]

    The number of ions of opposite charge surrounding
    an ion is the coordination number. The radius
    ratio is given by cation radius/anion radius.
    The cohesive energy of an ionic crystal is given

    by : $V = (-NMe^2/a) + A \exp (-a/\rho)$ where N is
    the Avogadro number, A and ρ are constants, a is
    the equilibrium lattice parameter and M is the

    Madelung constant. $M = \sum_{1}' \pm \frac{1}{r_1}$ where r_1's are the

    the distances from the origin to the points

of a lattice with unit lattice parameter.

* Ionic Radii of Pauling[1] (in A)

$Li^+0.60$ $Be^{++}0.31$ $B^{+3}0.20$ $C^{+4}0.15$ $O^=1.40$ $F^-1.36$

$Na^+0.95$ $Mg^{++}0.65$ $Al^{+3}0.50$ $Si^{+4}0.41$ $S^=1.84$ $Cl^-1.81$

$K^+1.33$ $Ca^{++}0.99$ $Sc^{+3}0.81$ $Ti^{+4}0.68$ $Se^=1.98$ $Br^-1.95$

$Rb^+1.48$ $Sr^{++}1.13$ $Y^{+3}0.93$ $Zr^{+4}0.80$ $Te^=2.21$ $I^-2.16$

$Cs^+1.69$ $Ba^{++}1.35$ $La^{+3}1.15$ $Ce^{+4}1.01$

(1) See L. Pauling, The Nature of the Chemical Bond, Cornell Univ Press, Ithaca, 1960.

* Heat capacities of Crystals

Einstein model $C_v = 3R(h\nu/2kT \, csch \, h\nu/2kT)^2$

Note: $csch \, x = 2/(e^x - e^{-x})$ and $e^x = 1 + x + (x^2/2!) + \cdots$

Debye Model

$$C_v = 3R(kT/h\nu)^3 \int_0^{h\nu/kT} e^x x^4 dx/(e^x-1)^2$$

where $x = h\nu/kT$

At low temperatures, $C_v = \propto T^3$

* Born-Haber Cycle

We shall consider the cycle for NaCl
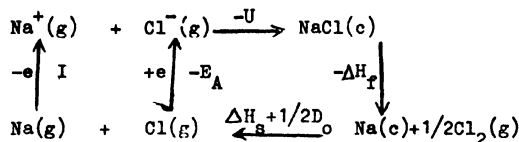
where U = the crystal energy, ΔH_f = standard heat of formation of NaCl(c), ΔH_s = Heat of sublimation of Na(c), D_o = dissociation energy of $Cl_2(g)$, I = ionization potential of Na and E_A = electron affinity of Cl.

$$U = -\Delta H_f + \Delta H_s + 1/2\ D_o + I - E_A$$

	$-\Delta H_f$	I	ΔH_s	$\frac{D_o}{}$	E_A	U
NaCl	99	117	26	54	88	181
NaBr	90	117	26	46	80	176
NaI	77	117	26	34	71	166
KCl	104	99	21	54	88	163
RbCl	105	95	20	54	88	159

II.8 Thermodynamics and Thermochemistry

In the most general terms, thermodynamics is a subject that is concerned with the understanding and interpretation of the properties of matter that are influenced by temperature changes. The approach does not take into account the atomic constitution of matter, but attempts to relate observed properties of matter in terms of the basic laws of thermodynamics. Thermodynamics does not provide explanations as to why a particular substance has certain properties or why a chemical reaction takes a certain path.

(1) Elementary Principles and Laws

* The Zeroth Law: If three or more bodies are in thermal contact by means of diathermal walls and are all in equilibrium, then any two taken separately are in equilibrium with one another.

* The First Law: Energy is conserved if heat is taken into account. That is, $dE = \delta q - \delta W$, where δq is the heat absorbed by a system δW is the work done by the system and dE is the increment in the internal energy. (δ denotes inexact differentials). In a cyclic process, $\oint dE = 0$

* Heat Content or Enthalpy

$$H = E + PV$$

* Heat Capacities

$$C_v = dq_v\ /dT = \left(\partial E/\partial T\right)_v$$

$$C_p = d\ q_p/dT = \left(\partial H/\partial T\right)_p$$

$$C_p - C_v = \left[P + (\partial E/\partial V)_T \right] (\partial V/\partial T)_p$$

(See also Section II.4)

* Joule-Thomson Coefficient

$$\mu = (\partial T/\partial P)_H = -1/C_p \, (\partial H/\partial P)_T$$

* For ideal gases

$$C_p - C_v = R \quad \text{per mole.}$$

$$\triangle E = E_2 - E_1 = \int_{T_1}^{T_2} C_v \, dT$$

$$\triangle H = H_2 - H_1 = \int_{T_1}^{T_2} C_p \, dT$$

For an isothermal reversible volume change,

$$q = -W = nRT \ln (V_2/V_1)$$

$$= nRT \ln (P_1/P_2)$$

For an adiabatic expansion,

$$dw = C_v dt = - PdV$$

$$(T_1/T_2) = (V_2/V_1)^{\gamma-1} \quad \text{where } \gamma = C_p/C_v$$

$$\text{and } PV^{\gamma} = \text{constant}$$

* Thermochemistry

$$\triangle H = \triangle E + \triangle (PV)$$

For ideal gases

$$\triangle H = \triangle E + \triangle n \, RT$$

As a consequence of the first law of thermodynamics, $\triangle E$ or $\triangle H$ for any chemical reaction is independent of the path. This principle is also referred to as the Law of constant heat summation.

The standard heat of formation of a compound is the heat
of the reaction by which it is formed from its elements
(the reactants and products all being in the standard
state at 25°C and 1 atm). The enthalpy of an element
is taken as zero.

Bond energy is the $\triangle H$ or $\triangle E$ required to form
a bond between two atoms.

The effect of temperature on heats of reaction
is given by :

$$d(\triangle H^\circ) = \triangle C_p dT = (A+BT+CT^2+\ldots)dT$$

$$\triangle H^\circ_T = \triangle H^\circ_o + AT + 1/2\ BT^2 + 1/3CT^3 + \ldots$$

Note that the experimental heat capacity data are
generally represented by a power series:

$$C_p = a+bT+cT^2+\ldots$$

* **The Carnot Cycle**
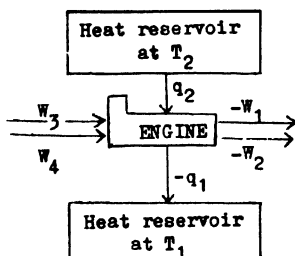
CARNOT CYCLE
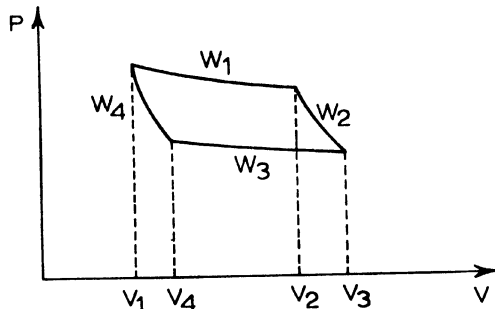
$$\triangle E = q+W = q_2+q_1+W_1+W_2+W_3+W_4 = 0$$

$$\text{Efficiency of the engine} = -W/q_2 = (q_2+q_1)/q_2$$

$$= (T_2-T_1)/T_2$$

* **The Second Law of Thermodynamics**

All reversible Carnot cycles operating between the same
initial and final temperatures must have the same efficiency.
(or) It is impossible to devise an engine which, working in
a cycle, shall produce no effect other than the extraction
of heat from a reservoir and the performance of an equal
amount of mechanical work.

* Entropy (S)

For a reversible Carnot cycle operating between T_2 and T_1, $(q_2/T_2) + (q_1/T_1) = 0$

(Reversible) $\oint dq/T = 0$

$ds = dq/T$

$\oint ds = \int_1^2 ds + \int_2^1 ds = S_2-S_1+S_1-S_2 = 0$

For an irreversible process,

$\oint dq/T < 0$ and $(q_2/T_2)+(q_1/T_1) < 0$.

Entropy change for a reversible process in an ideal gas: $ds = dq/T = (C_v dT/T)+(nRdv/V)$

$\triangle S = S_2-S_1 = C_v \ln(T_2/T_1)+nR\ln (V_2/V_1)$

At constant volume, $\triangle S = C_v \ln T_2/T_1$

At constant temperature, $\triangle S = nR\ln V_2/V_1$

Entropy change for a change of state:

$\triangle S = \triangle H_{tr}/T_{tr}$, where $\triangle H_{tr}$ and T_{tr} are the enthalpy and temperature of transformation (fusion, sublimation or vapourization).

Criterion for equilibrium: In a system, at constant E and V, S is maximum; at constant S and V, E is a minimum.

* Free energy, work function and thermodynamic relations

$A = E - TS$

$F = H - TS = A+PV$, where A and F (also designated by G) are the Helmholtz and Gibbs free energies respectively.

$\triangle F = \triangle A + P\triangle V$, at constant P

$\triangle F = \triangle A +\triangle nRT$

$\triangle A = \triangle E - T\triangle S$, at constant T

$$dE = TdS - PdV \; ; \; dA = - PdV - SdT$$

$$dH = TdS + VdP \; ; \; dF = - SdT + VdP$$

$$(\partial F/\partial P)_T = V \text{ and } \Delta F = \int_1^2 VdP$$

For an ideal gas, $\Delta F = nRT \ln P_2/P_1$

$$(\partial F/\partial T)_P = -S = (F-H)/T$$

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial F}{T}\right)\right]_P = \frac{-\Delta H}{T^2}$$

$$(\partial S/\partial P)_T = - (\partial V/\partial T)_P$$

                                        (Maxwell's Relation)

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V$$

At constant P, $S = \int C_p d\ln T + \text{constant} \; ; \; \Delta S = \int C_p d\ln T$

$$C_p = T (\partial S/\partial T)_P$$

$$C_v = T (\partial S/\partial T)_V$$

$$(\partial E/\partial V)_T + P = T (\partial P/\partial T)_V, \text{ which}$$

is also called the thermodynamic equation of state.

$$C_p - C_v = T (\partial P/\partial T)_V (\partial V/\partial T)_P$$

*   Chemical potential

$$\mu = (\partial F/\partial n_i)_{T, P, n_j}$$

At constant T and P, $dF = \sum \mu_i dn_i$, since

$dF = - SdT + VdP + \sum \mu_i dn_i$. Thus,

$\sum_i n_i d\mu_i = 0$ at constant T and P (Gibbs - Duhem Eqn.);

for a closed phase, $\sum \mu_i dn_i = 0$

*   Phase rule

   $f = c-p+2$ where f is the degrees of freedom, c the
number of components and p the number of phases.

* Clausius - Clapeyron equation

$$dP/dT = \Delta H_{tr}/T \cdot \Delta V_{tr}$$

For a liquid-vapour change,

$$d\ln P/dT = \Delta H_{vap}/RT^2$$

$$\ln P_2/P_1 = \left[-\Delta H_{vap}/R\right]\left[\left(1/T_2 - 1/T_1\right)\right]$$

Trouton's rule : $\Delta H_{vap}/T_{boiling} \approx 22$ e.u.

* The Third Law of Thermodynamics

If the entropy of each element in some crystalline state be taken as zero at absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature, the entropy may become zero, and does become so in the case of perfect crystalline substances.

If the entropy of a typical gaseous substance, Z is to be evaluated at 298.15°K the following steps will be necessary.

(i)   Extrapolation from 0-16°K (Debye theory), ΔS_1

(ii) $\int C_p \, d\ln T$ for solid form I of Z (16°-100°K), ΔS_2

(iii) Transition, solid I → Solid II; $\Delta H_{tr}/T_{tr}$ ($T_{tr}=100$°K) ΔS_3

(iv) $\int C_p \, d\ln T$ for solid II (100°-150°K), ΔS_4

(v)   Fusion, $\Delta H_{fusion}/T_{fusion}$ ($T_f=150$°K), ΔS_5

(vi) $\int C_p \, d\ln T$ for liquid from 150° to 200°K, ΔS_6

(vii) Vapourization, $\Delta H_v/T_B$ ($T_E=220$°K), ΔS_7

(viii) $\int C_p \, d\ln T$ for gas from 220° to 298.15°K, ΔS_8

$$S^0_{298.15} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$$

* Entropy and probability

S = k ln p + b   where p is the probability

$$\Delta S = S_2 - S_1 = k \ln p_2/p_1$$

(See Section II.11)

(11) Solutions and Phase Equilibria

* Measures of Composition

Mole fraction $X_A = n_A / n_T$ where n_A and n_T are the number of moles of A and total number of moles respectively.

Molarity, C, is the number of moles of the solute in a litre of solution.

Molarity, m, is the number of moles of the solute in 1000 grams of the solvent.

Weight per cent is the number of grams of the solute in 100 grams of the solution.

$$X_A = m_A / (1000/M_S) + m_A$$

where M_S is the molecular weight of the solvent.

$$X_A = C_A/(1000 \rho - C_A M_A)M_S + C_A$$

where ρ is the density of the solution.

$$X_A \approx C_A M_S / 1000 \rho_S .$$

For dilute aqueous solutions, $\rho \approx \rho_S \approx 1$ and $m_A \approx C_A$

Partial molar quantities

For a solution containing n_x moles of X and n_y moles of Y,

$$\overline{V}_x = (\partial V/\partial n_x)_{T,P,n_y}$$

$$dV = \overline{V}_x dn_x + \overline{V}_y dn_y$$

$$V = \overline{V}_x n_x + \overline{V}_x n_y$$

$$\overline{S}_x = (\partial S/\partial n_x)_{T,P,n_y} ; \quad \overline{H}_x = (\partial H/\partial n_x)_{T,P,n_y} ;$$

$$\overline{F}_x = (\partial F/\partial n_x)_{T,P,n_y}$$

$$(\partial \overline{F}_x/\partial P)_T = (\partial \mu_x/\partial P)_T = \overline{V}_x$$

$$(\partial \mu_x / \partial T)_P = - \bar{S}_x \quad ; \quad (\partial \bar{H}_x / \partial T)_P = (\bar{C}_p)_x$$

* Raoult's Law

$P_A = X_A P_A^o$ where P_A is the partial pressure of A above the solution in which its mole fraction is X_A and P_A^o is the vapour pressure of the pure liquid A. If B is added to pure A,

$$(P_A^o - P_A)/P_A^o = (1-X_A) = X_B$$

* Ideal Solutions

$$\mu_A = \mu_A^\theta + RT \ln P_A^o + RT \ln X_A$$

$$\bar{V}_A = \bar{V}_A^o \quad ; \quad \bar{H}_A = \bar{H}_A^o$$

$$\Delta S = - R \sum_1 X_i \ln X_i$$

* Henry's Law

$P_B = k \, X_B$ where P_A is the partial pressure of solute B.

* Boiling point elevation

$$\Delta T_B = (RT_o^2 / \Delta H_v) \ (m/1000) = K_B \, m \, ,$$

where T_o is the boiling point of the solvent, ΔH_v the heat of vapourization per gram, m the molarity and K_B, the molal boiling point elevation constant.

$$K_B = 0.514 \quad \text{for water}$$
$$= 0.1.67 \text{ for acetone}$$
$$= 2.67 \quad \text{for benzene.}$$

* Freezing point depression

$$\Delta T_f = (RT_o^2 / \Delta H_f) \ (m/1000) = K_f m \, ,$$

where T_o is the freezing point of the pure solvent, ΔH_f the heat of fusion and K_f the molal freezing point depression constant.

$$K_f = 1.855 \quad \text{for water}$$

$$= 5.12 \quad \text{for benzene}$$

$$= 40.0 \quad \text{for camphor}$$

* **Osmotic pressure**

  $\pi = C \ RT$ where C is the molarity of the solution

II. 9 Chemical Equilibrium, Electrochemistry and Kinetics

(i) Chemical Equilibrium

* **Equilibrium Constant**

  $aA + bH \rightleftharpoons cC + dD$

  $$[C]^c \ [D]^d \ / \ [A]^a \ [B]^b \ = k_f \ /k_b = K$$

* **Free energy**

  The standard free energy of formation of a compound
  is the free energy of the reaction by which it is formed
  from its elements when all the products and reactants
  are in the standard states.

  $$\Delta F^\circ = F^\circ \ (\text{Products}) - F^\circ \ (\text{reactants})$$

  $$\Delta F^\circ = - \ RT \ \ln K_p$$

  $$K_p = K_c \ (RT)^{\Delta n}$$

  $$\partial \ln K_p \ / \partial \ T = \Delta H^\circ \ / \ RT^2$$

  $$\ln K_2 \ / \ K_1 = -\Delta H^\circ \ /R \ (1/T_2 - 1/T_1)$$

  $$\ln K_p = -\Delta H^\circ \ / \ RT + A \ \ln T + BT + CT^2 \ \ldots +I$$

* **Fugacity and activity**

  For the general case of a component A in a nonideal
  solution, $d \mu_A = \overline{V}_A dP - \overline{S}_A dT$

  At constant temperature, $d \mu_A = \overline{V}_A dP$

  $$\mu_A = \mu^\circ_A + RT \ \ln f_A \ / \ f^\circ_A$$

  and $\mu_A = \mu^\circ_A + RT \ \ln a_A$,

where f_A and f_A^o are the fugacities and a_A the activity.

$$RT \ln f = RT \ln P - \int_0^P \alpha\, dP, \text{ where}$$

$$\alpha = RT/P - \bar{V}$$

Activity coefficient $\gamma = f/P$

$$K_f = f_C^c f_D^d \,/\, f_A^a f_B^b$$

$$= \left[\gamma_C^c \gamma_D^d / \gamma_A^a \gamma_B^b\right]\left[P_C^c P_D^d \,/\, P_A^a P_B^b\right]$$

$$K_f = K_\gamma\, K_P$$

$$K_a = a_C^c a_D^d \big/ a_A^a a_B^b = K_\gamma\, K_x$$

$$K_a = K_{\gamma'}, K_c = K_{\gamma''}\, K_m$$

(ii) Electrochemistry

* Faraday's laws

$m/M = It/ZF$ where m is the mass of an element of atomic weight M liberated at an electrode when a current I is passed through the solution for a time t.

* Conductivity

$R = \rho l/A$, where l and A stand for the length and cross-sectional area respectively and R and ρ are the resistance (in ohms) and resistivity (in ohm cm) respectively. The conductivity is given by : $\sigma = 1/\rho$.

Equivalent conductivity is defined as:

$\Lambda = 1000\, \sigma/C'$ where C' is the number of equivalents per cc. Λ extrapolated to zero concentration is called the equivalent conductivity at infinite dilution, Λ_0.

$$\Lambda_0 = \Lambda_+ + \Lambda_-$$

For strong electrolytes, $\Lambda = \Lambda_0 - kc^{1/2}$

* Dissociation theory of Arrhenius and the Debye-Hückel Postulates

The degree of dissociation $\alpha = \Lambda / \Lambda_0$.

$\alpha = i - 1/\nu - 1$ where i is the van't Hoff factor and ν is the number of ions produced by a solute molecule. For the reaction, $PQ \rightleftharpoons P^+ + Q^-$, $K = \alpha^2 c/(1-\alpha) = \Lambda^2 c/\Lambda_o(\Lambda_o - \Lambda)$.

According to the Debye-Hückel theory, in dilute solutions, strong electrolytes are completely dissociated. The factors that decrease the conductance at high concentrations are the interionic attractions (ion atmosphere) and frictional drag.

* Transport numbers

$$t_o^+ = \Lambda_o^+/\Lambda_o \; ; \; t_o^- = \Lambda_o^-/\Lambda_o$$

$\sigma = N Ze\mu$ where N is the number of charge carriers per unit volume, Ze is the absolute value of the charge and μ is mobility of an ion (given in $cm^2 sec^{-1} volt^{-1}$). $\sigma = F\mu = t\Lambda$ for each ion in solution.

* Activities

For an electrolyte giving ν ions on dissociation, the fugacity is given by, $f = k a^\nu$, where a is the activity ($a = \gamma m$).

$$a = a_+ a_- = a_{\pm}^2$$

$$a_+ = \gamma_+ m_+ \; ; \; a_- = \gamma_- m_-$$

For a general reaction, $A_{\nu_+} B_{\nu_-} \rightarrow \nu_+ A^+ + \nu_- B^-$,

$$\nu = \nu_+ + \nu_- \quad \text{and} \quad a = a_+^{\nu^+} a_-^{\nu^-} = a_{\pm}^{\nu}$$

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu+} \gamma_-^{\nu-}$$

$$a_{\pm} = a^{1/\nu} = (m_+^{\nu+} m_-^{\nu-} \gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu}$$

$$\gamma_{\pm} = a_{\pm} / (m_+^{\nu+} m_-^{\nu-})^{1/\nu}$$

From freezing point data activity coefficients can be obtained by the equation ,

$$\ln \gamma_{\pm} = -j - \int_0^m (j/m)dm, \text{ where}$$

$$j = 1 - (\Delta T_f /\nu m K_f).$$

From solubility data of sparingly soluble substances,

$$\gamma_{\pm} = K_{SP}^{1/2} / c.$$

* Ionic Strength

$$I_S = 1/2 \sum_i m_i z_i^2 \approx (1/\rho_0) \, 1/2 \sum_i c_i z_i^2,$$

where ρ_0 is the density of the solvent

* Debye-Hückel theory of activity coefficients

The limiting law is given by

$$\ln \gamma = - (e^2/\epsilon kT)^{3/2} (2\pi N/1000)^{1/2} \, z^2 \sqrt{I_s}$$

where ϵ is the dielectric constant. For aqueous solutions at 25°C,

$$\log \gamma_{\pm} = 0.5091 \, z_+ z_- \sqrt{I_s}$$

* Dissociation constants of acids and bases

$$HA + H_2O \rightleftharpoons A^- + OH_3^+$$
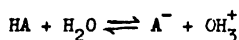
$$K_a = a_{A^-} \, a_{OH_3^+} / a_{HA} \, a_{H_2O}$$

$$= a_{A^-} \, a_{OH_3^+} / a_{HA} = (\alpha^2 c/1-\alpha) \, (\gamma_{H^+} \, \gamma_{A^-})$$

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$
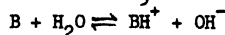
$$K_b = a_{BH^+} \, a_{OH^-} / a_B$$

$$K_a K_b = K_w = a_{OH_3^+} \, a_{OH^-}$$

$$BA + H_2O \rightleftharpoons HA + BOH$$
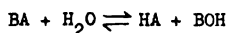
The hydrolysis constant is given by

$$K_h = a_{HA} \, a_{BOH} / a_{BA}$$

Salt of a weak acid and strong base: $K_h = K_w/K_a$

Salt of a weak base and strong acid: $K_h = K_w/K_b$

Salt of a weak base and weak acid: $K_h = K_w / K_a K_b$

* pH and pK

  $pH = - \log [H^+]$ and $pK = - \log K$ where K is the dissociation constant of an acid (K_a) or a base (K_b).

* Electrochemical Cells

  $\Delta F = - n FE$ where n is the number of faradays and E is the emf.

  $\Delta S = nF \left(\partial E / \partial T \right)_P$

  For a generalized cell reaction,

  $aA + bB \rightleftharpoons cC + dD$.

  $\Delta F = \Delta F^\circ + RT \ln a_C^c a_D^d / a_A^a a_B^b$

  $E = E^\circ - (RT/nF) \ln a_C^c a_D^d / a_A^a a_B^b$

                    (Nernst equation)

  $E^\circ = -\Delta F^\circ /nF = (RT/nF) \ln K_a$

  For $Pt\ (H_2)/HCl(m)/AgCl/Ag$,

  $E = E^\circ - (RT/F) \ln (a_{Ag} a_{H^+}\ a_{ct^-})/a_{AgCl} a_{H_2}^{1/2}$

  $E = E^\circ - (RT/F)\ln a_{H^+} a_{ct^-}$

  $E = E^\circ - (2RT/F) \ln \gamma_{\pm}\ m$

  $E +(2RT/F) \ln m = E^\circ - (2RTA/F)m^{1/2}$

  since $\gamma_{\pm} = Am^{1/2}$ where A is a constant.

  For electrode concentration cells,-

  $E = (-RT/F) \ln p_2/p_1$ where p_2 and p_1

  are the pressures of gas (eg. $Pt/H_2(p_1)/HCl(a)/H_2(p_2)/Pt$

  For the cell $M-Hg\ (a_1)/MSO_4/M-Hg(a_2)$

  $E = (-RT/2F) \ln a_2/a_1$

  For cells with liquid junctions as in

  $Pt/H_2/HCl\ (a_1)/HCl\ (a_2)/H_2/Pt$,
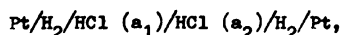
  $E = -0.11830\ t_-\log \left[(a_{\pm})_1/(a_{\pm})_2\right]$ since $F = 0$.

* Standard EMF values and electrode potentials

  The emfs of individual electrodes based on the arbitrary
  zero for the emf of the standard hydrogen electrode (hydrogen
  pressure of 1 atm and unit H^+ activity in solution) are often
  referred to as standard electrode potentials. They are the
  emfs of cells containing, on the left, the standard hydrogen
  electrode and, on the right, the elctrode being considered.

                 (See Section III for data)

* Types of electrodes

        Gas electrodes (e.g., $Pt/H_2(p\,atm)/HCl(c_1)$

        Oxidation-reduction electrodes (eg., $Pt/Fe^{++}(c_1), Fe^{+3}(c_2)$ or
        quinone-hydroquinone)

        Metal-metal ion electrodes (eg., $Ag/Ag^+(c)$)

        Amalgam electrodes (eg., Na in Hg at $c_1/Na^+(c_2)$)

        Metal-insoluble salt electrodes (eg., calomel electrode)

        Glass electrode

(iii) Chemical Kinetics

    * Order of a reaction
        $$-dc_A/dt = kc_A^a c_B^b c_D^d \ldots$$
        a+b+d = order of the reaction
    * The units of rate constants depend on the order.

        First order: $-dc/dt = k_1 c$; k_1 in (time unit)$^{-1}$

        Second Order: $-dc/dt = k_2 c^2$; k_2 in litre mole^{-1} time^{-1}

        ith order: $-dc/dt = k_i c^i$; k_i in time^{-1} (concentration)$^{1-i}$

    * Rate equations

        First order: $\ln a/(a-x) = k_1 t$, where a is the initial
        concentration of P and X is the concentration of Q or R in
        the reaction $P \rightarrow Q+R$.

              $\tau =$ half-time $= (\ln 2)/k_1$

        Second order: For the reaction, $P+Q \rightarrow R+S$

$$\left[1/(a-b)\right]\ln\left[b(a-x)/a(b-x)\right] = k_2 t$$

where a and b are the initial concentrations of P and Q respectively.

$$\mathcal{T} = 1/k_2 a$$

Opposing reactions: $P \rightleftharpoons Q$

$$dx/dt = k_1(a-x)-k_{-1}(b+x),$$

where k_1 and k_{-1} are both first order constants.

$$\ln w/\dot{w}-x = (k_1+k_{-1})t, \text{ where}$$

$$w = (k_1 a-k_{-1}b)/(k_1+k_{-1}).$$

* **Effect of temperature on reaction rates**

$$d\ln k/dT = E_a /RT^2$$

$$k = A \exp(-E_a /RT), \text{ where}$$

A is the frequency factor and E_a is the energy of activation (Arrhenius equation).

* **Absolute rate theory**

$$k = (kT/h) \exp (- \triangle F^{o*} /RT)$$

$$= (kT/h) \exp (\triangle S^{o*} /R)\exp(-\triangle H^{o*} /RT)$$

Potential energy vs Reaction Coordinate diagram showing Activated complex at the peak, Reactants at the lower left plateau, E_a measured from the reactant level to the peak, Products at the lower right plateau, and ΔH of reaction between the reactant and product levels.
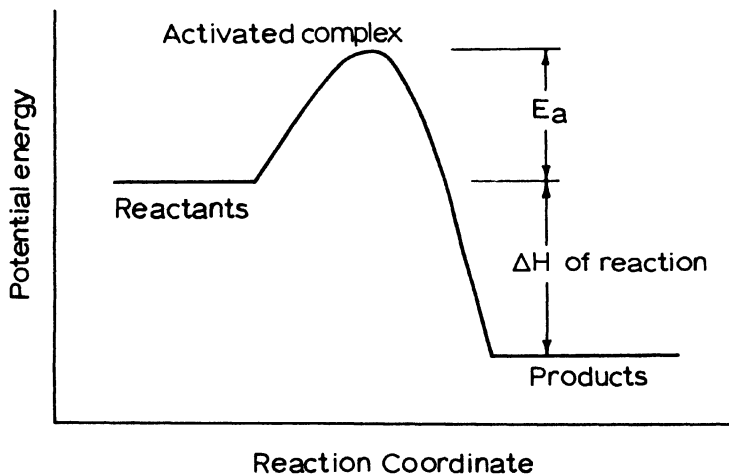
II.10 Surface Chemistry and Polymer Chemistry

(i) Surface Chemistry

* Surface concentration: $C_i^s = n_i^s / A^s$ (moles per unit area)

* Gibbs adsorption isotherm: $d\gamma = -C^* \, d\mu$, where C^* is the concentration of the component adsorbed and γ is the surface tension.

$$d\gamma = -RTC^* \, d \ln a$$

For an ideal solution, $d\gamma = -RTC^* \, d \ln x_2$ (x_2 is the mole fraction).

$$C^* = (-1/RT)(d\gamma / d \ln x_2)$$

* For condensed (monolayer) films, the surface pressure, f, is given by $f = b - aA$, where b and a are constants and A is the surface area.

* For adsorption from solution

$$x/m = kc^{1/n} \,,$$ where x and m are the masses of substance adsorbed and of the adsorbent respectively, c is the concentration of the solution and k is a constant (Freundlich).

* Langmuir isotherm equation for gas adsorption

$$\theta/1-\theta = P/P_0,$$ where θ is the fraction of sites covered and P_0 is a constant which measures the difficulty of desorption.

(ii) Physical chemistry of Polymers

* Molecular weight

number average molecular weight, $\bar{M}_n$ and mass average molecular weight, $\bar{M}_m$ are given by :

$$\bar{M}_n = \sum n_i M_i / \sum n_i \; ; \quad \bar{M}_m = \sum m_i M_i / \sum m_i$$

* Osmotic pressure

In dilute solutions, $\pi/C = (RT/\bar{M}_n) + BC$, where C is the mass concentration.

* Light scattering

$$KC/R_\theta = 1/M_m + 2BC/M^2,$$ where R_θ is the Rayleigh ratio at $90°$

* Ultracentrifuge:

   $M = RT_s /D(1-\bar{V}\rho)$ where s is the sedimentation constant, D
   is the diffusion coefficient, $\bar{V}$ is the partial specific volume
   is the density of the medium (Svedberg equation).

* Viscosity: $[\eta] = KM^{\alpha}$ (Staudinger)

* Classes of macromolecules

   (a) Addition polymers (eg. polyethylene) and condensation
   polymers (eg., nylon). Polymers may be atactic (random)
   or isotactic (stereospecific).

   (b) There are many inorganic polymers known (silicones,
   metaphosphate glasses, Sulfur).

   (c) Natural: Proteins (fibrous and globular, eg., keratin
   and hemoglobin respectively), Nucleic acids (eg., DNA),
   polysaccharides (eg., cellulose) and polyisoprene(natural
   rubber).

II.11 Statistical Mechanics

* Boltzmann distribution law (see Section II.7)

   $N_i/N = g_i \exp(-E_i/kT)/\sum_i g_i \exp(-E_i/kT)$,

   where g_i is the degeneracy or statistical weight of the ith level.

* Partition function: $\sum g_i \exp(-E_i/kT) = Q$

* Internal energy : $E = kT^2(\partial \ln Q/\partial T)$

   $\bar{C}_v = (k/T^2)\left[\partial^2 \ln Q/\partial(1/T^2)\right]$

* $S-S_0 = \int_0^T (C_v/T)dT$

   $= E/T + k \ln Q_{at\ T} + k \ln Q_{(at\ 0^\circ K)}$

   $S_0 = k \ln Q$ at $T = 0 = k \ln g_0$, where

   g_0 is the statistical weight of the lowest possible energy
   state of the system

   $S_0 = 0$ for crystalline solids (III law)
   S_0 due to mixing of random orientations is given by $= -R\sum X_i \ln X_i$.
   For two arrangements, $S_0 = R \ln 2$ (See Section II.8).

* Entropy and Probability

    $S = k \ln W$

    $W = N! \, / \, \prod_i N_i!$ (for distinguishable particles, with N_i
                        the number in i-th cell of phase space.)

    $S = k(n \ln N - N) - k \sum_i (N_i \ln N_i - N_i)$

    $\bar{S} = \bar{E} \, / \, \underline{T} + k \ln Q^{N_o}$, where N_o is the Avogadro
    number and $\bar{S}$ is the molar entropy.

* Free energy

    $A = - kT \ln Q$

    $P = kT \, (\partial \ln Q / \partial V)_T$

* Various partition functions

    $Q_{tr} = (2 \pi mkT)^{3/2} \, V/h^3$ (Translation)

    $Q_{rot} = 8 \pi^2 \, I \, kT/h^2$ (diatomic molecule)

    $Q_{rot} = 8 \pi^2 \, (8 \pi^3 ABC)^{1/2} (kT)^{3/2} / \sigma h^3$ (Polyatomic molecule)

    $Q_{vib} = \exp(-hv/2kT) \left[1 - \exp(-hv/kT) \right]^{-1}$ for each vibration

    $Q_{elec} = \sum_j g_j \exp(-E_j/kT)$

* Equilibrium constant for ideal gas reactions

    $F^\circ = -RT \ln K_p$

    $F^\circ = F^\circ_{Products} - F^\circ_{reactants}$

    $F^\circ = - RT \ln (Q^\circ/N_o)$

* Quantum statistics

    $N_i = g_i \, / \, \exp(\alpha + \beta \epsilon_i) \pm 1$

    For Fermi-Dirac case, +

    For Bose-Einstein case, −

II.12 Bibliography of Some Standard Books

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III. TABLES OF REFERENCE DATA AND SPECIFIC PROPERTIES
Fixed Points for Thermometer Calibration
Primary and Secondary Fixed Points

(Under a pressure of 1 standard atmosphere except for the triple points)

	I_n °C	Pressure correction and conditions
Equilibrium between liquid oxygen and its vapour (Oxygen point)	−182.970	Primary fixed point $+ 0.01254 \ (Pmm - 760) - 0.000006 \ (Pmm - 760)^2$
Equilibrium between solid carbon dioxide and its vapour	−78.5	$+ 0.01595 \ (Pmm - 760) - 0.000011 \ (Pmm - 760)^2$
Freezing Mercury	−38.87	. . . .
Equilibrium between ice and air saturated vapour (Ice Point)	0	Fundamental fixed point
Equilibrium between ice, water and its vapour (Triple Point)	+0.01000	Recommended for measurements of the highest precision
Equilibrium between liquid water and its vapour	100	$+ 0.03686 \ (Pmm - 760) - 0.000020 \ (Pmm - 760)^2$
Equilibrium between solid benzoic acid, its liquid and vapour (Triple Point)	122.36	. . . .
Freezing Tin	231.9	. . . .
Freezing Lead	327.3	. . . .
Equilibrium between liquid Mercury and its vapour	356.58	$+ 0.07309 \ (Pmm - 760) - 0.000040 \ (Pmm - 760)^2$
Freezing Zinc	419.5	. . . .
Equilibrium between liquid sulfur and its vapour		Primary fixed point
Sulfur Point	444.6000	$+ 0.09080 \ (Pmm - 760) - 0.000048 \ (Pmm - 760)^2$
Freezing Antimony	630.5	. . . .
Equilibrium between solid silver and its liquid (Silver Point)	960.8	Primary Point
Equilibrium between solid gold and its liquid (Gold Point)	1063.0	Primary fixed point

Freezing Mixtures:

The table below gives the percent of the anhydrous material in the eutectic mixture with ice. The eutectic temperature is the lowest temperature which can be obtained from a mixture of the substance with ice. To obtain the maximum cooling effect, the freezing mixture should be prepared with ice. Sodium chloride and ice, or calcium chloride and ice, mixtures are commonly used to attain temperatures of -21.2°C and -55°C respectively.

Formula of Substance	%	Eutectic Temp, °C	Formula of Substance	%	Eutectic Temp, °C
$BaCl_2$	22.5	- 7.8	$NH_4 NO_3$	41.2	-17.35
$CuCl_2$	36	-40	$(NH_4)_2 SO_4$	38.3	-19.05
$CuSO_4$	11.9	- 1.6	$NaBr$	40.3	-28
$FeCl_3$	33.1	-55	Na_2CO_3	5.9	- 2.1
HCl	24.8	-86	$NaOH$	19	-28
HNO_3	32.7	-43	$NaNO_3$	37	-18.5
K_2CO_3	39.5	-36.5	Na_2SO_4	12.7	- 3.55
KOH	31.5	-65	$Na_2S_2O_3$	30	-11
KNO_3	10.9	- 2.9	$ZnCl_2$	51	-62
$MgCl_2$	21.6	-33.6	$Zn(NO_3)_2$	39.4	-29
$Mg SO_4$	19	- 3.9	$Zn SO_4$	27.2	- 6.55
NH_4Cl	18.6	-15.8			

Non-Aqueous Baths

Low temperature may be produced by mixtures of various substances with carbon dioxide snow or by evaporation of low boiling liquids.

Substance	°C	Substance	°C
Alcohol - carbon dioxide	-72	Liquid air, boiling point	-190
Ammonia, boiling point	-33.4	Nitrogen, boiling point	-196
Chloroform-carbon dioxide	-77	Oxygen, boiling point	-183
Ethyl chloride, boiling point	+12.5	Sulfur dioxide boiling point	- 10

Standard Calibration Tables for Thermocouples

The tables given here represent arbitrary reference curves which show fairly well the relation between emf (in absolute millivolts) and temperature (in centigrade) and consequently should be used with an appropriate correction curve which must be determined for any individual thermocouple by means of a calibration at three or more fixed temperature points.

The tables which follow are for a fixed junction maintained at 0°C. If this fixed junction is not at 0°C, but at some other temperature (near 0°C), a correction should be applied as follows: $E_h = E_o + E$, where E_o is the observed emf, corresponding to the temperature of the fixed junction and E_h is the desired emf corrected for the temperature at which the fixed junction is being maintained. For more details, refer to National Bureau of Standards Circular 561 (1955); Journal Res. National Bureau of Standards 50,229 (1953).

COPPER – CONSTANTAN										
°C	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
-190°	-5.379	-5.205	-5.018	-4.817	-4.603	-4.377	-4.138	-3.887	-3.624	-3.349
-90°	-3.062	-2.764	-2.455	-2.135	-1.804	-1.463	-1.112	-0.751	-0.380	0.000
0	0.000	0.389	0.787	1.194	1.610	2.035	2.467	2.908	3.357	3.813
100°	4.277	4.749	5.227	5.712	6.204	6.703	7.208	7.719	8.236	8.759
200°	9.288	9.823	10.363	10.909	11.459	12.015	12.575	13.140	13.710	14.285
300°	14.864	15.447	16.035	16.626	17.222	17.821	18.425	19.032	19.642	20.257

CHROMEL – ALUMEL										
°C	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
-190°	-5.60	-5.43	-5.24	-5.03	-4.81	-4.58	-4.32	-4.06	-3.78	-3.49
-90°	-3.19	-2.87	-2.54	-2.20	-1.86	-1.50	-1.14	-0.77	-0.39	0.00
0°	0.00	0.40	0.80	1.20	1.61	2.02	2.43	2.85	3.26	3.68
100°	4.10	4.51	4.92	5.33	5.73	6.13	6.53	6.93	7.33	7.73
200°	8.13	8.54	8.94	9.34	9.75	10.16	10.57	10.98	11.39	11.80
300°	12.21	12.63	13.04	13.46	13.88	14.29	14.71	15.13	15.55	15.98
400°	16.40	16.82	17.24	17.67	18.09	18.51	18.94	19.36	19.79	20.22
500°	20.65	21.07	21.50	21.92	22.35	22.78	23.20	23.63	24.06	24.49
600°	24.91	25.34	25.76	26.19	26.61	27.03	27.45	27.87	28.29	28.72
700°	29.14	29.56	29.97	30.39	30.81	31.23	31.65	32.06	32.48	32.89
800°	33.30	33.71	34.12	34.53	34.93	35.34	35.75	36.15	36.55	36.96
900°	37.36	37.76	38.16	38.56	38.95	39.35	39.75	40.14	40.53	40.92
1000°	41.31	41.70	42.09	42.48	42.87	43.25	43.63	44.02	44.40	44.78
1100°	45.16	45.54	45.92	46.29	46.67	47.04	47.41	47.78	48.15	48.52
1200°	48.89	49.25	49.62	49.98	50.34	50.69	51.05	51.41	51.76	52.11
1300°	52.46	52.81	53.16	53.51	53.85	54.20	54.54	54.88	...	...

Specific Gravity of Air

This table gives the weight in grams $(\times 10^4)$ of one millilitre of air at 760 mm Hg. Density in grams per millilitre is the same as the specific gravity referred to water at 4°C as unity. To convert to density referred

to air at 70°F as unity, divide the value below by 12.00.

t°, C	Sp.Gr. x 10^4	t°, C	Sp.Gr. x 10^4
-25	14.240	40	11.274
-20	13.957	50	10.924
-10	13.424	60	10.596
0	12.931	80	9.995
+10	12.472	100	9.458
+20	12.046	200	7.457
30	11.647	400	5.248

Absolute density of water

This table gives the weight in grams of a cubic centimeter of water. Water attains its maximum density at 3.98°C at which temperature the density is 0.999973 (C.G.S.)

Temp °C	Density	Temp °C	Density
0	0.999841	12.0	0.999498
1.0	9900	14.0	9244
2.0	9941	16.0	8943
3.0	9965	18.0	8595
4.0	9973	20.0	8203
5.0	9965	22.0	7770
6.0	9941	24.0	7296
7.0	9902	26.0	6783
8.0	9849	28.0	6232
10.0	9700	30.0	5646

Vapour pressures of substances

For most compounds the constants A, B and C in the Antione equation(1) are given. For other compounds, constants B and C in equation (2) are given.

$$\log_{10} P = A - B/(C + t) \qquad \cdots \qquad \cdots \qquad (1)$$

$$\log_{10} P = -52.23 \, B/T + C \qquad \cdots \qquad \cdots \qquad (2)$$

(t = temperature in °C and T in °K)

Name	Range °C	A	B	C
Acetic Acid	0 to 36	7.80307	1651.2	225
Anhydride	36 to 170	7.18807	1416.7	221
Anhydride	100 to 140	Equation 2	45.585	8.688
Acetone	....	7.02447	1161.0	224
Acetonitrile	....	7.11988	1314.4	230
Aluminum chloride	70 to 190	Equation 2	115	16.24
Ammonium				
bromide	250 to 400	Equation 2	90.208	9.9404
chloride	100 to 400	Equation 2	83.486	10.0164
iodide	300 to 400	Equation 2	95.730	10.2700
Aniline	....	7.24179	1675.3	200
Anisole	....	6.98926	1453.8	200
Anthracene	100 to 160	Equation 2	72	8.91
Anthraquinone	224 to 286	Equation 2	110.05	12.305
Antimony	1070 to 1325	Equation 2	189	9.051
Argon	-207.62 to -189.19	Equation 2	7.8145	7.5741
Arsenic	440 to 815	Equation 2	133	10.800
Benzene	....	6.90565	1211.033	220.790
Bromine	....	6.83298	1133.0	228.3
n-butane	....	6.83029	945.90	240.00
iso-butane	....	6.74808	882.80	240.00
Camphor	0 to 180	Equation 2	53.559	8.799
Carbon dioxide	....	8.15406	799.02	230.0
disulfide	-10 to +160	6.85145	1122.50	236.46
monoxide	-210 to -165	6.24020	230.274	260
tetrachloride	....	6.93390	1242.43	230.0
Chlorine	....	6.86773	821.107	240
Chloroform	-30 to +150	6.90328	1163.03	227.4
Cresol(P)	....	7.00592	1493.0	160.0
Cyclohexane	-50 to +200	6.84498	1203.526	222.863
hexene	....	6.88617	1229.973	224.104
pentane	....	6.88676	1124.162	231.361
Decohydro naphthalene (cis)	15 to 95	7.41527	1898.13	225.0
	95 to 270	7.04387	1668.10	205.0

Name	Range °C	A	B	C
naphthalene (trans)	10 to 85	7.25013	1807.04	228.0
	85 to 250	6.88657	1583.28	208
Decane	10 to 80	7.31509	1705.60	212.59
Diethyl ether	....	6.78574	994.195	220.0
Diphenyl Amine	278.to 284	Equation 2	57.35	8.008
Ethyl acetate	−20 to +150	7.09808	1238.71	217.00
alcohol	....	8.04494	1554.3	222.65
amine	−70 to −20	7.09137	1019.7	225.0
	−20 to +90	7.05413	987.31	220.0
bromide	−50 to +130	6.89285	1083.8	231.7
chloride	−65 to +70	6.80270	949.62	230
Ethylene				
bromide	....	7.06245	1469.70	220.1
chloride	....	7.18431	1358.46	232.2
glycol	25 to 112	8.2621	2197.0	212.0
oxide	−70 to +100	7.40783	1181.31	250.60
Formic acid	....	6.94459	1295.26	218.0
Furan	−35 to +90	6.97523	1060.851	227.740
n.Heptane	....	6.90240	1268.115	216.900
n.Hexane	....	6.87776	1171.530	224.366
Hexene −1	....	6.86572	1152.971	225.849
Hydrazine	−10 to +39	8.26230	1881.6	238.0
Hydrogen	259.2 to −248	5.92088	71.615	276.337
bromide	−120 to −87*	8.4622	1112.4	270
	−120 to −60	6.88059	732.68	250
chloride	−127 to −60	7.06145	710.584	255.0
cyanide	−85 to −40	7.80196	1425.0	265.0
fluoride	−55 to +105	8.38036	1952.55	335.52
iodide	−97 to −51	Equation 2	24.16	8.259
	−50 to −34	Equation 2	21.58	7.630
peroxide	10 to 90	Equation 2	48.53	8.853
sulfide	−110 to −83	Equation 2	20.69	7.880
Iodine	....	7.26304	1697.87	204.0
Mercury	100 to 200	7.46905	2771.898	244.831
	200 to 300	7.7324	3003.68	262.482
	300 to 400	7.69059	2958.841	258.460

* Solid.

Name	Range °C	A	B	C
Mercury	400 to 800	7.7531	3068.195	273.438
Methyl acetate	....	7.20211	1232.83	228.0
alcohol	-20 to +140	7.87863	1473.11	230.0
amine	-93 to -45	6.91831	883.054	223.112
	-45 to +50	6.91205	838.116	214.237
benzoate	25 to 100	7.4312	1871.5	213.9
	100 to 260	7.07832	1656.25	195.23
chloride	-47 to -10	Equation 2	21.988	7.481
cyclohexane	0 to 120	6.82689	1272.864	221.630
ethylketone	....	6.97421	1209.6	216
Naphthalene	....	6.84577	1606.529	187.227
Nitric oxide	-200 to -161	Equation 2	16.423	10.048
	-16367 to -148	Equation 2	13.04	8.440
Nitrobenzene	112 to 209	Equation 2	48.955	8.192
methane	47 to 100	Equation 2	36.914	8.033
Nitrogen*	-210 to -180	6.86606	308.365	273.2
tetroxide	-100 to -40	Equation 2	55.16	13.400
	-40 to -10	Equation 2	45.44	11.214
	-8 to +43.2	Equation 2	33.43	8. 814
Oxygen	-210 to -160	6.98983	370.757	273.2
Ozone	....	6.72602	566.95	260.0
n-Pentane	....	6.85221	1064.63	232.000
iso-Pentane	....	6.78967	1020.012	233.097
Phenol	....	7.13617	1518.1	175.0
Phosgene	-68 to +68	6.84297	941.25	230
Phosphorous (white)	20 to 44.1	Equation 2	63.123	9.6511
Phosphorus (violet)	380 to 590	Equation 2	108.51	11.0842
Pentachloride	....	9.42740	2422.17	208.0
Phthalic anhydride	160 to 285	Equation 2	54.92	8.022
Silicon tetrachloride	-70 to +5	Equation 2	30.1	7.644
Sodium	180 to 883	Equation 2	103.3	7.553
Styrene	....	6.92409	1420.0	206
Sulfur				
dioxide	....	7.32776	1022.80	240.0
trioxide	24 to 48	Equation 2	43.45	10.022
Tetrachloroethylene	....	7.02003	1415.49	221.0

Name	Range °C	A	B	C
Toluene	....	6.95464	1344.800	219.482
Water	0 to 60	8.10765	1750.286	235.0
Xylene (m)	....	7.00908	1462.266	215.105
Xylene (p)	....	6.99052	1453.430	215.307
Zinc	250 to 419.4	Equation 2	133	9.200

Vapour pressure of mercury

Temp °C	mm of Hg	Temp °C	mm of Hg	Temp °C	mm of Hg
-30	0.0_5478	50	0.01267	160	4.189
-20	0.0_4181	60	0.02524	180	8.796
-10	0.0_4606	70	0.04825	200	17.287
0	0.0_3185	80	0.08880	220	32.133
+10	0.0_3490	90	0.1582	240	56.855
20	0.001201	100	0.2729	300	246.80
30	0.002777	120	0.7457	400	1574.1
40	0.006079	140	1.845	600	22.87 atm.

Vapour pressure of water

Temp °C	mm of Hg	Temp °C	mm of Hg	Temp °C	mm of Hg
-10	2.149	14.0	11.987	32.0	35.663
-5	3.163	16.0	13.634	34.0	39.898
0.0	4.579	18.0	15.477	40.0	55.324
2.0	5.294	20.0	17.535	50.0	92.51
4.0	6.101	22.0	19.827	60.0	149.38
6.0	7.013	24.0	22.377	70.0	233.7
8.0	8.045	26.0	25.209	80.0	355.1
10.0	9.209	28.0	28.349	90.0	525.76
12.0	10.518	30.0	31.824	100.0	760.00

Vapour pressure of ice in mm.Hg

t °C	mm of Hg	t °C	mm of Hg	t °C	mm of Hg
-90	0.000070	-40	0.0966	-10	1.950
-70	0.00194	-30	0.2859	-5	3.013
-50	0.0296	-20	0.776	0.0	4.579

Efficiency of drying agents

(Weight of residual water per litre of gas dried at 25°C)

Drying Agent	Milligrams of water	Drying Agent	Milligrams of Water
P_2O_5	2×10^{-5}	H_2SO_4	3×10^{-3}
BaO	1×10^{-4}	$CaSO_4$	4×10^{-3}
$Mg(ClO_4)_2$	5×10^{-4}	$CaCl_2$(granular)	0.14 - 0.25
KOH (fused)	2×10^{-3}		

Correction of boiling points at various pressures to 760 mm Hg

*To correct for small differences in barometric pressure the following formula is employed

$$T_c = T_0 + C (760 - Pmm) \qquad \ldots\ldots(\text{applicable only to liquids})$$

where T_c = corrected boiling point, T_0 = observed boiling point, P = atmospheric pressure in millimetre of mercury and C = a constant having the value of 0.037 at 25-40°C; 0.043 at 41-75°C; 0.044 at 76-100°C; 0.046 at 101-120°C; 0.048 at 121-140°C; 0.051 at 141-155°C; 0.055 at 156-220°C; 0.057 at 221-300°C; 0.064 at 310-325°C.

*The Sydney Young equation is as follows:

$$\text{For Centigrade scale: } G_c = 0.00012 (760-P)(273 + t_c)$$
$$\text{For Fahrenheit scale: } G_f = 0.00012 (760-P(460 - t_f)$$

in which G_c and G_f are, respectively, corrections to be made on the observed temperatures t_c or t_f, and P is the actual barometric pressure in millimetres of mercury.

The Sydney Young equation is applicable only to non-polar substances with low dielectric constants (e.g.; hydrocarbons). For other types of compounds a more exact value can be obtained by use of the following equations and constants:

$$\text{For Centigrade scale: } C_c = K (760-P)(273 + t_c)$$
$$\text{For Fahrenheit scale: } C_f = K (760-P)(460 + t_f)$$

where the value of the constant K is for: Hydrocarbons = 0.000125; Halogen-dervatives = 0.000125; Ethers = 0.000125; Aldehydes = 0.000125; Esters = 0.000121; Ketones = 0.000121; Amines = 0.000118; and Alcohols = 0.000100. The variation of K in the case of acids is very wide.

*Dreisbach method

$$dt/dp = B \ 2.3062 \ p \ (A - \log p)^2$$

This equation will give an accurate value for dt/dp at any pressure but can not be used to correct boiling points at various barometric readings to boiling points at 760 mm pressure since the dt/dp value varies with pressure. For the values of A and B for a number of organic compounds, see Dreisbach's P-V-T RELATIONSHIPS OF ORGANIC COMPOUNDS Published by Handbook Publishers, Inc. Sandusky, Ohio, U.S.A.

Linear expansion coefficients (Room Temperature)

Substance	(per °C)	Substance	(per °C)
Aluminum	23×10^{-6}	Ice	51×10^{-6}
Brass	19×10^{-6}	Lead	29×10^{-6}
Copper	17×10^{-6}	Magnesium	26.4×10^{-6}
Cast iron	8×10^{-6}	Nickel	13.1×10^{-6}
Diamond	1.2×10^{-6}	Palladium	12.4×10^{-6}
Glass(Ordinary)	9×10^{-6}	Platinum	9.0×10^{-6}
Glass(Pyrex)	3.2×10^{-6}	Silver	19.4×10^{-6}
Graphite	0.6×10^{-6}	Steel	11×10^{-6}
Gold	14.2×10^{-6}	Tin	29×10^{-6}
Hard rubber	80×10^{-6}	Zinc	16×10^{-6}

Volume expansion coefficients (Room Temperature)

Substance	(per °C)	Substance	(per °C)
Acetic Acid	1.071×10^{-3}	Iodine	204×10^{-6}
Acetone	1.487×10^{-3}	Mercury	0.182×10^{-3}
Benzene	1.237×10^{-3}	Nickel	38.2×10^{-6}
Cadmium	91×10^{-6}	Pentane	1.608×10^{-3}
Carbon tetr- chloride	1.236×10^{-3}	Phenol	1.090×10^{-3}
Chloroform	1.273×10^{-3}	Selenium	175×10^{-6}
Cobalt	35.6×10^{-6}	Tin	68×10^{-6}
Ether	1.656×10^{-3}	Water	0.207×10^{-3}
Glycerin	0.505×10^{-3}	Zinc	89×10^{-6}

Thermal conductivity data

*metals and alloys

Metal or Alloy	Temp °C	λ	Metal or Alloy	Temp °C	λ
Aluminum 99%	18	0.504	Constantin 60 Cu + 40 Ni	18	0.05401
Antimony	0	0.0538	Copper	-183	1.111
Brass, red	0	0.246	Copper	0	0.920
Brass, red	100	0.2827	Copper	100	0.92
Brass, yellow	0	0.2041			

Metal or Alloy	Temp °C	λ	Metal or Alloy	Temp °C	λ
Platinum	-252.8	0.93	Silver 99.98%	18	1.006
Platinum	-183	0.182	Tin	0	0.1528
Platinum	0-200	0.167	Tungsten	0	0.383
Rhodium	17	0.210	Zinc	18	0.2653
Wood metal	7	0.0319			

*common solids

Substance	Temp °C	$\lambda \times 10^3$	Substance	Temp °C	$\lambda \times 10^3$
Aluminum oxide	46.8	1.62	Graphite Powder Sp.G =0.7	40	2.85
Asbestos board	20	1.78	Gypsum	0	3.1
Asbestos fabric	20	0.666	Ice	—	5.7
Asbestos fiber	0	0.267	Lamp black Sp.G=0.165	40	0.156
Asbestos paper	20	0.345	Leather, Cowhide	84	0.42
Asphalt	20	1.7e	Marble white	...	7.8
Brick common	20	1.5	Mica	41.3	0.860
Chalk	20	2.2	Paper	20	0.3
Clay(fire-hardened)	360 to 600	2.09 to 2.21	Paraffin	0	0.688
Coal	< 0	0.405	Plaster of Paris	20	0.70
	1427	20.1	Porcelain	95	2.48
Concrete	20	2.2	Potassium chloride	0	16.6
Cork Sp.G=0.204	30	0.128	Quartz, glass	0	3.32
Cotton Sp.G=0.081	0	0.136	Rock salt	0	16.67
Diatomaceous earth	20	0.13	Rubber,hard,gray	49	0.55
Earth's crust average	20	4.0	Rubber, soft,red	49	0.34
Ebonite	0	0.378	Sand, dry	20	0.93
Felt (dark gray)	40	0.149	Wax, bees?	20	0.207
Fire brick	20	1.1	Wood, Pine‖to face(Sp.G=0.551)	20	0.834
Flannel	50	0.0355	Wood, Pine,⊥ to face(Sp.G=0.546)	15	0.361
Flint	20	2.4	Wood,teak,‖ to face(Sp.G=0.604)	15	0.903
Glass, Jena	22	2.27	Wood, teak ⊥ to face(Sp.G=0.642)	15	0.417
Glass, Soda	20	1.7			
Graphite Sp.G = 1.58	50	105.5			

*Liquid and solutions

Liquid or solution	Temp °C	$\lambda \times 10^3$	Liquid or solution	Temp °C	$\lambda \times 10^3$
Acetic acid	25	0.43	Ethyl ether	12	0.303
Acetone	0	0.4228	Glycerol	12	0.670
Ammonia 26%	18	1.09	Heptane	4	0.337
Aniline	12	0.408	Hexane	4	0.364
Benzene	12	0.333	Hydrochloric acid 25%	32	1.151
Calcium chloride 30%	32	1.315	Octane	4	0.375
Carbon tetrachloride	12	0.252	Paraffin oil	17	0.346
Ethyl acetate	12	0.348	Sulfuric acid 30%	32	1.244
Ethyl alcohol	5.2	0.487	Water	12	1.36

*Gases and vapours

Gas or vapour	Temp °C	$\lambda \times 10^5$	Gas or Vapour	Temp °C	$\lambda \times 10^5$
Acetone	0	2.301	Helium	-191.7	14.84
Acetone	100	3.96	Helium	0	33.60
Acetylene	0	4.40	Helium	100	39.85
Air	0	5.572	n-Heptane	100	4.136
Air	100	7.197	Hydrogen	0	39.60
Ammonia	0	5.135	Hydrogen	100	49.94
Argon	-182.6	1.42	Mercury (Vapour)	203	1.846
Argon	0	3.88	Methane	0	7.200
Argon	100	5.087	Neon	0	10.87
Benzene	0	2.094	Nitrogen	-191.4	1.829
Carbondioxide	-78.5	2.546	Nitrogen	0	5.68
Carbondioxide	0	3.393	Nitrogen	100	7.18
Carbondioxide	100	5.06	Oxygen	-191.4	1.721
Carbondisulfide	0	1.615	Oxygen	0	5.70
Carbon tetrachloride	46	1.666	Oxygen	100	7.427
Ethyl ether	0	3.101	Water vapour	46	4.580
Helium	-252.2	5.18	Water vapour	100	5.510

Critical constants of gases

Name	t_c, °C	p_c, atm	d_c, g/cc
Acetic acid	321.6	57.1	0.351
Acetone	235.5	46.6	0.273
Air	140.6	37.2	0.313
Argon	-122	48.0	0.531
Benzene	289	48.6	0.300
Carbon dioxide	31.0	72.9	0.468
monoxide	-140	34.5	0.301
tetrachloride	283.2	45.0	0.558
Chlorine	144	76.1	0.573
Chloroform	263.4	54	0.50
Cyclo-hexane	280	40.0	0.273
Diethyl ether	194	35.6	0.264
Ethane	32.3	48.2	0.203
Ethyl alcohol	243	63.0	0.276
Helium	-267.9	2.26	0.0693
n-Heptane	267.0	27.0	0.235
Hydrogen (normal)	-239.9	12.80	0.0310
Hydrogen(equilibrium)	-240.2	12.8	0.0308
Hydrogen chloride	51.4	81.5	0.42
sulfide	10C.4	88.9	0.349
Iodine	512	....	.....
Mercury	900	180	.....
Neon	-228.7	26.9	0.484
Nitrogen	-147.0	33.5	0.311
Oxygen	-118.4	50.1	0.41
Sulfur	1040	116	.....
dioxide	157.5	77.8	0.524
Water	374.2	218.3	0.32

van der Waals' constants for gases

To use the values of a and b in the table, P must be in atm., V in litres per mole, T in °K and R=0.08207 lit atm per mole per degree.

van der Waals' constants for gases (contd.)		
Name	$\dfrac{a}{(\text{litres})^2 \times \text{atm}}$ $\dfrac{}{(\text{mole})^2}$	$\dfrac{b}{\text{litres}}$ $\dfrac{}{\text{mole}}$
Argon	1.345	0.03219
Carbon dioxide	3.592	0.04267
Carbon monoxide	1.485	0.03985
Carbon tetrachloride	20.39	0.1383
Chlorine	6.493	0.05622
Chloroform	15.17	0.1022
Ethyl ether	17.38	0.1344
Ethylene	4.471	0.05714
Heptane(n)	31.51	0.2654
Hydrogen	0.2444	0.2661
Hydrogen chloride	3.667	0.04081
Mercury	8.093	0.01696
Methane	2.253	0.04278
Neon	0.2107	0.01709
Nitrogen	1.390	0.03913
Oxygen	1.360	0.03183
Water	5.464	0.03049

*Surface Tensions of liquids

The nature of the gas in contact with the liquid is given in paren-
thesis. The temperature (in °C) is indicated by the superscript. Eotvos
constant ($dr/dt = K_E$) values are also given.

	Surface Tension in Dynes per cm.		k_E
Benzene (vapour)	$31.7^{0°}$	$29.02^{20°}$	....
n-Butyl alcohol (air or vapour)	$26.2^{0°}$	$24.6^{20°}$	1.91
Chlorobenzene (air)	$34.4^{10°}$	$33.2^{20°}$	2.21
Chlorobenzene (vapour)	$34.8^{10°}$	$33.6^{20°}$	....
Chloroform (air)	$28.5^{10°}$	$27.1^{20°}$	2.1
Ethyl acetate (air)	$26.5^{0°}$	$23.9^{20°}$	2.3
Ethyl acetate (vapour)	$26.90°$	$24.3^{20°}$	2.3
Ethyl alcohol (air)	$24.05^{0°}$	$22.27^{20°}$	1.0
Ethyl alcohol (vapour)	$22.75^{20°}$	$20.14^{50°}$	1.3
Glycerol (air)	$63^{20°}$	$59^{90°}$	

* Surface tension of water

Surface tension in Dynes/cm	Surface tension in Dynes/cm
$75.64^{(0)°}$ $74.22^{(10)°}$ $73.49^{(15)°}$	$71.97^{(25)°}$ $71.18^{(30)°}$ $67.91^{(50)°}$

Viscosity of Substances

Viscosity of liquids is given in millipoises (1000_n) at the temperature (in °C) indicated by the superscript. Value in centipoises = value in milli-poises/$10d^t$ where d^t is the density at the temperature.

* Liquids

Name	1000	Name	1000
Acetone	$3.311^{(20)°}$ $2.561^{(50°)}$	Carbon tetrchloride	$9.578^{(21.21°)}$ $7.928^{(35.21°)}$
Aniline	$44.67^{(20°)}$ $29.3^{(32°)}$	Ethyl acetate	$4.546^{(20°)}$ $3.668^{(40°)}$
Benzene	$6.47^{(20°)}$ $5.61^{(30°)}$	Ethyl alcohol	$11.943^{(20°)}$ $8.309^{(40°)}$
n-butyl alcohol	$29.48^{(20°)}$ $17.816^{(40°)}$	Methyl acetate	$3.880^{(20°)}$

* Gases and Vapours (in micropoises)

Name	$\times 10^6$	Name	$\times 10^6$
Acetone	$78.0^{(18°)}$ $94.27^{(100°)}$	Hydrogen	$93.1^{(20°)}$
Air	$170.9^{(0°)}$ $180.8^{(20°)}$ $217.5^{(100°)}$	Iodine	$239.7^{(247.10°)}$
		Nitrogen(chemical)	$184^{(20°)}$ $189.4^{(53.50°)}$
Argon	$221.0^{(23°)}$	Water vapour	$100.6^{(28.9°)}$ $127^{(100°)}$
Benzene	$75.9^{(16.8°)}$ $100.7^{(70.1°)}$		

*Aqueous Sucrose solutions (in centipoises)

t °C	20 wt %	40 wt %	60 wt %
10	2.652	9.794	109.8

t°C	20 wt %	40 wt %	60 wt %
20	1.960	6.200	56.5
30	1.504	4.382	33.78
40	1.193	3.249	21.28
50	0.970	2.497	14.01

*Aqueous Ethyl alcohol solutions (in centipoises)

% by wt	10	20	40	60	80	100
% by vol	12.36	24.09	45.83	65.56	83.59	100
t°C						
20	1.538	2.183	2.91	2.67	2.008	1.200
25	1.323	1.815	2.35	2.24	1.748	1.096
30	1.160	1.553	2.02	1.93	1.531	1.003
40	0.907	1.160	1.482	1.447	1.203	0.834

* Water in centipoises from 0° to 100°C

Calculated by the formula:

$$n = 2.1482 \ (t - 8.435 + 8078.4 + (t - 8.435)^2 \ -120$$

Liquid standards for refractive index determinations			
$n^{20°}_D$	Liquid	$n^{20°}_D$	Liquid
1.3289	Methyl alcohol	1.4663	Cyclohexanol
1.3330	water	1.4950	Toluene
1.3585	Acetone	1.5005	Benzene
1.3725	Ethyl acetate	1.5165	Anisole
1.3875	n-Heptane	1.5246	Chlorobenzene
1.3986	n-Butyl alcohol	1.5300	Methyl iodide
1.4015	n-Butyl chloride	1.5520	Nitrobenzene
1.4221	Dioxan (1,4)	1.5859	Aniline
1.4225	Methylcyclohexane	1.5960	Bromoform
1.4314	Ethylene glycol	1.6200	Iodobenzene
1.4500	Cyclohexanone	1.7400	Methylene iodide

Magnetic Susceptibility Data

The following tables give values of specific susceptibility (x) for various substances in 1x10⁻6 cgs units. Relation to volume susceptibility k is shown by the equation x = k/d, where d is the density of the substance. Values of positive for parame ntic substances

*Elements and Inorganic Compounds

Substance	Temp °C	Susceptibility 10^{-6} cgs	Substance	Temp °C	Susceptibility 10^{-6} cgs
Aluminum	18	0.65	Manganese	18	9.9
Aluminum oxide	....	-0.098	Manganese dioxide	21	38.4
Ammonia	16 gas	-1.1	Mercury	-80 sol	-0.15
Antimony	18 sol	-0.87	Neodymium	18	36
Argon	20 gas	-0.45	Neodymium oxide	....	30.3
Arsenic	18	-0.31	Nickel bromide	18	19
Carbon(graphite)	20	-3.5	Nickel Carbonyl	19	-0.481
Carbon dioxide	20 gas	-0.423			
Ceric Oxide	....	0.39	Nitrogen	20 gas	-0.342
Cerous chloride	19	6.1	Nitrogen dioxide	22 gas	48.66
Chromium	18	3.6	Nitrogen monoxide	12 liq	-0.429
Chromic Oxide	18	25.5			
Chromium trioxide	17	0.51	Oxygen	20 gas	106.2
			Platinum	18	1.10
Cobaltic oxide	....	34.3	Platinum tetrachloride	22	0.0
Copper	18	-0.086	Potassium	18	0.52
Cupric bromide	31	3.10	Silicon	18	-0.13
Cupric Sulfate 5H$_2$O	....	8.6 5.9	Silver	18	-0.20
Dysprosium oxide	16	229	Silver chloride	17	-0.35
Ferric Chloride	20	86.2	Sulfur (rhombic)	18	-0.49
Ferric oxide	18	20.6	Tatanium dioxide	....	0.066
Ferric Sulfate	23	57.3	Uranium	18	2.6
Gadolinium oxide	20	130.1	Vanadium	18	1.4
Gold	18	-0.15	Vanadium Pentoxide	15	0.85
Iron Carbonyl	19	-0.40	Vanadium trioxide	15	13.9
Lanthanum chloride	15	5.6	Zinc oxide	....	-0.362
Lead bromide	20	-0.28	Zirconium dioxide	15	-0.112

*Organic Compounds

Substance	Susceptibility 10^{-6} cgs	Substance	Susceptibility 10^{-6} cgs.
Acetic acid	−0.526	Cyclohexane	−0.810
Acetone	−0.581	Ethyl acetate	−0.607 (−6°)
Anthracene	−0.726	Glycerol	−0.538
Benzene	−0.712 (16.8°)	Hexane	−0.888
Benzoic acid	−0.556	Pyridine	−0.623
Carbon tetrachloride	−0.429	Toluene	−0.729
Chloroform	−0.488	Urea	−0.560

Standard Electrode Potentials for Aqueous Solutions at 25°C

Electrode	Electrode reaction	(Volts)
ACID SOLUTION		
Li/Li^+	$Li = Li^+ + e^-$	−3.045
K/K^+	$K = K^+ + e^-$	−2.925
Ba/Ba^{++}	$Ba = Ba^{++} + 2e^-$	−2.906
Ca/Ca^{++}	$Ca = Ca^{++} + 2e^-$	−2.866
Na/Na^+	$Na = Na^+ + e^-$	−2.7142
Mg/Mg^{++}	$Mg = Mg^{++} + 2e^-$	−2.363
Al/Al^{3+}	$Al = Al^{3+} + 3e^-$	−1.662
Mn/Mn^{++}	$Mn = Mn^{++} + 2e^-$	−1.180
Zn/Zn^{++}	$Zn = Zn^{++} + 2e^-$	−0.7628
Cr/Cr^{3+}	$Cr = Cr^{3+} + 3e^-$	−0.744
Fe/Fe^{++}	$Fe = Fe^{++} + 2e^-$	−0.4402
Cd/Cd^{++}	$Cd = Cd^{++} + 2e^-$	−0.4409
$Pb/PbSO_4/SO_4^=$	$Pb + SO_4^= = PbSO_4 + 2e^-$	−0.3588
Pb/Pb^{++}	$Pb = Pb^{++} + 2e^-$	−0.126
$Pt/H_2/H^+$	$H_2 = 2H^+ + 2e^-$	0.0000
$Ag/AgBr/Br^-$	$Ag + Br^- =$	+0.0713
$Cu/CuCl/Cl$	$Cu + Cl^- = CuCl + e^-$	+0.137
$Pt/Cu^+, Cu^{++}$	$Cu^+ + Cu^{++} + e^-$	+0.153
$Ag/AgCl/Cl^-$	$Ag + Cl^- = AgCl + e^-$	+0.2225
$Pt/Hg/Hg_2Cl_2/Cl^-$	$2Cl^- + 2Hg = Hg_2Cl_2 + 2e^-$	+0.2676
Cu/Cu^{++}	$Cu = Cu^{++} + 2e^-$	+0.337
$Pt/I_2/I^-$	$3I = I_3^- + 2e^-$	+0.536
$Pt/Fe^{++}, Fe^{3+}$	$Fe^{++} = Fe^{3+} + e^-$	+0.771
Ag/Ag^+	$Ag = Ag^+ + e^-$	+0.7991
$Au/AuCl_4^-, Cl^-$	$Au + 4Cl^- = AuCl_4^- + 3e^-$	+1.00
$Pt/Cl_2/Cl^-$	$2Cl^- = Cl_2 + 2e^-$	+1.3595
$Pt/Mn^{++}, MnO_4^-$	$Mn^{++} + 4H_2O = MnO_4^- + 8H^+ + 5e^-$	+1.51
$Pt/F_2/F^-$	$2F^- = F_2(g) + 2e^-$	+2.87

Electrode	Electrode reaction	(Volts)
BASIC SOLUTION		
$Pt/SO_3^=$, $SO_4^=$	$SO_3^= + 2OH^- = SO_4^= + H_2O + 2e^-$	-0.93
$Pt/H_2/OH^-$	$H_2 + 2OH^- = 2H_2O + 2e^-$	-0.82806
$Pt/S/S^=$	$S^= = S + 2e^-$	-0.447
$Pt/O_2/OH^-$	$4OH^- = O_2 + 2H_2O + 4e^-$	+0.401
$Pt/MnO_2/MnO_4^-$	$MnO_2 + 4OH^- = MnO_4^- + 2H_2O + 3e^-$	+0.588

Electrical Conductivity of Standard Solutions

In the table below, the normal KCl solution was prepared by dissolving 74.59g of KCl in water and diluting to one litre at 18°C. The specific gravity of such a solution is 1.0449 at 18°C. The concentrations of H_2SO_4 and of Mg SO_4 are those of maximum conductivity at 18°C

Conductivity in mhos/centimeter, or ohm^{-1} cm^{-1}

Temp °C	KCl Normal	KCl 0.1 normal	KCl 0.01 normal	H_2SO_4 Sp.G 1.223 (18°)	NaCl saturated Sp.G 1.2014 (18°)	$MgSO_4$ Sp.G. 1.190 (18°)
0	0.06541	0.00715	0.000776	0.5184	0.1345	0.02877
10	0.08319	0.00933	0.001020	0.6408	0.1779	0.03963
20	0.10207	0.01167	0.001278	0.7645	0.2260	0.05171
30	....	0.01412	0.001552	0.8860	0.2774	0.06459

Ionisation Constants of Acids and Bases at 25°C

*Acids

Acid	-log K	Acid	-log K
Acetic	4.76	Formic	3.75
Adipic	4.43	Fumaric	K_1 3.03
Aluminum			K_2 4.47
hydroxide	12.20	Glutaric	4.34
Barbituric	3.98	Glycine	9.78
Benzoic	4.20	Hydrazoic	4.59
Boric	9.24	Hydrocyanic	9.14
Bromoacetic	2.87	Hydrofluoric	3.14
n-Butyric	4.82	Hydrosulfuric (H_2S)	K_1 7.24; K_2 14.92
Carbonic	K_1 6.37	Maleic	K_1 2.00
	K_2 10.25		K_2 6.26
Chloroacetic	2.86	Malic	K_1 3.40
p-Chlorobenzoic	3.98		K_2 5.05
Chromic	6.49	Malonic	K_1 2.85
Cinnamic (cis)	3.88		K_2 6.10
Cinnamic (trans)	4.43	Methoxybenzoic	4.47
Citric	K_1 3.06	Nitrobenzoic	3.42
	K_2 4.74	Nitrous	4.47
	K_3 5.40	Oxalic	K_1 1.19
Cyanuric	6.74		K_2 4.21
Dichloroacetic	1.30	Periodic	1.64

Acid	$-\log K$	Acid	$-\log K$
Phenol	9.89	Silicic	ca 9.7
Phenylacetic	4.31	Succinic	K_1 4.19
Phosphoric	K_1 2.12		K_2 5.57
	K_2 7.21	Sulfanilic	3.19
	K_3 12.32	Sulfuric	K_1 0.40
Phosphorous	K_1 1.80		K_2 1.92
	K_2 6.15	Sulfurous	K_1 1.76
Phenolphthalein	9.70		K_2 7.20
o-Phthalic	2.89	Tartaric	K_1 3.02
	5.41		K_2 4.54
Picric	0.38	Thiosulfuric	2.00
Propionic	4.87	Trichloroacetic	0.89
Saccharin	1.60	Uric	3.89
Salicytic	2.97		

*Bases

Base	$-\log K$	Base	$-\log K$
Acetanilide	13.39	Hydrazine	5.52
Ammonium		Hydraxylamine	7.97
hydroxide	(25°) 4.74	Methylamine	3.36
Aniline	9.42	Morphine	6.13
Benzidine	K_1 9.03	Phenylhydrazine	(40°) 8.80
	K_2 10.25	Piperidine	2.80
n-Butylamine	3.39	Pyridine	8.85
tert-Butylamine	3.55	Quonoline	9.20
Diethylamine	2.90	Thiourea	14.96
Enthanolamine	4.56	p-Toluidine	8.70
Ethylamine	3.25	Triethylamine	3.25
Ethylenediamine	4.07	Urea	13.82
Glycine	11.65	Zinc hydroxide	4.36

Ionic properties of water

	Temperature, °C						
	0	10	20	25	30	50	100
Specific conductivity $(\text{ohm}^{-1}\text{cm}^{-1} \times 10^8)$	1.2	2.3	4.2	5.5	7.0	17	--
Ionic product $(K_w \times 10^{15})$	1.14	2.92	6.81	10.08	14.7	56	513

Acid-Base Indicators

Name	Concentration of solution	Colour low pH–high pH	pH range	$pK_a = -\log K_a$
Thymol blue	0.1% in water	red-yellow	1.2– 2.8	1.7
Methyl yellow	0.1% in 90% alc.	red-yellow	2.9– 4.0	——
Methyl orange	0.1% in water	red-yellow	3.1– 4.4	3.7
Bromocresol green	0.1% in water	yellow-blue	3.8– 5.4	4.7
Methyl red	0.1% in water	red-yellow	4.4– 6.2	5.1
Bromocresol purple	0.1% in water	yellow-red	5.2– 6.8	6.3
Azolitmin(litmus)	0.5% in water	red-blue	5.0– 8.0	——
Bromothymol blue	0.1% in water	yellow-blue	6.0– 7.6	7.0
Phenol red	0.1% in water	yellow-red	6.8– 8.4	7.9
Cresol red	0.1% in water	yellow-red	7.2– 8.8	8.3
Thymol blue	0.1% in water	yellow-blue	8.0– 9.6	8.9
Phenolphthalein	0.1% in 70% alc.	colourless-red	8.3–10.0	9.6
Alizarin yellow	0.1% in water	yellow-lilac	10.1–12.0	——

Solubility Products at 25°C

Name	Formula	Solubility Product
aluminium hydroxide	$Al(OH)_3$	1×10^{-33}
antimony(III) sulphide	Sb_2S_3	*
arsenic(III) sulphide	As_2S_3	**
barium carbonate	$BaCO_3$	5×10^{-9}
barium sulphate	$BaSO_4$	1×10^{-10}
bismuth sulphide	Bi_2S_3	1×10^{-97}
cadmium hydroxide	$Cd(OH)_2$	4×10^{-15}
cadmium sulphide	CdS	8×10^{-27}
calcium carbonate	$CaCO_3$	3×10^{-9}
calcium hydroxide	$Ca(OH)_2$	4×10^{-6}
calcium fluoride	CaF_2	3×10^{-11}
calcium oxalate	CaC_2O_4	2×10^{-9}
calcium sulphate	$CaSO_4$	9×10^{-6}
chromium(II) hydroxide	$Cr(OH)_2$	1×10^{-17}

Name	Formula	Solubility Product
chromium(III) hydroxide	$Cr(OH)_3$	1×10^{-33}
cobalt(II) hydroxide	$Co(OH)_2$	6×10^{-15}
cobalt(III) hydroxide	$Co(OH)_3$	3×10^{-41}
cobalt(II) sulphide	CoS	$4 \times 10^{-21}(\alpha)$
		$2 \times 10^{-25}(\beta)$
copper(I) chloride	CuCl	2×10^{-7}
copper(II) hydroxide	$Cu(OH)_2$	2×10^{-19}
copper(I) iodide	CuI	1×10^{-12}
copper(II) sulphide	CuS	4×10^{-36}
copper(I) thiocyanate	CuSCN	ca.1×10^{-14}
iron(II) hydroxide	$Fe(OH)_2$	8×10^{-16}
iron(III) hydroxide	$Fe(OH)_3$	4×10^{-40}
iron(II) sulphide	FeS	5×10^{-18}
lead carbonate	$PbCO_3$	6×10^{-14}
lead chloride	$PbCl_2$	2×10^{-5}
lead hydroxide	$Pb(OH)_2$	8×10^{-16}
lead sulphate	$PbSO_4$	2×10^{-8}
magnesium carbonate	$MgCO_3$	3×10^{-8}
magnesium hydroxide	$Mg(OH)_2$	1×10^{-11}
manganese(II) hydroxide	$Mn(OH)_2$	2×10^{-13}
mercury(I) chloride	Hg_2Cl_2	1×10^{-18}
mercury(I) sulphate	Hg_2SO_4	7×10^{-7}
mercury(II) sulphide	HgS	1×10^{-52}
nickel hydroxide	$Ni(OH)_2$	2×10^{-15}
scandium hydroxide	$Sc(OH)_3$	2×10^{-30}
silver acetate	$AgCH_3COO$	3×10^{-3}
silver carbonate	Ag_2CO_3	8×10^{-12}
silver chloride	AgCl	2×10^{-10}
silver chromate	Ag_2CrO_4	2×10^{-12}
silver cyanide	AgCN	$1 \times 10^{-16}(***)$
silver hydroxide	AgOH	2×10^{-8}
silver iodide	AgI	8×10^{-17}
silver sulphide	Ag_2S	6×10^{-50}
silver thiocyanate	AgSCN	1×10^{-12}
strontium carbonate	$SrCO_3$	1×10^{-10}

Name	Formula	Solubility Product
tin(II) hydroxide	$Sn(OH)_2$	8×10^{-29}
tin(II) sulphide	SnS	1×10^{-26}
titanium(IV) hydroxide	$TiO(OH)_2$	1×10^{-29}
zinc hydroxide	$Zn(OH)_2$	2×10^{-16}
zinc sulphide	ZnS	$2 \times 10^{-24} (\alpha)$
		$3 \times 10^{-22} (\beta)$

$$* \tfrac{1}{2} Sb_2S_3(s) + 3H_2O \rightleftharpoons Sb(OH)_3 + 3/2 \ H_2S(g) \quad 2 \times 10^{-15}$$
$$** \tfrac{1}{2} As_2S_3(s) + 3H_2O \rightleftharpoons As(OH)_3 + 3/2 \ H_2S(g) \quad 5 \times 10^{-12}$$
$$*** 2AgCN \rightleftharpoons Ag^+ + Ag(CN)_2^- \quad 2 \times 10^{-11}$$

Stepwise stability constants at $\sim 27°C$

K_n = the equilibrium constant for the reaction

$$ML_{n-1} + L \rightleftharpoons ML_n.$$
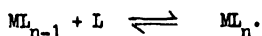
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Ammines						
Ni^{2+}	2.8	2.2	1.6	1.2	0.7	-0.01
Cu^{2+}	4.1	3.5	2.9	2.1	-0.5	——
Zn^{2+}	2.3	2.3	2.4	2.0	——	——
Ag^+	3.4	3.8	——	——	——	——
Cyanides						
Hg^{2+}	18.0	16.7	3.8	3.0	——	——
Fluorides						
Al^{3+}	6.1	5.0	3.9	2.7	1.6	0.5
Chlorides						
Fe^{3+}	1.5	0.7	-1.4	-1.9	——	——

Stability Constants of Complex ions at 25°C

K = the equilibrium constant referred to the reaction as written.

Equilibrium	$\log K$
$Al^{3+} + 6F^- \rightleftharpoons AlF_6^{3-}$	20
$Fe2+ + 6CN- \rightleftharpoons Fe(CN)_6^{4-}$	24

Stability Constants

Equilibrium	log K
$Fe^{3+} + 6CN^- \rightleftharpoons Fe(CN)_6^{3-}$	31
$Fe^{3+} + 4Cl^- \rightleftharpoons FeCl_4^-$	-1
$Co^{3+} + 6CN^- \rightleftharpoons Co(CN)_6^{3-}$	64
$Co^{2+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{2+}$	5
$Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$	35
$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	31
$Ni^{2+} + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{2+}$	9
$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{3-}$	30
$Cu^+ + 2NH_3 \rightleftharpoons Cu(NH_3)_2^+$	11
$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$	13
$Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$	17
$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$	9
$\frac{1}{2}As_2S_3(s) + \frac{1}{2}S^{2-} \rightleftharpoons AsS_2^-$	1
$AsS_2^- + H^+ \rightleftharpoons HAsS_2$	4
$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$	21
$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$	7
$AgCl(s) + Cl^- \rightleftharpoons AgCl_2^-$	-5
$AgI(s) + I^- \rightleftharpoons AgI_2^-$	-5
$AgI(s) + 2I^- \rightleftharpoons AgI_3^{2-}$	-3
$Cd^{2+} + 4CN^- \rightleftharpoons Cd(CN)_4^{2-}$	19
$Cd^{2+} + 4I^- \rightleftharpoons CdI_4^{2-}$	6
$SnS_2(s) + S^{2-} \rightleftharpoons SnS_3^{2-}$	5
$Hg^{2+} + 4CN^- \rightleftharpoons Hg(CN)_4^{2-}$	41
$HgS(s) + S^{2-} \rightleftharpoons HgS_2^{2-}$	0.6
$HgS_2^{2-} + 2H^+ \rightleftharpoons Hg(SH)_2$	7.0
$PbCl_2(s) + Cl^- \rightleftharpoons PbCl_3^-$	-4

Dielectric Constant Data

(See also Section II.5 for some data)

The values of a or α may be used for interpolating or for extrapolating over a limited range of temperature by means of the equations:

$$E_t' = E_t - a\ (t'-t) \qquad \cdots\cdots\cdots(1)$$

$$\log_{10}E_t' = \log_{10}E_t - \alpha(t'-t) \qquad \cdots\cdots\cdots(2)$$

Liquid (°C)	E	a(or α) x10^2	Liquid (°C)	E	a (or α) x 10^2
Acetic acid(20°)	6.15	......	Ethylene bromide(25°)	4.78	0.60
Acetone (25°)	20.7	0.205(α)	diamine(20°)	14.2	10
Acetonitrile(20°)	37.5	16	glycol(25°)	37.7	0.224(α)
Aniline(20°)	6.89	0.148(α)	Formic acid(16°)	58.5[a]	......
Bromine(20°)	3.09	0.7	amide(20°)	109	72
Bromoform(20°)	4.39	0.105(α)	Heptane (n)(20°)	1.924	0.140
Butyl acetate(n) (20°)	5.01	1.4	Methanol(25°)	32.63	0.264(α)
alcohol(n)(25°)	17.1	0.335(α)	Methyl acetate (25°)	6.68	2.2
Carbon disulfide (20°)	2.641	0.268			
Carbon tetrachloride (20°)	2.238	0.200	Methylenechloride (20°)	9.08	......
Chloroform (20°)	4.806	0.160(α)	Nitro-methane(30°)	35.87	0.189(α)
Cyclo-hexane(20°)	2.023	0.160	benzene(25°)	34.82	0.225(α)
hexanol (25°)	15.0	0.437(α)	Tetrachloro-ethylene(25°)	2.30	0.20
hexanone(20°)	18.3	....	Tetrahydrofuran (25°)	7.4	......
Decane (n)(20°)	1.991	0.130			
Dimethylsulfoxide (20°)	45	....	Toluene(25°)	2.379	0.243
Dioxane (1,4)(25°)	2.21	0.170	Tributyl Phosphate (30°)	7.95	2.74
Ethyl acetate(25°)	6.02	1.5	Water (200°)	34.59*	....
alcohol (25°)	24.3	0.270(α)			
ether (20°)	4.34	0.217(α)			

* $E = 5321/T + 233.76 - 0.9297\ T + 0.001417\ T^2$; E(25°), 78.54

Index of Refraction Calculations For Organic Liquids

In the Lorentz-Lorenz formula:

$$\frac{n^2 - 1}{n^2 + 2} \; x \; \frac{1}{d} = k$$

n is the index of refraction of a liquid at a given temperature, d is the density of the substance at the same temperature, and k (which is nearly independent of the temperature) is the constant called the "specific refraction". The product M x k, where M is the molecular weight of the substance, is the "molecular refraction"; this quantity (Mk) is additive and can be calculated for most organic liquid compounds from empirically deduced atomic, and structural refractive constants.

	k (sodium D light)
C	2.418
H	1.100
O	(i) 1.525; (ii) 2.221; (iii) 1.643; (iv) 1.64
S	(v) 7.69 (vi) 7.97 (vii) 7.91 (viii) 8.11
Hal	(ix) 0.95; (x) 1.1; (xi) 5.967; (xii) 8.865 (xiii) 13.900
N	2.45^1; 3.21^2; 2.65^3; 3.59^4; 3.00^5; 4.36^6; 2.48^7; 2.47^8; 3.05^9; 3.79^{10} 3.93^{11}; 2.65^{12}; 2.27^{15}; 2.71^{14}; 3.776^{15}; 3.901^{16}; 4.10^{17}; 3.46^{18}.
NO_2	7.59^{19}; 7.44^{20}; 6.72^{21}; 7.30^{22}; 7.51^{23}

In the form of : (i) (OH); (ii) C:O; (iii) ether OR; (iv) ester OR (v) SH; (vi)RSR; (vii) RCNS; (viii) RSSR; (ix) One F on carbon; (x) F in polyfluorides; (xi) Cl; (xii) Br; (xiii) I; (1) aliph.prim.amine; (2) arom.primamine; (3)aliph. sec. amine (4) arom.sec.amine (5) aliph.tert.amine (6)arom.tert.amine; (7)hydroxylmine; (8) hydrozine (9)aliph.cynide (10) aromatic cynide (11)alip.oxime (12) prim.amide (13) sec.amide (14)tert.amide; (15) imidine (16)oximido (17) carbimido; (18) hydrazone; (19) alkyl nitrate; (20) alkyl nitrite (21) nitroparaffin; (22) nitroaromatics, (23) nitramine.

Crystal structures and unit cell dimensions (in Å) of selected solids (25°C)

(All the data are from NBS Circular 539)

Aluminum	cubic (F.C.C.)	4.0494
Aluminum oxide (α)	hexagonal	a=4.7580; c; 12.9910
Ammonium chloride	cubic (Pm3m)	3.8756
Calcium carbonate(calcite)	hexagonal	a=4.989; c=17.0620
Calcium fluoride(Fluorite)	cubic.(Fm3m)	5.4626
Carbon (diamond)	cubic.(F.C.C.)	3.5667
Cesium chloride	cubic (B.C.C.)	4.1230
Copper	cubic (F.C.C.)	3.6150
Iron (α)	cubic (Im3m)	2.8664

Magnesium oxide	cubic (F.C.C.)	4.2130
Molybdenum	cubic (B.C.C.)	3.1472
Platinum	cubic (Pm3m)	3.9231
Potassium chloride	cubic (Pm3m)	5.3470
Silicon dioxide(∝)	Tetragonal	a=4.9730; c=6.9500
Silver	cubic (Pm3m)	4.0862
Sodium chloride	cubic (F.C.C.)	5.6402
Tungsten	cubic (Im3m)	3.1648
Zinc sulfide (form)	hexagonal	ᵃ 3.8200; c=6.2600

Elastic Moduli

Material	Composition and condition	Young's Modulus $10''$ dyns/cm	Poisson's ratio	Rigidity Modulus $10''$ dynes/cm	Tensile breaking stress 10^8 dynes/cm
Silver	Pure	7.1 – 7.8	0.37	2.6	——
Platinum	Pure	16.67	0.39	6.42	12 – 13
Beryllium	Pure	29.4	——	——	12 – 15
Molybdenum	Pure	34	——	14.7	69
Silicon	Pure	11.26	——	——	——
Titanium	Pure	11.6	——	——	54
Tungsten	Pure (drawn)	34	——	13.5	80
Gold	Pure (annealed)	8	0.42	——	13.1
Aluminium	Pure and alloyed	6.89	0.33	2.65	4.74
Copper	(with 0.0016 sulfur)	12.77	0.364	4.68	35
Brass	Various composition	9-11.7	0.33	3.5-4.7	30 – 60
Lead	Rolled	1.47-1.67	0.40-0.45	0.54	1 – 2
Magnesium	Pure	4.48	0.35	1.67	——
Tin	Rolled	3.92-5.39	0.33	1.67	1.45-2.14
Iron	Cast(2.5-3.5% carbon and other impurities	8.27-17.2	0.17	5.10-8.6	15.5-39.3
Steel	Carbon(0.8% other impurities;drawn)	19.22	——	8.11	——
Steel	Other compositions	18-20	0.2-0.3	7-9	30 – 60
Zinc	Pure	7.8 – 10.2	——	2.9-3.73	——

Thermochemical Data of Selected Elements and Compounds

$\triangle H_f^o$ = Standard enthalpy of formation, for 1 mole of the substance in its standard state (stable form at 1 atm) at 298°K from its elements in their standard states (in Kcal mole^{-1}).

$\triangle F_f^o$ = Standard Gibbs free energy of formation at 298°K (in Kcal mole^{-1}).

S^o = the standard entropy (in cal deg^{-1} mole^{-1}) at 298°K

C_p^o = the molar heat capacity at constant pressure (in cal deg^{-1} mole^{-1}) at 298°K.

State: S, Solid; l, liquid and g, gas.

Formula	State	$\triangle H_f^o$	$\triangle F_f^o$	S^o	C_p^o
Aluminum	S	0	0	6.8	5.8
Al_2O_3	S(form)	−399.1	−376.8	12.2	18.9
$AlCl_3$	S	−166.2	−148.2	26.3	21.3
$Al_2(SO_4)_3$	S	−821.0	−739.0	57.2	62.0
AlN	S	−76.5	−69.1	5.0	7.7
Antimony					
Sb	S	0	0	10.5	6.1
Sb_2O_3	S	−168.4	−149.0	29.4	24.2
Sb_2O_5	S	−215.0	−181.2	29.9	28.1
$Sb\,Cl_3$	g	−75.2	−72.3	80.8	18.5
	S	−91.3	−77.6	44.5	25.6
Sb_2S_3	S	−43.5	−42.9	30.3	28.2
Argon					
Ar	g	0	0	37.0	5.0
Arsenic					
As	S( )	0	0	8.4	6.0
As_4	g	35.7	25.2	69	——
$As_4O_6(As_2O_3)$	S	−313.9	−275.4	51.2	45.7
As_2O_5	S	−218.6	−184.6	25.2	27.8
AsH_3	g	41.0	41.6	53.2	——
As_2S_3	S	−35.0	——	——	——
Barium					
Ba	S	0	0	16.0	6.3

Formula	State	$\triangle H_i^o$	$\triangle F_f^o$	S^o	C_p^o
BaO	S	−133.4	−126.3	16.8	11.3
BaCl$_2$	S	−205.6	−193.8	30.0	18.0
BaCl$_2$·2H$_2$O	S	−349.3	−309.7	48.5	37.1
Ba SO$_4$	S	−350.2	−323.4	31.6	24.3
Ba CO$_3$	S	−291.3	272.2	26.8	20.4
Bismuth					
Bi	S	0	0	13.6	6.1
Bi$_2$O$_3$	S	−137.9	−118.7	36.2	27.2
BiCl$_3$	g	−64.7	−62.2	85.3	19.0
	S	−90.6	−76.2	45.3	—
BiOCl	S	−87.3	−77.0	20.6	—
Bi$_2$S$_3$	S	−43.8	−39.4	35.3	30.7
Boron					
B	S	0	0	1.6	2.9
B$_2$O$_3$	S	−302.2	−283.0	12.9	14.9
Bromine					
Br$_2$	l	0	0	36.4	17.1
	g	7.3	0.7	58.6	8.6
Cadmium					
Cd	S(α)	0	0	12.3	6.2
CdO	S	−60.9	−53.8	13.1	10.4
CdCl$_2$	S	−93.0	−82.8	31.2	18.3
CdS	S	−34.5	−33.6	17.0	13.2
CdSO$_4$	S	−221.4	−195.0	29.4	24.0
Caesium					
Cs	S	0	0	19.8	7.4
CsCl	S	−103.5	−96.8	23.9	12.6
Calcium					
Ca	S	0	0	9.9	6.3
CaO	S	−151.9	−144.4	9.5	10.2
CaH$_2$	S	−45.1	−35.8	10.0	—
Ca(OH)$_2$	S	−235.8	−214.3	18.2	20.2
CaCl$_2$	S	−190.0	−179.3	27.2	17.4
CaSO$_4$	S	−342.4	−315.6	25.5	23.8
CaSO$_4$·2 H$_2$O	S	−483.1	−429.2	46.4	44.5

Formula	State	ΔH_f^0	ΔF_f^0	S^0	C_p^0
$CaCO_3$	S Calcite	-288.4	-269.8	22.2	19.6
Carbon					
C	S(graphite)	0	0	1.4	2.1
	S(diamond)	0.5	0.7	0.6	1.4
CO	g	-26.4	-32.8	47.3	7.0
CO_2	g	-94.1	-94.3	51.1	8.9
CH_4	g	-17.9	-12.1	44.5	8.5
C_2H_6	g	-20.2	-7.9	54.8	12.6
C_3H_8	g	-24.8	-5.6	64.5	17.6
$n-C_6H_{14}$	g	-40.0	0.05	—	92.45
C_2H_4	g	12.50	16.3	52.5	——
C_2H_2	g	54.2	50.0	48.0	——
C_6H_6	l	11.7	29.8	41.3	——
$Cyclo-C_6H_{12}$	l	-36.7(18°)	6.8	——	——
$C_{10}H_8$	S	16.0(18°)	45.2	——	——
$C_{14}H_{10}$	S	27.6(18°)	64.8	——	——
HCHO	g	-27.7	-26.3	52.3	8.4
CH_3CHO	g	-39.8	-32.0	63.5	——
H COOH	g	-86.7	-80.2	60.0	——
CH_3COOH	l	-104.7	-91.2	34.5	——
CH_3OH	l	-57.0	-39.7	30.3	——
CH_3OCH_3	g	-44.3	-27.3	63.7	——
CH_3COCH_3	l	-59.3	-37.2	——	——
CH_3CN	l	12.7	24.0	——	——
C_6H_5COOH	S	-93.2(18°)	-61.9	——	——
$C_6H_5NH_2$	l	7.3(18°)	35.4	——	——
CCl_4	l	-33.3	-16.4	51.2	31.5
$COCl_2$	g	-53.3	-50.3	69.1	14.5
$CHCl_3$	l	-31.5	-17.1	48.5	27.8
CS_2	l	21.1	15.2	36.1	18.1
Chlorine					
Cl_2	g	0	0	53.3	8.1
Cl	g	29.0	25.2	39.5	5.2

Formula	State	ΔH_f^o	ΔF_f^o	S^o	C_p^o
Chromium					
Cr	s	0	0	5.7	5.6
Cr_2O_3	s	−269.7	−250.2	19.4	28.4
CrO_3	s	−138.4	−119.9	17.2	—
$CrCl_3$	s	−134.6	−118.0	30.0	21.5
Cobalt					
Co	s	0	0	7.2	6.1
CoO	s	−57.2	−51.5	12.6	—
Co_3O_4	s	−216.3	−188.0	24.5	—
$CoCl_2$	s	−77.8	−67.5	−25.4	18.8
$CoCl_2 \cdot 6H_2O$	s	−508.9	—	—	—
$CoSO_4$	s	−207.5	−182.1	27.1	—
$CoSO_4 \cdot 7H_2O$	s	−713.8	—	—	—
Copper					
Cu	s	0	0	8.0	5.8
Cu_2O	s	−39.8	34.4	22.4	16.7
CuO	s	−37.1	−30.4	10.2	10.6
CuCl	s	−32.2	−28.4	21.9	11.6
$CuCl_2$	s	−49.2	−39.0	27.0	19.0
$CuCl_2 \cdot 2H_2O$	s	−193.0	—	—	—
Cu_2S	s	−19.0	−20.6	28.9	18.2
CuS	s	−11.6	−11.7	15.9	11.4
$CuSO_4$	s	−184.0	−158.2	27.1	24.1
$CuSO_4 \cdot 5H_2O$	s	−544.5	−449.3	73.0	67.2
Fluorine					
F_2	g	0	0	48.6	7.5
Germanium					
Ge	s	0	0	10.1	6.2
GeO_2	amorph.	−128.3	−114.4	12.5	—
Gold					
Au	s	0	0	11.4	6.0
Au_2O_3	s	19.3	39.0	30.0	—
$AuCl_3$	s	−28.3	−11.6	35.4	—
Helium					
He	g	0	0	30.1	5.0

Formula	State	ΔH_f^0	ΔF_f^0	S^0	C_p^0
Hydrogen					
H_2	g	0	0	31.2	6.9
H_2O	g	−57.8	−54.6	45.1	8.0
	l	−68.3	−56.7	16.7	18.0
H_2O_2	g	−32.3	−24.5	54.2	——
HF	g	−64.2	−64.7	41.5	6.9
HCl	g	−22.1	−22.8	44.6	7.0
H Br	g	−8.7	−12.7	47.4	7.0
HI	g	6.2	0.3	49.3	7.0
H_2S	g	−4.8	−7.9	49.1	8.1
Iodine					
I_2	s	0	0	27.9	13.1
	g	14.9	4.6	62.3	8.8
I	g	25.5	16.8	43.2	5.0
Iron					
Fe	s	0	0	6.5	6.0
Fe_2O_3	S(haema-tite)	−196.5	−177.1	21.5	25.0
$FeCl_2$	s	−81.5	−72.2	28.6	18.2
$FeCl_3$	s	−96.8	−80.6	32.2	22.8
FeS	s(α)	−22.7	−23.3	16.1	13.1
FeS_2	S(Pyri-tes)	−42.5	−39.8	12.7	14.8
$FeSO_4$	s	−220.5	−194.8	25.7	——
Fe_3C	S(cemen-tite)	5.0	3.5	25.7	25.3
Lead					
Pb	s	0	0	15.5	6.4
Pb O	S(red)	−52.4	−45.2	16.2	11.8
	S(yellow)	−52.1	−45.0	16.6	11.6
Pb O_2	s	−66.1	−52.3	18.3	15.4
Pb_3O_4	s	−175.6	−147.6	50.5	35.1
Pb Cl_2	s	−85.8	−75.0	32.6	18.4
Pb I_2	s	−41.8	−41.5	42.3	19.4
Pb S	s	−22.5	−22.1	21.8	11.8
$PbSO_4$	s	−219.5	−193.9	35.2	24.9
$Pb(NO_3)_2$	s	−107.3	——	——	——

Formula	State	ΔH_f^o	ΔF_f^o	S^o	C_p^o
Lithium					
Li	s	0	0	6.7	5.6
	g	37.1	29.2	33.1	5.0
Li_2O	s	-142.4	-133.8	9.1	13.0
LiH	g	30.7	25.2	40.8	7.1
LiCl	s	-97.7	-91.9	13.9	12.0
Li_2SO_4	s	-342.8	-316.0	29.0	————
Magnesium					
Mg	s	0	0	7.8	5.7
MgO	s	-143.8	-136.1	6.4	8.9
$Mg(OH)_2$	s	-221.0	-199.3	15.1	18.4
$MgCl_2$	s	-153.4	-141.6	21.4	17.0
$MgCl_2 \cdot 6H_2O$	s	-597.4	-505.6	87.5	75.5
$Mg\,SO_4$	s	-305.5	-280.5	21.9	23.0
$Mg\,CO_3$	s	-266.0	-246.0	15.7	18.0
Manganese					
Mn	$s(\alpha)$	0	0	7.6	6.3
MnO	s	-92.0	-86.8	14.4	10.3
MnO_2	s	-124.5	-111.4	12.7	12.9
Mn_2O_3	s	-229.4	-210.8	26.4	25.8
Mn_3O_4	s	-331.4	-306.0	35.5	33.3
MnF_2	s	-189.0	-179.0	22.2	16.2
$MnCl_2$	s	-112.0	-102.2	28.0	17.4
$MnSO_4$	s	-254.2	-228.5	26.8	23.9
Mercury					
Hg	l	0	0	18.2	6.6
	g	14.5	7.6	41.8	5.0
HgO	s(red)	-21.7	-14.0	16.8	10.9
	s(yellow)	-21.6	-14.1	17.5	———
Hg_2Cl_2	s	-63.3	-50.3	46.8	24.3
$HgCl_2$	s	-55.0	-44.0	34.5	18.3
HgS	s(red)	-13.9	-11.7	18.6	11.1
	s(black)	-12.9	-11.1	19.9	11.1
Molybdenum					
Mo	s	0	0	6.8	5.6

Thermochemical Data

Formula	State	ΔH_f^0	ΔF_f^0	S^0	C_p^0
MoO_2	S	-139.5	-126.9	13.6	———
MoO_3	S	-180.3	-161.9	18.7	17.6
MoS_2	S	-55.5	-53.8	15.1	15.2
Mo_2S_3	S	-102.0	-99.5	28.0	———
Neon					
Ne	g	0	0	34.9	5.0
Nickel					
Ni	S	0	0	7.2	6.2
NiO	S	-58.4	-51.7	9.2	10.6
$NiCl_2 \cdot 6H_2O$	S	-505.8	-410.5	75.2	———
$NiSO_4 \cdot 6H_2O$	S(blue)	-642.5	-531.0	73.1	82.0
$Ni(CO)_4$	g	-144.7	-140.3	96.0	———
Nitrogen					
N_2	g	0	0	45.8	7.0
NO	g	21.6	20.7	50.3	7.1
NO_2	g	8.1	12.4	57.5	9.1
N_2O	g	19.5	24.8	52.6	9.3
N_2O_4	g	2.3	23.5	72.7	18.9
N_2O_5	g	3.6	——	——	——
NH_3	g	-11.0	-4.0	46.0	8.5
HNO_3	l	-41.4	-19.1	37.2	26.3
NH_4Cl	S	-75.4	-48.7	22.6	20.1
$(NH_4)_2SO_4$	S	-281.9	-215.2	52.6	44.6
Oxygen					
O_2	g	0	0	49.0	7.0
O_3	g	34.0	39.1	56.8	9.1
Phosphorous					
P	S(white)	0	0	10.6	5.5
	S(red)	-4.4	——	——	——
	g	75.2	66.7	39.0	5.0
P_4	g	13.1	5.8	66.9	16.0
$P_4O_{10}(P_2O_5)$	S	-740.0	-673.6	65.0	49.1
PH_3	g	4.1	6.2	50.4	8.1

Formula	State	ΔH_f^o	ΔF_f^o	S^o	C_p^o
H_3PO_4	s	-306.2	—	—	—
$P Cl_3$	g	-66.7	-61.9	74.6	17.2
PCl_5	g	-95.3	-77.6	84.3	27.0
$POCl_3$	g	-141.5	130.3	77.6	20.2
Platinum					
Pt	s	0	0	10.0	6.3
Potassium					
K	s	0	0	15.2	7.0
KOH	s	-101.8	—	—	—
KCl	s	-104.2	-97.6	19.8	12.3
$KClO_3$	s	-93.5	-69.3	34.2	24.0
KBr	s	-93.7	-90.6	23.0	12.8
KI	s	-78.3	-77.0	24.9	13.2
K_2SO_4	s	-342.7	-314.6	42.0	31.1
KNO_3	s	-117.8	-94.0	31.8	23.0
K_2CO_3	s	-273.9	—	—	—
$KMnO_4$	s	-194.4	-170.6	41.0	28.5
Silicon					
Si	s	0	0	4.5	4.7
SiO_2	s(quartz)	-205.4	-192.4	10.0	10.6
$Si H_4$	g	-14.8	9.4	48.7	10.2
$SiCl_4$	g	-145.7	-136.2	79.2	21.7
SiC	s	-12.4	-11.8	3.9	6.4
Silver					
Ag	s	0	0	10.2	6.2
Ag_2O	s	-7.3	-2.6	29.1	15.7
AgCl	s	-30.4	-26.2	23.0	12.1
AgBr	s	-23.8	-22.9	25.6	12.5
Ag I	s	-14.9	-15.8	27.3	13.0
$Ag NO_3$	s	-29.4	-7.7	33.7	22.2
Ag_2CO_3	s	-120.9	-104.5	40.0	26.8
Sodium					
Na	s	0	0	12.2	6.8
Na_2O_2	s	-123.0	-107.0	22.6	—

Formula	State	ΔH_f^0	$\Delta F_f^{\bullet}$	S^0	C_p^0
NaOH	s	−102.0	−91.0	15.3	14.3
Na F	s	−136.5	−129.3	12.3	11.0
NaCl	s	−98.6	−92.2	17.4	11.9
NaBr	s	−86.0	−82.9	20.0	12.5
Na I	s	−68.8	−67.5	21.8	—
Na_2SO_4	s	−330.9	−302.8	35.7	30.5
$Na_2SO_4 \cdot 10H_2O$	s	−1033.5	−870.9	141.7	140.4
$NaNO_3$	s	−111.5	87.5	27.8	22.2
$NaNO_2$	s	−85.9	—	—	—
Na_3PO_4	s	−460.0	—	—	—
Na_2CO_3	s	−270.3	−250.4	32.5	26.4
$NaH CO_3$	s	−226.5	−203.6	24.4	20.9
Strontium					
Sr	s	0	0	13.0	6.0
$Sr(OH)_2$	s	−229.3	—	—	—
$SrCl_2$	s	−198.0	−186.7	28.0	18.9
$Sr SO_4$	s	−345.3	−318.9	29.1	—
$SrCO_3$	s	−291.2	−271.9	23.2	19.5
Sulphur					
S	S(rhombic)	0	0	7.6	5.4
	S(mono-clinic)	0.1	0	7.8	5.6
	g	52.4	43.6	40.1	5.7
S_8	g	24.4	11.9	102.8	—
SO_2	g	−71.0	−71.8	59.4	9.5
SO_3	g	−94.4	−88.5	61.2	12.1
H_2SO_4	l	−193.9	—	—	32.9
SF_6	g	−262.0	−237.0	69.5	—
Tin					
Sn	S(white)	0	0	12.3	6.3
	S(grey)	0.6	1.1	10.7	6.2
SnO	s	−68.4	−61.5	13.5	10.6
SnO_2	s	−138.7	−123.9	11.6	12.6
$SnCl_4$	l	−130.3	−113.3	61.8	39.5

Formula	State	ΔH_f^o	ΔF_f^o	S^o	C_p^o
Titanium					
Ti	s	0	0	7.2	6.0
TiO$_2$	s(rutile)	-218.0	-203.8	12.0	13.2
TiCl$_4$	l	-191.5	-175.3	59.6	37.5
Tungsten					
W	s	0	0	8.0	6.0
WO$_3$	s(yellow)	-200.8	-182.5	19.9	19.5
Uranium					
U	s	0	0	12.0	6.6
UO$_2$	s	-270.0	-257.0	18.6	15.3
UF$_6$	g	-505.0	-485.0	90.8	—
Vanadium					
V	s	0	0	7.0	5.8
V$_2$O$_3$	s	-290.0	-271.0	23.6	24.8
V$_2$O$_5$	s	-373.0	-344.0	31.3	31.0
Zinc					
Zn	s	0	0	9.9	6.0
ZnO	s	-83.2	-76.0	10.5	9.6
Zn(OH)$_2$	s	-153.5	—	—	17.3
ZnCl$_2$	s	-99.4	-88.3	25.9	18.3
ZnS	s(zinc blende)	-48.5	-47.4	13.8	10.8
	s(wurtzite)	-45.3	—	—	—
ZnSO$_4$	s	-233.9	-208.3	29.8	28.0
ZnSO$_4$·7H$_2$O	s	-735.1	-611.9	92.4	93.7
Zirconium					
Zr	s	0	0	9.2	6.2
ZrO$_2$	s	-258.2	-244.4	12.0	13.4

Heats of Combustion of selected organic Compounds

Heats of combustion ($- \triangle H$) = the heat evolved per mole of the subs-
tance when combustion takes place at atmospheric pressure, the final pro-
ducts being CO_2 (g). H_2O (l) and N_2 (g). The heats of formation of CO_2 (g) =
-94.1 K cal and H_2O(1) = -68.3 K cal.

Name	State	Heat of com-bustion(at 298°K) in Kcal mole-1	Name	State	Heat of com-bustion(at 298°K) in Kcal mole⁻1
Hydrocarbons			Ethanol	l	326.7
Methane	g	212.8	Propanol-1	l	480.5
Ethane	g	372.8	Diethyl ether	l	652.8
Propane	g	530.6	Acetaldehyde	l	279.0
n-butane	g	687.7	Acetone	l	426.8
n-pentane	l	838.8	Formic acid	l	64.6
n-hexane	l	995.0	Acetic acid	l	209.4
Cyclo-Pentane	l	786.5	Oxalic acid	S	58.9
Cyclo-hexane	l	936.9	Benzaldehyde	l	841.3
Ethylene	g	337.2	Benzoic acid	S	771.4
1:3-butadiene	g	607.5	Glucose	S	673.0
Acetylene	g	310.6	Phenol	S	732.0
Benzene	l	781.0	Sucrose	S	1,348.9
Toluene	l	934.5	**Nitrogen containing compounds**		
Naphthalene	S	1,228.2	Aniline	l	811.9
Oxygen Containing Compounds			Nitrobenzene	l	739.6
Methanol	l	173.6			

Latent Heats and Heats of Atomization

Latent heat of fusion ($\triangle H_{fus}$) = $\triangle H$ for the transition solid $\longrightarrow$ liquid.

Latent heat of evaporation ($\triangle H_e$) = $\triangle H$ for the transition liquid $\longrightarrow$ vapour

Latent heat of sublimation ($\triangle H_s$) = $\triangle H_{fus}$ + $\triangle H_e$ = $\triangle H$ for the transition

solid $\longrightarrow$ vapour

Heat of atomization ($\triangle H$ at) = the standard heat of formation of the gaseous
element at 25°C.

Substance	ΔH_{fus} at m.p. (K cal mole^{-1})	ΔH_e at b.p. (K cal mole^{-1})	ΔH_s at 25°C (K cal mole^{-1})	ΔH_{at} (K cal mole^{-1})
H	0.014	0.108	—	52.1
Li	0.70	35.3	37.9	38.4
B	—	—	138 (ΔH_s)	141
C	—	—	171.7 (ΔH_s)	171.7
N	0.086	0.666	—	112.9
O	0.053	0.81	—	59.2
F	0.19	0.75	—	18.3
Na	0.63	23.7	25.7	26.0
Mg	2.1	30.5	33.6	35.9
Al	2.5	69.6	—	75.0
Si	12.1	72.5	—	105
P	0.15	3.1	3.4	75.2
S	0.29	2.5	—	52.4
Cl	C.77	2.44	—	29.0
K	0.57	18.9	21.0	21.5
Ca	2.2	39.9	43.1	46.0
Ti	3.7	1C2.5	—	112.6
V	4.2	109.6	—	122.8
Cr	3.5	82.9	92.3	95.0
Mn	3.5	52.5	—	66.7
Fe	3.7	83.9	89.4	99.8
Co	3.7	91.4	—	101.6
Ni	4.2	88.9	—	101.3
Cu	3.1	72.8	79.4	81.1
Zn	1.76	27.6	29.5	31.2
Ge	7.6	79.9	84.8	90.0
As	6.6	—	7.7 (ΔH_s)	60.6
Se	1.25	3.3	—	48.4
Br	1.26	3.65	3.8	26.7
Rb	0.53	18.1	20.0	20.5
I	1.88	4.98	5.78	25.5
H_2O	1.44	9.82	10.5	—
H_2O_2	2.92	10.3	12.2	—

Substance	ΔH_{fus} at m.p. (K cal mole^{-1})	ΔH_e at b.p. (K cal mole^{-1})	ΔH_e at 25°C (K cal mole^{-1})	ΔH_{at} (K cal mole^{-1})
HF	0.94	1.8	——	——
H_2S	0.59	4.46	——	——
HCl	0.48	3.86	——	——
HBr	0.58	4.21	——	——
HI	0.69	4.72	——	——
C_6H_6	2.35	7.35	8.09	——
CS_2	1.05	6.5	6.65	——
CCl_4	0.60	7.28	7.88	——
NH_3	1.35	5.58	——	——
NaF	8.0	48.1	59.9	——
NaCl	6.9	40.7	50.5	——
Na Br	6.1	38.0	45.5	——
Na I	5.3	38.1	47.1	——
$Mg\ Cl_2$	10.3	32.7	46.6	——
SO_2	1.77	5.96	——	——
KCl	6.1	39.0	47.2	——
KBr	7	37.2	46.6	——
KI	——	34.7		——

Lattice Energy and Hydration Energy for Alkali Halides at 25°C

Lattice (crystal)energy = ΔH for the formation of gaseous ions (infinitely separated) from one mole of compound in the crystalline state.

Hydration energy = ΔH for the formation of gaseous ions, (infinitely seperated) from one mole of compound in aqueous solution at infinite dilution.

Salt	Lattice energy (Kcal mole^{-1})	Hydration energy (Kcal mole^{-1})	Salt	Lattice energy (Kcal mole^{-1})	Hydration energy (Kcal mole^{-1})
LiF	244	243	KBr	160	155
LiCl	202	211	KI	149	144
LiBr	191	203	RbF	182	188
LiI	178	193	RbCl	161	157
NaF	215	215	RbBr	154	149
NaCl	184	183	RbI	145	138
NaBr	175	175	CsF	172	181
NaI	163	-164	CsCl	155	151
KF	190	194	CsBr	149	143
KCl	167	163	CsI	140	132

Heats of formation of Aqueous ions

$\triangle H_f^o$ = the standard enthalpy of formation of the aqueous ions at 25°C (Kcal mole^{-1})

Ion	$\triangle H_f^o$	Ion	$\triangle H_f^o$
H^+	0	Ca^{2+}	-129.8
CO_3^{2-}	-161.6	CrO_4^{2-}	-206.3
HCO_3^-	-165.2	$Cr_2O_7^{2-}$	-349.1
NH_4^+	-31.7	Mn^{2+}	-52.3
NO_2^-	-25.4	Fe^{2+}	-21.0
NO_3^-	-49.4	Fe^{3+}	-11.4
OH^-	-55.0	Cu^+	+12.4
F^-	-78.7	Cu^{2+}	+15.4
Na^+	-57.3	Zn^{2+}	-36.4
Mg^{2+}	-110.4	Br^-	-28.9
Al^{3+}	-125.4	Ag^+	+25.3
S^{2-}	+10.0	I^-	-13.4
SO_4^{2-}	-216.9	Ba^{2+}	-128.7
Cl^-	-40.0	Pb^{2+}	+0.4
K^+	-60.0		

Variation of selected Equilibrium constants with temperature

Equilibrium	log K_p (at °K)						
	298	400	500	600	700	900	1100
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI(g)$	2.9		2.2		1.8	1.6	1.4
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3(g)$	5.8		-1.0		-4.1	-6.0	-7.3
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO (g)$	-30.4				-12.3		-7.4
$2NO(g) + O_{2(g)} \rightleftharpoons 2NO_2(g)$	12.3		4.2		0.7	-1.3	-2.5
$2SO_2(g) + O_{2(g)} \rightleftharpoons 2SO_3(g)$	24.4		10.4		4.5	1.2	-0.9
$2C(s) + O_{2(g)} \rightleftharpoons 2CO(g)$	48.2		32.5		26.1	22.5	20.2
$C(s) + O_{2(g)} \rightleftharpoons CO_2(g)$	69.2		41.2		29.4	22.8	18.7
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	-22.7		-10.1		-4.8	-1.9	0.0

Equilibrium	log K_p (at °K)						
	298	400	500	600	700	900	1100
$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$	-4.0	1.0	3.9	5.8	——	——	.
$CuSO_4 \cdot 3H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s) + 2H_2O(g)$	-4.6	0.6	3.6	5.6	——	——	——
$CuSO_4 \cdot H_2O(s) \rightleftharpoons CuSO_4(s) + H_2O(g)$	-4.7	-1.4	0.4	1.7	——	——	——

Heats of Solution

Values are given in kilocalories per gram mole for the dilution indicated. Positive values indicate evolution of heat. To convert to BTU multiply by the factor 3.9685.

Name	Dilution in moles of water	Heat of solution	Temp °C
Acetic acid	200	+ 0.375	18
Aluminum chloride	1250	+ 76.845	18
Ammonium chloride	200	- 3.88	18
Barium chloride	400	- 4.93	18
Barium hydroxide	....	+ 12.26	18
Calcium chloride	300	+ 17.41	18
Calcium chloride	400	- 4.31	19.3
Calcium hydroxide	2500	+ 2.79	18
Calcium oxide	2500	+ 18.33	18
Copper sulfate	400	+ 9.34	18
Hydrobromic acid	....	+ 20.0	15
Hydrochloric acid	....	+ 17.4	15
Hydrogen sulfide	....	+ 4.56	15
Iron chloride (ous)	1100	+ 8.7	20
Iron chloride (ic)	1000	+ 32.68	18
Iron sulfate (ous)	400	- 4.51	18
Lead acetate	440	+ 1.4	16
Lead nitrate	400	- 7.61	18
Lithium bromide	....	+ 11.25	15
Lithium chloride	230	+ 8.37	15

Name	Dilution in moles of water	Heat	Temp °C
Magnesium Chloride	800	+ 35.92	18
Magnesium chloride	400	+ 2.95	18
Phosphorous Pentoxide	550	+ 35.6	15
Potassium chloride	100	- 4.19	21
Potassium dichromate	400	- 16.70	18
Potassium hydroxide	250	+ 13.29	18
Potassium nitrate	200	- 8.52	18.
Silver nitrate	200	- 5.44	18
Sodium acetate	200	+ 3.87	18
Sodium acetate	400	- 4.81	18
Sodium bicarbonate	....	- 4.3	15
Sodium carbonate	400	+ 5.64	18
Sodium chloride	100	- 1.18	18
Sodium hydroxide	200	+ 9.94	18
Zinc chloride	300	+ 15.63	18
Zinc sulfate	400	+ 18.43	18

Heats of Neutralisation

Enthalpy of neutralisation ($\triangle H$) at 25°C for equal volumes of reactants (each 1 molar)

Reaction	$\triangle H$ K cal mole^{-1}
$HCl + NaOH \longrightarrow NaCl + H_2O$	13.84
$HNO_3 + NaOH \longrightarrow NaNO_3 + H_2O$	13.76
$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$	13.42
$HCl + NH_3 \longrightarrow NH_4Cl$	12.76
$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$	12.04
$HCl + NaF \longrightarrow HF + NaCl$	-2.45
$HCl + \frac{1}{2} MgO(Solid) \longrightarrow \frac{1}{2} MgCl_2 + \frac{1}{2} H_2O$	17.45

Heat capacity standards

*Water °C	C_p at 1atm.pres.,cal	°C	C_p at 1atm.pres.,cal
0	1.00804	30	0.99866
10	1.00194	50	0.99919
20	0.99947	60	1.00008

°C	C_p at 1atm. pres.,cal	°C	C_p at 1atm. pres. cal
80	1.00295	100	1.00763

*Mercury

°C	Liquid			Vapour
	C_{satd}	C_p	C_v	C_p
-20	0.033534	0.033534	0.02941	0.02476
0	0.033817	0.033817	0.02920	0.02476
20	0.033240	0.033240	0.02876	0.02476
40	0.033110	0.033110	0.02845	0.02476
80	0.032877	0.032877	0.02789	0.02476
100	0.032776	0.032776	0.02764	0.02476
140	0.032606	0.032606	0.02716	0.02476

*Aluminum oxide

°K	C_p, Cal	°K	C_p, Cal
20	0.000178	300	0.18615
40	0.001619	500	0.24860
60	0.006517	600	0.26374
100	0.03010	800	0.28207
200	0.11988	1000	0.29241

Kopp's rule

Kopp's rule is used only where experimental values are lacking. It states that the specific heat of a compound is approximately equal to the sum of the heat capacities of the constituent elements and that an APPROXI-MATE value expressed in gram calories per gram weight is calculated by assigning the following atomic heat capacities to the elements:

For solids: C, 1.8; H, 2.3; 0, 4.0; S, 5.4; P, 5.4; F, 5.0; Si, 3.8; B, 2.7; all other elements 6.2.

For liquids: C, 2.8; H, 4.8; 0, 6.0, S, 7.4; P, 7.4, F. 7.0; Si, 5.8, B, 4.7; all other elements 8-0.

Example: For $BaCO_3$, 6.2 + 1.8 + (3 x 4.0) = 20.0g cal/g formula weight; or 20.0 /197.37 = 0.1013g cal/g. Found by experiment, 0.0999.

IV ATOMIC AND MOLECULAR STRUCTURE AND PROPERTIES

IV.1 Quantum Mechanics:

* **Postulates** a) The state of an atomic or molecular system is described by the function $\Psi(q_1, \ldots q_n, t)$ where Ψ is the <u>state function</u> of the system. $q_1 \ldots q_n$ are the n-coordinates, the corresponding momenta being $p_1 \ldots p_n$. $\Psi\Psi^* d\tau \, dt$ is the probability for the system having q values lie within the volume element $d\tau$ at time t; that is q between q_1 and $q_1 + dq_1$ etc. at time t.

$$\int \Psi^*(q_1 \ldots q_n t) \; \Psi(q \ldots q_n, t) \, d\tau = 1$$

Ψ is also referred to as the wave function.

b) A linear operator α can be assigned to every dynamical variable A.

Example:

Variable	Operator
q_i	multiplication by q_i
t	multiplication by t
p_i	$-i\hbar \dfrac{\partial}{\partial q_i}$ (q_i is conjugate to p_i)

$\hbar = h/2\pi$ where h is Planck's constant. The linear operators chosen are Hermitian. ($\int \varphi^*(\alpha \Psi) \, d\tau = \int \Psi(\alpha^* \varphi^*) \, d\tau$)

c) The time-dependent equation satisfied by the Ψ's is

$$H(q, -i\hbar \partial/\partial q, t) \Psi(q,t) = -i\hbar \frac{\partial}{\partial t} \Psi(q,t)$$

H is the Hamiltonian operator for the system. The above equation is also referred to as the Schrödinger time-dependent equation.

d) The precise value <u>a</u> of a dynamical variable A for a system is

$$\alpha \Psi(q, t) = a \; \Psi(q, t)$$

where α is the corresponding operator and $\Psi(q, t)$ is the eigen function of α. <u>a</u> is also called the <u>expectation</u> value. The energy value E of the system, in particular, is given by the Hamiltonian operator

$$H \Psi(q, t) = E \Psi(q, t)$$

For a stationary state

$$H \psi(q) = E \psi(q)$$
$$\Psi(q, t) = \psi(q) \exp -(\frac{iEt}{\hbar})$$

e) If a state for which the function is Ψ can be represented as a superposition of say two eigen functions i.e. $\Psi = c_1 \varphi_1 + c_2 \varphi_2$ where c_1,

c_2 are coefficients and φ_1 and φ_2 are eigen functions of the operator α then the expectation value of the operator α is $c_1^* c_1 a_1 + c_2^* c_2 a_2$. Here a_1 and a_2 are the expectation values of the operator for the eigen functions φ_1 and φ_2 separately. In general, if a state function is expanded in terms of a set of eigen functions with $\Psi = \sum c_1 \varphi_1$ then

$$\langle \Psi | \alpha | \Psi \rangle = \int \Psi^* \alpha \Psi \, d\tau = \sum_i c_i^* c_i \, a$$

* **Uncertainty principle**

$$(pq - qp)\Psi = - i \hbar \Psi$$

p and q are conjugate variables (momentum and coordinate; time and energy). p and q do not commute. Two operators α and β are said to commute if $\alpha\beta = \beta\alpha$.

* **Angular momentum operators**

$$M_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$M_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$M_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

$$M^2 = M_x^2 + M_y^2 + M_z^2 .$$

Commutation Relations

$$M_y M_z - M_z M_y = i \hbar M_x$$

$$M_z M_x - M_x M_z = i \hbar M_y$$

$$M_x M_y - M_y M_x = i \hbar M_z$$

$$M^2 M_x - M_x M^2 = 0$$

$$M^2 M_y - M_y M^2 = 0$$

$$M^2 M_z - M_z M^2 = 0$$

The above relations hold for a single particle as well as a system of particles. The expressions apply to orbital as well as spin angular momenta. The eigen functions of the angular momentum operator will be denoted by $Y_{\ell,m}$ ($\ell \geqslant m \geqslant -\ell$ with ℓ and m integers or half integers).

$$M^2 Y_{\ell,m} = k_\ell Y_{\ell,m} = \ell(\ell+1)\hbar^2 Y_{\ell,m}$$

$$M_z Y_{\ell,m} = k_m Y_{\ell,m} = m\hbar Y_{\ell,m}.$$

$$(M_x + iM_y)Y_{\ell,m} = M_+ Y_{\ell,m} = \hbar \left[(\ell+m+1)(\ell-m) \right]^{1/2} Y_{\ell,\,m+1}$$

$$= \hbar \left[\ell(\ell+1)-m(m+1) \right]^{1/2} Y_{\ell,\,m+1}$$

$$(M_x - iM_y) Y_{\ell,m} = M_- Y_{\ell,m} = \hbar \left[(\ell(\ell+1) - m(m-1) \right]^{1/2} Y_{\ell,m-1}$$

$$= \hbar \left[(\ell+m)(\ell-m+1) \right]^{1/2} Y_{\ell,m-1}$$

$$\langle Y_{\ell,m} | M_x | Y_{\ell,m} \rangle = -\frac{\hbar}{2} \left\{ \left[\ell(\ell+1) - m(m+1) \right]^{1/2} \delta_{m,m+1} \right. $$

$$\left. + \left[\ell(\ell+1) - m(m+1) \right]^{1/2} \delta_{m,m-1} \right\} \cdot \delta_{\ell',\ell}$$

$$\langle Y_{\ell'm'} | M_y | Y_{\ell,m} \rangle = \frac{i\hbar}{2} \left\{ \left[\ell(\ell+1) - m(m+1) \right]^{1/2} \delta_{m,m+1} \right. $$

$$\left. - \left[\ell(\ell+1) - m(m-1) \right]^{1/2} \delta_{m,m-1} \right\} \cdot \delta_{\ell'\ell}$$

$$\langle Y_{\ell'm'} | M_z | Y_{\ell,m} \rangle = \hbar m \, \delta_{m'm} \, \delta_{\ell'\ell}$$

where $\delta_{rs} = 1$ for $r = s$, zero otherwise. The $Y_{\ell,m}$'s here are the spherical harmonic functions appearing in the solutions of hydrogenic systems.

$$Y_{\ell,m} = \left[2\pi \right]^{-1/2} \Theta_{\ell,m}(\theta) \exp (im\phi)$$

$\Theta_{\ell,m}(\theta)$ is the associated Legendre polynomial ($0 \leq \theta \leq \pi$); ($0 \leq \phi \leq 2\pi$).

*Electron spin angular momentum

The spin angular momentum operator $\underline{S}$ is similar to $\underline{M}$ above. Eigenvalue for $\underline{S}^2$ operator is $S(S+1)$. Two eigenvalues for S_z namely $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. The spin eigen functions are correspondingly α and β i.e. $\underline{S}\alpha = \frac{1}{2}\hbar\alpha$, $\underline{S}\beta = -\frac{1}{2}\hbar\beta$

$$S^2\alpha = 3/4 \, \hbar^2\alpha \; ; \; S^2\beta = 3/4 \, \hbar^2\beta \; .$$

$$S_+ = (S_x - iS_y); \; S_- = (S_x - iS_y)$$

$$S_+\alpha = 0; \; S_-\alpha = \hbar\beta$$

$$S_+\beta = \hbar\alpha \; ; \; S_-\beta = 0$$

*Free particle (Potential V = 0)

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E_x \psi$$

$$\psi = N(E_x) \exp - \left[\frac{1}{\hbar} (2mxE_x)^{1/2} \right]$$

m = mass of particle; E_x = energy value; $N(E_x)$ = normalization factor. Since values of x can range from $-\infty$ to $+\infty$ E_x values from 0 to $+\infty$ are possible, in other words, a continuous spectrum of energy values is possible.

*Particle in a Box

$$\left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + V \right] \psi = \frac{-\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

Potential V is zero inside the box while at the boundary and elsewhere it is infinite, i.e.

$$V_x = 0, \quad 0 < x < a; \quad V_x = \infty \quad \text{elsewhere}$$

$$V_y = 0, \quad 0 < y < b; \quad V_y = \infty \quad \text{elsewhere}$$

$$V_z = 0, \quad 0 < z < c; \quad V_z = \infty \quad \text{elsewhere}$$

a, b and c are the box dimensions. $\psi = \sqrt{\dfrac{8}{abc}} \, Sin \dfrac{n_x \pi}{a} x \, Sin \dfrac{n_y \pi}{b} y \, Sin \dfrac{n_z \pi}{c} z$.

$E = E_x + E_y + E_z = \dfrac{h^2}{8m} \left(\dfrac{n_x^2}{a^2} + \dfrac{n_y^2}{b^2} + \dfrac{n_z^2}{c^2} \right)$. For a one dimensional box

$\psi = A \exp \dfrac{ix}{\hbar} \left(2m (E-V) \right)^{\frac{1}{2}}$

If V is not infinitely high and not infinitely wide ψ is _not zero_ outside the box. There is a finite probability of finding the particle _outside_ the box. This phenomenon is called _tunnelling_.

* _Rigid Rotator_ $(V = 0)$

Two mass points (atoms) separated by a distance R form the rotator. Let the atom coordinates be a, θ, ϕ and b, θ, ϕ respectively with masses m_1 and m_2. The moment of inertia $I = m_1 a^2 + m_2 b^2$

$$-\frac{h^2}{2I} \left[\frac{1}{Sin\theta} \frac{\partial}{\partial\theta} \left(Sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{Sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right] = E\psi$$

$$\psi = \Theta_{l,m}(\theta) \, \Phi_m(\phi) = Y_{l,m}(\theta,\phi)$$

$$E = \frac{\hbar^2}{2I} l(l+1) \qquad l = 0, 1, 2, 3 \ldots$$

* _Rigid Rotator in a plane_ $(V = 0)$

This case is similar to that of the rigid rotator problem above but here θ is constant and equal to 90°. (rotator in the xy plane)

$$-\frac{\hbar^2}{2I} \frac{d^2\psi}{d\phi^2} = E\psi \; ; \qquad \psi = \frac{1}{\sqrt{2\pi}} \exp \pm (im\phi), \; (m=0,1,2 \ldots)$$

$$E = \frac{\hbar^2}{2I} m^2$$

*_Harmonic Oscillator_

one - dimensional case: $(V = \frac{1}{2} kx^2; \; k = \text{force constant})$

$$-\frac{h^2}{2m} \left[\frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] \psi = E\psi$$

$$\psi = \psi_n(\xi) \frac{\sqrt[4]{(\beta/\pi)}}{(2^n n!)^{1/2}} H_n(\xi) \exp - (\xi^2/2)$$

$$\xi = \sqrt{\beta}\, x \qquad ; \qquad \beta = (mk)^{\frac{1}{2}} \hbar^{-1}$$

$H_n(\xi)$ is the <u>Hermite</u> polynomial with $n = 0, 1, 2 \dots$

$$E = \hbar\,(k/m)^{\frac{1}{2}}(n + 1/2) = (n + 1/2)\, h\nu$$

For $n = 0$ case $E = \frac{1}{2} h\nu$ (<u>zero-point energy</u>).

<u>Three-dimensional case:</u>

$$\psi = \psi_{n_x, n_y, n_z}(x, y, z)$$

$$= \left[(\beta_x \beta_y \beta_z)^{\frac{1}{2}} \Big/ \left(\pi^{3/2}\, 2^{n_x + n_y + n_z}\, n_x!\, n_y!\, n_z! \right) \right]^{\frac{1}{2}}$$

$$\cdot\; H_{n_x}(\xi_x)\, H_{n_y}(\xi_y)\, H_{n_z}(\xi_z)$$

$$\cdot\; \exp. -\frac{1}{2}\left(\xi_x^2 + \xi_y^2 + \xi_z^2 \right)$$

$$E = \hbar \left[\left(\frac{k_x}{m}\right)^{1/2}(n_x + 1/2) + \left(\frac{k_y}{m}\right)^{1/2}(n_y + 1/2) + \left(\frac{k_z}{m}\right)^{1/2}(n_z + 1/2) \right]$$

$$= h \left[(n_x + 1/2)\,\nu_x + (n_y + 1/2)\,\nu_y + (n_z + 1/2)\,\nu_z \right]$$

For the isotropic case $k_x = k_y = k_z$

$$E = h\,(n_x + n_y + n_z + 3/2)\,\nu = (n + 3/2)\, h\nu.$$

<u>Hermite Polynomials</u>

$$H_n(\xi) = (-1)^n \exp(\xi^2)\; \frac{d^n \exp - (\xi^2)}{d\xi^n}$$

$H_0(\xi) = 1$; $H_1(\xi) = 2\xi$; $H_2(\xi) = 4\xi^2 - 2$; $H_3(\xi) = 8\xi^3 - 12\xi$;
$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$; $H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$; $H_6(\xi) = 64\xi^6$
$- 480\xi^4 + 720\xi^2 - 120$; $H_7(\xi) = 128\xi^7 - 1344\xi^5 + 336\xi^3 - 1680\xi$; $H_8(\xi) =$
$256\xi^8 - 3584\xi^6 + 13440\xi^4 - 13440\xi^2 + 1680$; $H_9(\xi) = 512\xi^9 - 9216\xi^7 +$
$48384\xi^5 - 80640\xi^3 + 30240\xi$; $H_{10}(\xi) = 1024\xi^{10} - 23040\xi^8 + 161280\xi^6 -$
$403200\xi^4 + 302400\xi^2 - 30240.$

<u>IV. 2 Atomic Orbitals</u>

* <u>Schrödinger equation for hydrogenic atoms</u>

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{r} \right] \Psi = E\,\Psi$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Ψ = wave function of the electron; E = energy eigenvalue

In spherical polar co-ordinates

$$\Psi (r, \theta, \phi) = R(r) \Theta (\theta) \Phi (\phi)$$

and the Schrodinger equation for a hydrogenic system can be written as

$$\frac{1}{r^2 R} \frac{d}{dr} (r^2 \frac{dR}{dr}) + \frac{1}{r^2 \sin^2\theta \Phi} \frac{d^2 \Phi}{d \phi^2}$$

$$+ \frac{1}{r^2 \sin\Theta} \frac{d}{d\theta} (\sin\theta \frac{d\Theta}{d\theta}) + \frac{2\mu}{\hbar^2} r^2 \left[E - \frac{Ze^2}{r} \right] = 0$$

The functions $R(r)$, $\Theta (\theta)$ and $\Phi (\phi)$ are defined in terms of quantum numbers n, ℓ and m. The hydrogenic wave functions are therefore written usually as $\Psi n \ell m$.

* Hydrogenic Wave Functions($\Psi_{n \ell m}$)

n = Principal quantum number; ℓ = Azimuthal quantum number; m = Magnetic quantum number.

$$\Psi_{n \ell m} = R_{n \ell} (r) \Theta_{\ell m} (\theta) \Phi_m (\phi) \quad \text{(polar coordinates } r, \theta, \phi)$$

$$R_{n\ell}(r) = - \left[(\frac{2Z}{n a_o})^3 \frac{(n - \ell - 1)!}{2n \{(n+\ell)!\}^3} \right]^{\frac{1}{2}} e^{-x/2} x^\ell \mathcal{L}_{n+\ell}^{2\ell+1}(x)$$

where $x = \frac{2Zr}{n a_o}$;   Z = effective nuclear charge (Z = 1 for hydrogen atom).

$a_o = \hbar^2 (\mu e^2)^{-1}$ = (Bohr radius) and $\mathcal{L}_{n+\ell}^{2\ell+1}(x)$ is the associated Laguerre polynomial of order (2ℓ+ 1) and degrees (n + ℓ) - (2 ℓ+1).

$$\mathcal{L}_{n+\ell}^{2\ell+1} (x) = \sum_{k=0}^{n-\ell-1} (-1)^{k+1} \frac{\left[(n + \ell)! \right]^2 x^k}{(n - \ell - 1 - k)! (2\ell + 1 + k)! \, k!}$$

$$\Theta_{\ell,m}(\theta) = \left[\frac{(2\ell+1) (\ell - |m|)!}{2(\ell + |m|)!} \right]^{\frac{1}{2}} P_\ell^{|m|} (\cos \theta)$$

where $P_\ell^{|m|}(\cos \theta)$ is the associated Legendre polynomial of order $|m|$ and degree ℓ .

$$\Phi (\phi) = (2\pi)^{-\frac{1}{2}} \exp (im \phi)$$

Table of $R_{n \ell} (r)$ Functions (Normalized), $x = 2Zr/(n a_o)$			
n	l	Symbol	$R_n (r)$
1	0	1s	$(Z/a_o)^{3/2} \, 2 \exp (-x/2)$
2	0	2s	$(2 \sqrt{2})^{-1} (Z/a_o)^{3/2} (2 - x) \exp (-x/2)$
2	1	2p	$(2 \sqrt{6})^{-1} (Z/a_o)^{3/2} x \exp (-x/2)$

$R_{nl}(r)$ as a function of $x = \dfrac{2Zr}{na_0}$
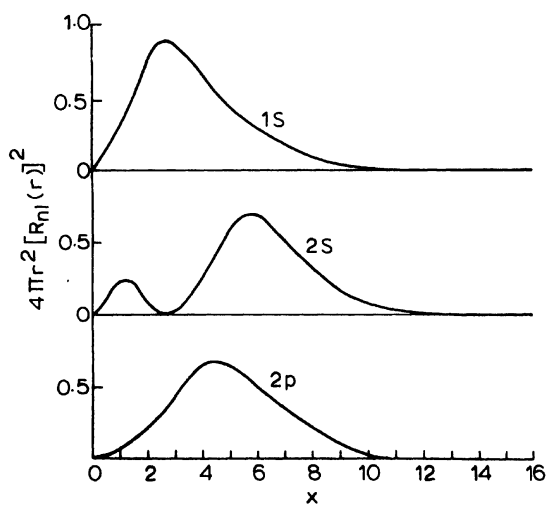
Electron distribution function $4\pi r^2\left[R_{nl}(r)\right]^2$
as a function of x

n	l	Symbol	$R_n(r)$
3	0	3s	$(9\sqrt{3})^{-1}(Z/a_o)^{3/2}(6 - 6x + x^2)\exp(-x/2)$
3	1	3p	$(9\sqrt{6})^{-1}(Z/a_o)^{3/2}(4 - x)\,x\exp(-x/2)$
3	2	3d	$(9\sqrt{30})^{-1}(Z/a_o)^{3/2}(x^2\exp(-x/2)$
4	0	4s	$(96)^{-1}(Z/a_o)^{3/2}(24 - 36x + 12x^2 - x^3)\exp(-x/2)$
4	1	4p	$(32\sqrt{15})^{-1}(Z/a_o)^{3/2}(20 - 10x + x^2)x\exp(-x/2)$
4	2	4d	$(96\sqrt{5})^{-1}(Z/a_o)^{3/2}(6 - x)\,x^2\exp(-x/2)$
4	3	4f	$(96\sqrt{35})^{-1}(Z/a_o)^{3/2}x^3\exp(-x/2)$
5	0	5s	$(300\sqrt{5})^{-1}(Z/a_o)^{3/2}(120 - 240x + 120x^2 - 20x^3 + x^4)\cdot\exp(-x/2)$
5	1	5p	$(150\sqrt{30})^{-1}(Z/a_o)^{3/2}(120 - 90x + 18x^2 - x^3)\,x\cdot\exp(-x/2)$
5	2	5d	$(150\sqrt{70})^{-1}(Z/a_o)^{3/2}(42 - 14x + x^2)\,x^2\exp(-x/2)$
5	3	5f	$(300\sqrt{70})^{-1}(Z/a_o)^{3/2}(8-x)\,x^3\exp(-x/2)$
5	4	5g	$(900\sqrt{70})(Z/a_o)^{3/2}x^4\exp(-x/2)$

Table of $\ominus_{lm}$ Functions (Normalized)

l	m	Symbol	$\ominus_{lm}(\theta)$
0	0	s	$\sqrt{2}/2$
1	0	p_0	$(\sqrt{6}/2)\cos\theta$
1	±1	$p_{\pm 1}$	$(\sqrt{3}/2)\sin\theta$
2	0	d_0	$(\sqrt{10}/4)(3\cos^2\theta - 1)$
2	±1	$d_{\pm 1}$	$(\sqrt{15}/2)\sin\theta\cos\theta$
2	±2	$d_{\pm 2}$	$(\sqrt{15}/4)\sin^2\theta$
3	0	f_0	$[(3\sqrt{14})/4](5/3\cos^3\theta - \cos\theta)$
3	±1	$f_{\pm 1}$	$(\sqrt{42}/8)\sin\theta(5\cos^2\theta - 1)$
3	±2	$f_{\pm 1}$	$(\sqrt{105}/4)\sin^2\theta\cos\theta$
3	±3	$f_{\pm 3}$	$(\sqrt{70}/8)\sin^2\theta$

Table of $\bar{\Phi}_m(\phi)$ Functions (Normalized)

m	$\Phi_m(\phi)$ (imaginary)	$\Phi_m(\phi)$ (real)
0	$(2\pi)^{-\frac{1}{2}}$ (real)	$(2\pi)^{-\frac{1}{2}}$
1	$(2\pi)^{\frac{1}{2}}\exp(i\phi)$	$(2\pi)^{-\frac{1}{2}}\cos\phi$
-1	$(2\pi)^{-\frac{1}{2}}\exp(-i\phi)$	$(2\pi)^{-\frac{1}{2}}\sin\phi$
2	$(2\pi)^{\frac{1}{2}}\exp(i2\phi)$	$(2\pi)^{\frac{1}{2}}\cos 2\phi$
-2	$(2\pi)^{-\frac{1}{2}}\exp(-i2\phi)$	$(2\pi)^{-\frac{1}{2}}\sin 2\phi$

* __Alternative expressions for p and d orbitals (see also Table of $\Box_{\ell m}(\theta)$__ functions)

$$\Psi_{p_x} = \Psi_{p_1} + \Psi_{p-1}$$

$$\Psi_{p_y} = \Psi_{p_1} - \Psi_{p_{-1}}$$

$$\Psi_{p_z} = \Psi_{p_0}$$

$$\Psi_{d_{xy}} = \frac{1}{i\sqrt{2}}\left[\Psi_{d_2} - \Psi_{d_{-2}}\right]$$

$$\Psi_{d_{xz}} = \frac{1}{\sqrt{2}}\left[\Psi_{d_1} - \Psi_{d_{-1}}\right]$$

$$\Psi_{d_{yz}} = -\frac{1}{i\sqrt{2}}\left[\Psi_{d_1} + \Psi_{d_{-1}}\right]$$

$$\Psi_{d_{z^2}} = \Psi_{d_0}$$

$$\Psi_{d_{x^2-y^2}} = \frac{1}{\sqrt{2}}\left[\Psi_{d_2} + \Psi_{d_{-2}}\right]$$

__*Energy levels of the hydrogenic atom__

The energy values of the free hydrogenic atom depend only on the principal quantum number n.

$$E_n = -\frac{\mu_z^2 e^4}{2\hbar^2 n^2} = -\frac{R\,Z^2\,hc}{n^2} = -\frac{Z^2}{n^2}E_H$$

(E_H = energy of the hydrogen atom)

__*Expectation values of r^n using hydrogenic wave functions__

$$\langle \Psi_{n\ell m}| r^n |\Psi_{n\ell m}\rangle = \langle r^n\rangle$$

$$\langle r\rangle = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}\left(1 - \frac{\ell(\ell+1)}{n^2}\right)\right]$$

Shapes (Boundary surfaces) of atomic orbitals

s

p_x p_y p_z

d_{xz} d_{xy} d_{yz}

$d_{x^2-y^2}$ d_{z^2}
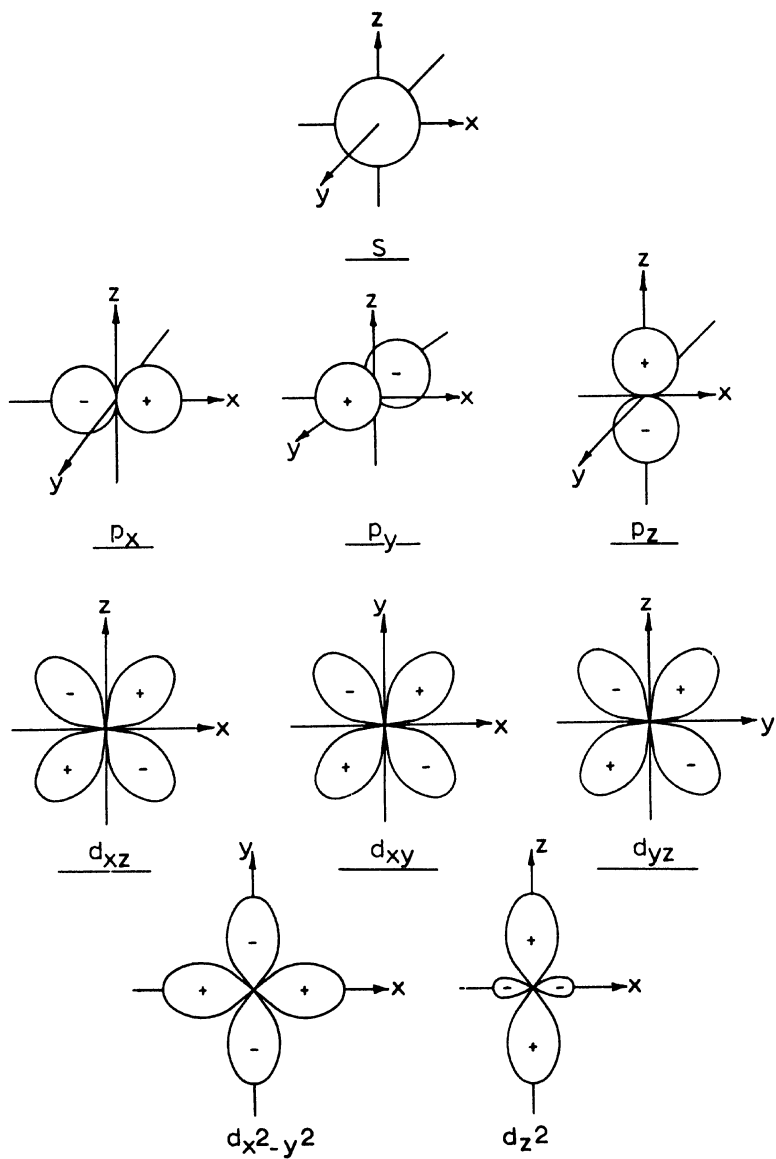
$$\langle r^2 \rangle = \frac{n^4 a_0^2}{z^2} \left[1 + \frac{3}{2} \left(1 - \frac{\ell(\ell+1) - \frac{1}{3})}{n^2} \right) \right]$$

$$\langle r^{-1} \rangle = \frac{z}{(n^2 a_0)}$$

$$\langle r^{-2} \rangle = z^2 / \left[n^3 a_0^2 (\ell + 1/2) \right]$$

$$\langle r^{-3} \rangle = z^3 / \left[n^3 a_0^3 \ell (\ell + 1/2)(\ell + 1) \right]$$

$$\langle r^{-4} \rangle = \frac{3}{2} z^4 (1 - \frac{\ell(\ell+1)}{3n^2}) / \left[n^3 a_0^4 (\ell + 3/2)(\ell + 1)(\ell + 1/2) \ell (\ell - 1/2) \right]$$

* Slater Atomic Orbitals

Orbital			Function
1s	Ψ_{1s}	=	$\frac{(Z^*)^{3/2}}{\sqrt{\pi}} \exp(-Z^* r/2)$
2s	Ψ_{2s}	=	$\frac{(Z^*)^{5/2}}{\sqrt{96\pi}} r \exp(-Z^* r/2)$
$2p_x$	Ψ_{2px}	=	$\frac{(Z^*)^{5/2}}{\sqrt{32\pi}} r \exp(-Z^* r/2) \sin\theta \cos\phi$
$2p_y$	Ψ_{2py}	=	$\frac{(z^*)^{5/2}}{\sqrt{32\pi}} r \exp(-Z^* r/2) \sin\theta \sin\phi$
$2p_z$	Ψ_{2pz}	=	$\frac{(Z^*)^{5/2}}{\sqrt{32\pi}} r \exp(-Z^* r/2) \cos\theta$
3s	Ψ_{3s}	=	$\frac{(2Z^*)^{7/2}}{(5.3^9 \pi)^{\frac{1}{2}}} r^2 \exp(-Z^* r/3)$
$3p_x$	Ψ_{3px}	=	$\frac{(2Z^*)^{7/2}}{(5.3^8 \pi)^{1/2}} r^2 \exp(-Z^* r/3) \sin\theta \cos\phi$
$3p_y$	$\bar\Psi_{3py}$	=	$\frac{(2Z^*)^{7/2}}{(5.3^8 \pi)^{1/2}} r^2 \exp(-Z^* r/3) \sin\theta \sin\phi$
$3p_z$	Ψ'_{3pz}	=	$\frac{(2Z^*)^{7/2}}{(5.3^8 \pi)^{1/2}} r^2 \exp(-Z^* r/3) \cos\theta$
$3d_{xy}$	$\Psi_{3d_{xy}}$	=	$\frac{(Z^*)^{7/2}}{(2.3^9 \pi)^{1/2}} 2 r^2 \exp(-Z^* r/3) \sin^2\theta \sin\phi \cos\phi$
$3d_{xz}$	$\Psi_{3d_{xz}}$	=	$\frac{(Z^*)^{7/2}}{(2.3^9 \pi)^{1/2}} 2 r^2 \exp(-Z^* r/3) \sin\theta \cos\theta \cos\phi$
$3d_{yz}$	$\Psi_{3d_{yz}}$	=	$\frac{(Z^*)^{7/2}}{(2.3^9 \pi)^{1/2}} 2 r^2 \exp(-Z^* r/3) \sin\theta \cos\theta \sin\phi$

$$3d_z^2 \qquad \Psi_{3d_z^2} = \frac{(Z^*)^{7/2}}{(2.3^9 \pi)^{1/2}} \frac{r^2}{\sqrt{3}} \exp(-Z^* r/3)(3\cos^2\theta - 1)$$

$$3d_{x^2-y^2} \qquad \Psi_{3d_{x^2-y^2}} = \frac{(Z^*)^{7/2}}{(2.3^9 \pi)^{1/2}} r^2 \exp(-Z^* r/3)\sin^2\theta(2\cos^2\phi - 1)$$

Z^* = effective atomic number = $Z - S$ where S is the screening constant.
To obtain the screening constant S use Slater's rules.

* Slater's Rules for S

1. Consider s and p orbitals of a given shell as one group and the d and f orbitals as a separate group.

2. Shells are arranged from inside to outside as follows:

Group 1: 1s; Group 2: 2s, 2p; Group 3: 3s, 3p; Group 4: 3d; Group 5: 4s, 4p; Group 6: 4d; Group 7: 4f; Group 8: 5s, 4p; Group 9: 5d; Group 10:5f etc.

3. Value of S is the sum of all contributions from electrons in the same shell as well as those within. Contribution from electrons outside a given shell is zero.

4. S = 0.35 from each electron in the same group. However, S=0.30 for Group 1.

5. In the case of electrons in s-p shells (Groups 2, 3, 5, 8 etc.) S=0.85 from all electrons in the next inner shell. S=1.00 from all electrons further inside.

6. In the case of electrons in d or f shells (group 4, 6, 9 etc.) S = 1.00 from every electron inside the shell considered.

* Antisymmetry and Pauli Principle

The electron coordinates may be said to consist of space and spin parts. The total wave function of a system of electrons should be anti-symmetric (Pauli Principle). This implies that if electrons are exchanged, that is, if the space and spin coordinates of two electrons are exchanged the original wave function Ψ of the system becomes $-\Psi$ after exchange.

* Slater Determinants and antisymmetry

The wave function of a many-electron system can be written as a determinant so that if a pair of electrons are exchanged the wave function of the system changes sign owing to the property of determinants. Wave functions thus written in the form of determinants are called Slater determinants.

$$\Psi(1, 2 \ldots N) = A \begin{vmatrix} \psi_a(1) & \psi_a(2) & \ldots\ldots\ldots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \ldots\ldots\ldots & \psi_b(N) \\ \vdots & \vdots & & \vdots \\ \psi_N(1) & \psi_N(2) & \ldots\ldots\ldots & \psi_N(N) \end{vmatrix}$$

ψ_a, ψ_b ..... ψ_N are wave functions of electrons 1, 2 .....N.

*Self Consistent Field and Many-electron Atoms

Due to the electron repulsion term (e^2/r_{ij}) in the potential for a many-electron atom exact analytical solutions of the Schrödinger equation are not possible. The self-consistent field (S.C.F.) method takes into account the interaction between electrons in the form of a(spherically) averaged potential. Thus, in the case of helium, for example, this potential is $e^2 \int \frac{\psi_1^2}{r_{12}} d\tau_1$ due to electron 1 at the site of electron 2. The introduction of this potential modifies the wave function ψ_2. Since the potential at the site of electron 1 is to be calculated with the modified ψ_2 function the two wave functions have to be made self consistent in terms of the interelectron repulsion potential. The problem for a many-electron atom, in general, involves the solution of a set of integro-differential equations and the procedure is termed the S.C.F. procedure. Since the wave function and consequently the potentials are modified successively to reach a desired limit of self-consistency the method is called the self-consistent field procedure or Hartree method after D.R. Hartree who employed the method successfully for many atoms. The inclusion of exchange integrals in the set of equations mentioned above was due to V. Fock and S.C.F. method with exchange interaction included is known as Hartree-Fock method. For details see D.R. Hartree, "The Calculation of Atomic Structures," John Wiley, New York (1957).

The method has also been formulated and applied to molecules (see C.C.J. Raothaan, Rev. Mod. Phys., 23, 69 (1951).

*Correlation Energy: The individual probability functions of the S.C.F. type discussed above may be used to write a total function. For two electrons, for example, $P(r_1, r_2) = P(r_1) \cdot P(r_2)$. The function $P(r_1 \cdot r_2)$ includes no correlation since $P(r_1)$ and $P(r_2)$ were obtained by averaging over all positions of the other particle. The difference between the Hartree-Fock SCF energy value and the energy value obtained by exact solution of the non-relativistic Schrodinger equation is designated as the correlation energy.

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* Ground State Electronic Configuration of Atoms

Atom	Atomic no.	Electronic Configuration	Term symbol	Atom	Atomic no.	Electronic Configuration	Term symbol
H	1	$1s^1$	$^2S_{1/2}$	K	19	$Ar\ 4s^1$	$^2S_{1/2}$
He	2	$1s^2$	$^1S_0$	Ca	20	$Ar\ 4s^2$	$^1S_0$
Li	3	$1s^2\ 2s^1$	$^2S_{1/2}$	Sc	21	$Ar\ 3d^1\ 4s^2$	$^2D_{3/2}$
Be	4	$1s^2\ 2s^2$	$^1S_0$	Ti	22	$Ar\ 3d^2\ 4s^2$	$^3F_2$
B	5	$1s^2\ 2s^1\ 2p^1$	$^2P_{1/2}$	V	23	$Ar\ 3d^3\ 4s^2$	$^4F_{3/2}$
C	6	$1s^2\ 2s^2 2p^2$	$^3P_0$	Cr	24	$Ar\ 3d^5\ 4s^1$	$^7S_3$
N	7	$1s^2\ 2s^2\ 2p^3$	$^4S_{3/2}$	Mn	25	$Ar\ 3d^5\ 4s^2$	$^6S_{5/2}$
O	8	$1s^2\ 2s^2\ 2p^4$	$^3P_2$	Fe	26	$Ar\ 3d^6\ 4s^2$	$^5D_4$
F	9	$1s^2\ 2s^2\ 2p^5$	$^2P_{3/2}$	Co	27	$Ar\ 3d^7\ 4s^2$	$^4F_{9/2}$
Ne	10	$1s^2\ 2s^2\ 2p^6$	$^1S_0$	Ni	28	$Ar\ 3d^8\ 4s^2$	$^3F_4$
Na	11	$Ne\ 3s^1$	$^2S_{1/2}$	Cu	29	$Ar\ 3d^{10}\ 4s^1$	$^2S_{1/2}$
Mg	12	$Ne\ 3s^2$	$^1S_0$	Zn	30	$Ar\ 3d^{10}\ 4s^2$	$^1S_0$
Al	13	$Ne\ 3s^2\ 3p^1$	$^2P_{1/2}$	Ga	31	$Ar\ 3d^{10}\ 4s^2 4p^1$	$^2P_{1/2}$
Si	14	$Ne\ 3s^2\ 3p^2$	$^3P_0$	Ge	32	$Ar\ 3d^{10}\ 4s^2 4p^2$	$^3P_0$
P	15	$Ne\ 3s^2\ 3p^3$	$^4S_{3/2}$	As	33	$Ar\ 3d^{10}\ 4s^2 4p^3$	$^4S_{3/2}$
S	16	$Ne\ 3s^2\ 3p^4$	$^3P_2$	Se	34	$Ar\ 3d^{10}\ 4s^2 4p^4$	$^3P_2$
Cl	17	$Ne\ 3s^2\ 3p^5$	$^2P_{3/2}$	Br	35	$Ar\ 3d^{10}\ 4s^2 4p^5$	$^2P_{3/2}$
Ar	18	$Ne\ 3s^2\ 3p^6$	$^1S_0$	Kr	36	$Ar\ 3d^{10}\ 4s^2 4p^6$	$^1S_0$

Atom	Atomic No.	Electronic Configuration	Term Symbol	Atom	Atomic No.	Electronic Configuration	Term Symbol
Rb	37	Kr $5s^1$	$^2S_{1/2}$	La	57	Xe $5d^1\ 6s^2$	$^2D_{3/2}$
Sr	38	Kr $5s^2$	$^1S_0$	Ce	58	Xe $4f^1\ 5d\ 6s^2$	$^3H_4$
Y	39	Kr $4d^1\ 5s^2$	$^2D_{3/2}$	Pr	59	Xe $4f^2\ 5d^1\ 6s^2$	$^4K_{11/2}$
Zr	40	Kr $4d^2\ 5s^2$	$^3F_2$	Nd	60	Xe $4f^3\ 5d^1\ 6s^2$	$^5L_6$
Nb	41	Kr $4d^4\ 5s^1$	$^6D_{1/2}$	Pm	61	Xe $4f^4\ 5d^1\ 6s^2$	$^6L_{9/2}$
Mo	42	Kr $4d^5\ 5s^1$	$^7S_3$	Sm	62	Xe $4f^5\ 5d^1\ 6s^2$	$^7K_4$
Tc	43	Kr $4d^5\ 5s^2$	$^6S_{5/2}$	Eu	63	Xe $4f^6\ 5d^1\ 6s^2$	$^8H_{3/2}$
Ru	44	Kr $4d^7\ 5s^1$	$^5F_5$	Gd	64	Xe $4f^7\ 5d^1\ 6s^2$	$^9D_2$
Rh	45	Kr $4d^8\ 5s^1$	$^4F_{9/2}$	Tb	65	Xe $4f^8\ 5d^1\ 6s^2$	$^8H_{17/2}$
Pd	46	Kr $4d^{10}$	$^1S_0$	Dy	66	Xe $4f^9\ 5d^1\ 6s^2$	$^7K_{10}$
Ag	47	Kr $4d^{10}\ 5s^1$	$^2S_{1/2}$	Ho	67	Xe $4f^{10}\ 5d^1\ 6s^2$	$^6K_{19/2}$
Cd	48	Kr $4d^{10}\ 5s^2$	$^1S_0$	Er	68	Xe $4f^{11}\ 5d^1\ 6s^2$	$^5L_{10}$
In	49	Kr $4d^{10}\ 5s^2\ 5p^1$	$^2P_{1/2}$	Tm	69	Xe $4f^{12}\ 5d^1\ 6s^2$	$^4K_{17/2}$
Sn	50	Kr $4d^{10}\ 5s^2\ 5p^2$	$^3P_0$	Yb	70	Xe $4f^{13}\ 5d^1\ 6s^2$	$^3H_6$
Sb	51	Kr $4d^{10}\ 5s^2\ 5p^3$	$^4S_{3/2}$	Lu	71	Xe $4f^{14}\ 5d^1\ 6s^2$	$^2D_{3/2}$
Te	52	Kr $4d^{10}\ 5s^2\ 5p^4$	$^3P_2$	Hf	72	Xe $4f^{14}\ 5d^2\ 6s^2$	$^3F_2$
I	53	Kr $4d^{10}\ 5s^2\ 5p^5$	$^2P_{3/2}$	Ta	73	Xe $4f^{14}\ 5d^3\ 6s^2$	$^4F_{3/2}$
Xe	54	Kr $4d^{10}\ 5s^2\ 5p^6$	$^1S_0$	W	74	Xe $4f^{14}\ 5d^4\ 6s^2$	$^5D_0$
Cs	55	Xe $6s^1$	$^2S_{1/2}$	Re	75	Xe $4f^{14}\ 5d^5\ 6s^2$	$^6S_{5/2}$
Ba	56	Xe $6s^2$	$^1S_0$	Os	76	Xe $4f^{14}\ 5d^6\ 6s^2$	$^5D_4$

Atom	Atomic No.	Electronic Configuration	Term Symbol	Atom	Atomic No.	Electronic Configuration	Term Symbol
Ir	77	Xe $4f^{14}5d^{7}6s^{2}$	$^4F_{9/2}$	At	85	Xe $4f^{14}5d^{10}6s^{2}6p^{5}$	$^2P_{3/2}$
Pt	78	Xe $4f^{14}5d^{9}6s^{1}$	$^3D_{3}$	Rn	86	Xe $4f^{14}5d^{10}6s^{2}6p^{6}$	$^1S_{0}$
Au	79	Xe $4f^{14}5d^{10}6s^{1}$	$^2S_{1/2}$	Fr	87	Rn $7s^{1}$	$^2S_{1/2}$
Hg	80	Xe $4f^{14}5d^{10}6s^{2}$	$^1S_{0}$	Ra	88	Rn $7s^{2}$	$^1S_{0}$
Tl	81	Xe $4f^{14}5d^{10}6s^{2}6p^{1}$	$^2P_{1/2}$	Ac	89	Rn $6d^{1}7s^{2}$	$^2D_{3/2}$
Pb	82	Xe $4f^{14}5d^{10}6s^{2}6p^{2}$	$^3P_{0}$	Th	90	Rn $6d^{2}7s^{2}$	$^3F_{2}$
Bi	83	Xe $4f^{14}5d^{10}6s^{2}6p^{3}$	$^4S_{3/2}$	Pa	91	Rn $6d^{3}7s^{2}$	$^4F_{3/2}$
Po	84	Xe $4f^{14}5d^{10}6s^{2}6p^{4}$	$^3P_{2}$	U	92	Rn $6d^{4}7s^{2}$	$^5D_{0}$

IV. 3. Atomic Spectra

* Units

Wavelength (λ): Infrared region - unit of λ is usually μ ($1\,\mu = 10^{-4}$ cm);
Optical region - unit of λ is usually Å ($1\text{Å} = 10^{-8}$ cm).

Frequency (ν'): $= \frac{c}{\lambda}$ where c is the velocity of light. Unit is usually
cycles per second. Since ν' is generally a large number one uses ν, the value
of frequency in wave numbers. $\nu = \lambda^{-1}$. Unit of ν is usually cm^{-1}, i.e. λ in cm.
If measurements are made in air the values can be referred to $C_{vac.}$ and $\lambda_{vac.}$
the values corresponding to propagation in vacuum, as follows:

$$\nu' = \frac{C_{air}}{\lambda_{air}} = \frac{C_{vac}}{\lambda_{vac}} ; \quad \nu = \frac{1}{\lambda_{vac.}} = \frac{1}{n_{air} \cdot \lambda_{air}}$$

since $\lambda_{vac} = n_{air}\,\lambda_{air}$. ($n_{air}$ = refractive index of air for that wave lenth λ_{air}).

Energy (E):

$$E = h\nu' = hc\,\nu ; \quad h = \text{Planck's constant} = 6.6239 \times 10^{-27} \text{ erg.sec.}$$

Table of Conversion Factors of Energy Units

Unit	cm^{-1}	ergs/molecule	cal/mole	e.v.
1 cm^{-1}	1	1.9865×10^{-16}	2.859	1.2398
1 erg/molecule	5.0348×10^{15}	1	1.43956×10^{16}	6.2421×10^{11}
1 cal/mole	0.34975	6.9467×10^{-17}	1	4.3361×10^{-5}
1 e.v.	8065.8	1.6020×10^{-12}	2.306×10^{4}	1

* **Frequency of Hydrogen Series**

$$\nu \ (cm^{-1}) = R(\frac{1}{n_2^2} - \frac{1}{n_1^2})$$

$$(R = Rydberg = 109, \ 677.581 \ cm^{-1})$$

Lyman Series: $(n_2 = 1; \ n_1 = 2, \ 3, \ 4 \ \ldots\ldots)$ (Far ultraviolet)

Balmer Series: $n_2 = 2; \ n_1 = 3, \ 4, \ 5 \ \ldots\ldots$ (Visible and near u.v.)

Ritz-Paschen Series: $n_2 = 3; \ n_1 = 4, \ 5, \ 6 \ \ldots\ldots$ (Infrared)

Brackett Series: $n_2 = 4; \ n = 5, \ 6, \ 7 \ \ldots\ldots$ (Infrared)

Pfund Series: $n_2 = 5; \ n = 6, \ 7, \ 8 \ \ldots\ldots$ (Infrared)

* **Earlier atomic models**

Bohr Model and Atomic Spectra

Bohr condition for the angular momentum of an electron in a circular orbit around the nucleus:

$$mvr = n\hbar \ , \qquad n = 1, \ 2, \ 3 \ \ldots\ldots$$

n = principal quantum number; m = mass of electron; v = velocity of electron; r = radius of electron orbit.

Bohr radius, r.

$$r = \frac{n^2 \hbar^2}{me^2 Z} \qquad e = \text{electronic charge}; \quad Z = \text{atomic number}$$

For $n = 1$, $r = a_H = 0.529$ Å. (a_0)

Energy values

$$E_n = \frac{-2\pi^2 \mu e^4}{h^2} \frac{Z^2}{n^2}$$

where $\mu = \frac{mM}{m+M}$ with M = mass of nucleus. (μ = reduced mass).

Spectral frequencies

$$\nu \ (\text{in } cm^{-1}) = \frac{1}{hc} (E_{n_1} - E_{n_2}) = \frac{2\pi^2 \mu e^4 Z^2}{ch^3} (\frac{1}{n_2^2} - \frac{1}{n_1^2}) = RZ^2 (\frac{1}{n_2^2} - \frac{1}{n_1^2})$$

where $R = Rydberg = 2\pi^2 \mu e^4/(ch^3)$; $R = R_\infty (\frac{M}{M+m})$; R_∞ = value of Rydberg for infinitely heavy nucleus.

Bohr - Sommerfeld Model

According to this model the electron is supposed to move in elliptic orbits. The linear momentum p_r in the direction of r is quantized.

$$\oint p_r \ dr = n_r h; \quad n_r = 0, \ 1, \ 2 \ \ldots\ldots = \text{radial quantum number}$$

The angular momentum p_ϕ is also quantized

$$\oint p_\phi \, d\phi = k h ; \quad k = 1, 2, 3 \ldots\ldots = \text{azimuthal quantum number.}$$

Principal quantum number $n = k + n_r$.; $n \geqslant k$. ($k = 0$ not allowed); circular orbits are obtained when $k = n$ and the ellipticity increases for a given k as the difference between n and k increases.

Sommerfeld Relativistic correction for energy of Bohr atom

$$E(n,k) = -\frac{2\pi^2 \mu e^4}{h^2} \cdot \frac{z^2}{n^2} \left[1 + \frac{\alpha^2 z^2}{n} \left(\frac{1}{k} - \frac{3}{4n} \right) \right]$$

where $\alpha = \dfrac{2\pi e^2}{hc}$ = fine structure constant.

* **De Broglie Relation:** The wavelength λ associated with a moving particle having a velocity v is

$$\lambda = h/(mv) = h/p ; \quad h = \text{Planck's constant}$$

* **Planck - Bohr relation:** The frequency of a transition between two levels of energy E_1 and E_2 is

$$\nu = \frac{E_2 - E_1}{h} = \Delta E/h$$

* **Term Symbols:** Total orbital and spin angular momenta of electrons in an atom are designated L and S. In the Russell - Saunders (LS) coupling to "scheme, L and S are vectorailly coupled" to yield the resultant J. J values range from L + S, to L - S in the following manner: L + S, $|L + S - 1|$, $|L + S - 2| \ldots\ldots |L - S + 1|$, $|L - S|$. The number of such values which J takes is known as multiplicity and the corresponding energy levels constitute a multiplet. The term symbols for a given electronic configuration indicate the L values by means of term letters S, P, D, F ...... for L = 0, 1, 2, 3 ..... respectively. An example of such a term symbol is $2_{P_{3/2}}$. P indicates that the value of L = 1. The left-hand superscript shows the value of 2S+1, the spin multiplicity. In the present example S = ½ hence 2S+1 = 2. S values range from 1 onwards and are called singlet, doublet etc. The right hand subscript in the term symbol shows the value of J. In the above example L = 1, S = ½ hence J = 3/2.

Usually a state with the lowest J value in a given multiplet corresponds to the lowest energy. (normal multiplet). However, in some cases the situation is reversed and the highest J value corresponds to the lowest energy. (inverted multiplet). In general, for a given set of atomic states the state with the highest spin multiplicity and largest L value corresponds to lowest (ground state) energy. (Hund's rule)

* **Zeeman and Paschen - Back Effects:** The application of magnetic field in atoms gives rise to a set of new energy levels (magnetic splitting) characterized by the different values of J. (that is,M values which range as J, J-1 ...... -J). One thus obtains a set of 2J+1 levels for each multiplet. The interaction between the component electron magnetic moment along the field direction (μ_z) and the external magnetic field H_z results in the splitting which depends on the M value since $\mu_z = e\hbar/(2mc) M = \beta M$ where m = mass of

electron and β = Bohr magneton. The J vector is thought of as precessing
around H with a frequency (Larmor frequency) $\omega = 2\pi\nu = eH/(2mc)$. Tran-
sitions between various levels of a pair of multiplets differing in J value
by 1 are allowed subject to the condition $\Delta M = 0, \pm 1$. If one is dealing
with spin singlet levels one observes three components (Zeeman components)
one σ and two π which are polarized perpendicular and parallel to the field
respectively. This is the normal Zeeman effect. For levels which are not
singlets more than three components are observed (anomalous Zeeman effect)
which can be explained by postulating that μ_z = gβM where g is the Lande
g - factor.

$$g = 1 + \left\{ \left[J(J+1) + S(S+1) - L(L+1) \right] / (2J(J+1)) \right\}$$

If the magnetic field is increased to a high value such that the magnetic
splitting becomes greater than the splitting between levels of different
J value in the absence of a field (that is, multiplet separation) then the
anomalous Zeeman effect goes over to the normal type. This effect is known
as the Paschen - Back effect.

The Paschen - Back effect can be interpreted in terms of the uncoupling
of L and S vectors.

Stark Effect: The splitting of atomic spectral lines due to an electric
field was originally discovered by J. Stark and the phenomenon is known as Stark
effect. The total angular momentum vector J is quantized along the electric
field direction. Levels with +M and -M quantum numbers have the same energy
(degenerate). The number of term components is $J+\frac{1}{2}$ if J is half-integral and
J+1 if J is integral. In very strong fields L and S may be uncoupled similar
to the magnetic Paschen - Back effect. The interaction in Stark effect is
that of the electric field (E) with the induced electric dipole (μ) of the
atom. [$\mu_z = \alpha_{zz}E_z$ where α_{zz} is the polarizability tensor; interaction
term $= - \mu_z E_z = - \alpha_{zz}E_z^2$.]

*Hyperfine Structure of Atomic Spectral Lines

Under very high resolution multiplet components may show "splittings"
of the order of a few cm^{-1} and this is called hyperfine structure (h.f.s.).
These additional lines may be due to close-lying spectral lines of different
isotopes of the atom in question (isotope effect) or due to nuclear-electron
interactions. The nuclear h.f.s. can be explained in terms of the magnetic
and electrical properties of the nuclei and the nature of interaction between
electrons and nuclei. Thus, since the probability of finding an s-electron of
an atom at its nucleus is non-zero we have the Fermi-contact interaction. The
nucleus may have, besides a magnetic moment, an electric quadrupole moment if its
spin angular momentum quantum number $I > \frac{1}{2}$. p,d,f... electrons may interact
with the nuclear electric quadrupole moment J and I can be added vectorially
to yield F and the h.f.s. analyzed in terms of the quantum numbers of F.

* X-ray Spectra: The emission of X-rays ($\lambda = 10^{-2}$ to 10 $\overset{o}{A}$) from atoms
is due to transitions of electrons from outer orbitals to inner orbitals
from which electrons had been ejected by bombardment of the solid containing
the atoms (targets) with high-speed electrons or high energy photons.

Characteristic frequencies (in cm^{-1}) of X-ray emission by atoms depend on
$Z; \bar{\nu}^{1/2} = a \, (Z-b)$ where a and b are constants   (Moseley). The X-ray
emission lines are labelled K,L ... depending on the inner orbital principal
quantum number ($n_1 = 1,2$ ...) and further classified as α_1, α_2 ...,
β_1, β_2 ... etc. depending on the quantum numbers of the outer orbitals
concerned with the transitions.

$$\bar{\nu} = R \, Z'^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

R = Rydberg; $Z' = (Z-S)$ where S = screening constant. Thus for K_α :
$Z' = (Z-1)$, $n_1 = 1$, $n_2 = 2$; for L_α : $Z' = (Z-7.4)$, $n_1 = 2$, $n_2 = 3$ and so on.
The early investigations of X-ray spectra by Moseley were largely responsible
for the subsequent development of atomic models.
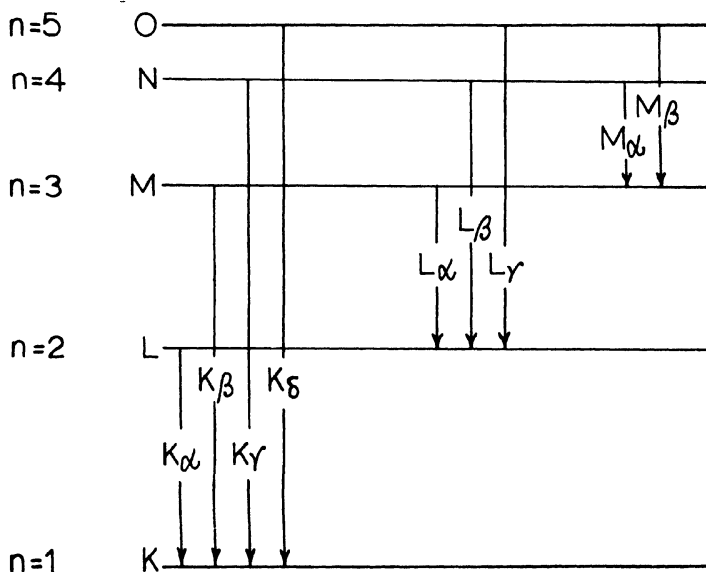
Origin of X-ray Spectra

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For an extensive collection of data on atomic energy levels see C.E.
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Atomic Radii of Elements

Element	Atomic No.	Radius Å	Element	Atomic No.	Radius Å	Element	Atomic No.	Radius Å
H	1	0.37	Co	27	1.16	I	53	1.33
He	2	0.93	Ni	28	1.15	Xe	54	1.90
Li	3	1.25	Cu	29	1.17	Cs	55	2.35
Be	4	0.89	Zn	30	1.25	Ba	56	1.98
B	5	0.8	Ga	31	1.25	La	57	1.69
C	6	0.77	Ge	32	1.22	Ce	58	1.65
N	7	0.74	As	33	1.21	Pr	59	1.65
O	8	0.74	Se	34	1.17	Nd	60	1.64
F	9	0.72	Br	35	1.14	Pm	61	
Ne	10	1.12	Kr	36	1.69	Sm	62	1.66
Na	11	1.57	Rb	37	2.16	Eu	63	1.85
Mg	12	1.36	Sr	38	1.91	Gd	64	1.61
Al	13	1.25	Y	39	1.62	Tb	65	1.59
Si	14	1.17	Zr	40	1.45	Dy	66	1.59
P	15	1.10	Nb	41	1.34	Ho	67	1.58
S	16	1.04	Mo	42	1.30	Er	68	1.57
Cl	17	0.99	Tc	43	1.27	Tm	69	1.56
Ar	18	1.54	Ru	44	1.24	Yb	70	1.70
K	19	2.03	Rh	45	1.25	Lu	71	1.56
Ca	20	1.74	Pd	46	1.28	Hf	72	1.44
Sc	21	1.44	Ag	47	1.34	Ta	73	1.34
Ti	22	1.32	Cd	48	1.41	W	74	1.30
V	23	1.22	In	49	1.50	Re	75	1.28
Cr	24	1.18	Sn	50	1.40	Os	76	1.26
Mn	25	1.17	Sb	51	1.41	Ir	77	1.26
Fe	26	1.17	Te	52	1.37	Pt	78	1.30

Atomic Radii of Elements (contd.)

Element	Atomic No.	Radius Å	Element	Atomic No.	Radius Å	Element	Atomic No.	Radius Å
Au	79	1.34	Po	84	1.53	Ac	89	
Hg	80	1.44	At	85		Th	90	1.65
Tl	81	1.55	Rn	86		Pa	91	
Pb	82	1.54	Fr	87		U	92	1.42
Bi	83	1.52	Ra	88				

First Ionization Potentials (I_1) of Elements

Element	Atomic No.	I_1(e.v.)	Element	Atomic No.	I_1(e.v.)	Element	Atomic No.	I_1(e.v.)
H	1	13.6	Mn	25	7.4	In	49	5.8
He	2	24.6	Fe	26	7.9	Sn	50	7.3
Li	3	5.4	Co	27	7.9	Sb	51	8.6
Be	4	9.3	Ni	28	7.6	Te	52	9.0
B	5	8.3	Cu	29	7.6	I	53	10.5
C	6	11.3	Zn	30	9.4	Xe	54	12.1
N	7	14.5	Ga	31	6.0	Cs	55	3.9
O	8	13.6	Ge	32	8.1	Ba	56	5.2
F	9	17.4	As	33	9.8	La	57	5.6
Ne	10	21.6	Se	34	9.8	Ce	58	6.9
Na	11	5.1	Br	35	11.8	Pr	59	5.8
Mg	12	7.6	Kr	36	14.0	Nd	60	6.3
Al	13	6.0	Rb	37	4.2	Pm	61	–
Si	14	8.2	Sr	38	5.7	Sm	62	5.6
P	15	11.0	Y	39	6.4	Eu	63	5.7
S	16	10.4	Zr	40	6.8	Gd	64	6.2
Cl	17	13.0	Nb	41	6.9	Tb	65	6.7
Ar	18	15.8	Mo	42	7.1	Dy	66	6.8
K	19	4.3	Tc	43	7.3	Ho	67	–
Ca	20	6.1	Ru	44	7.4	Er	68	–
Sc	21	6.5	Rh	45	7.5	Tm	69	–
Ti	22	6.8	Pd	46	8.3	Yb	70	6.2
V	23	6.7	Ag	47	7.6	Lu	71	5.0
Cr	24	6.8	Cd	48	9.0	Hf	72	7.0

Element	Atomic No.	I_1 (e.v.)	Element	Atomic No.	I_1 (e.v.)	Element	Atomic No.	I_1 (e.v.)
Ta	73	7.9	Hg	80	10.4	Fr	87	-
W	74	8.6	Tl	81	6.1	Ra	88	5.3
Re	75	7.9	Pb	82	7.4	Ac	89	6.9
Os	76	8.7	Bi	83	7.3	Th	90	-
Ir	77	9.0	Po	84	8.4	Pa	91	-
Pt	78	9.0	At	85	-	U	92	4.0
Au	79	9.2	Rn	86	10.7			

Successive Ionization Potentials* (in e.v.) of Some Elements (Starting from outermost electron to the innermost)

Element	I_2	I_3	I_4	I_5	I_6	I_7	I_8	I_9	I_{10}
H									
He	54.4								
Li	75.6	122.3							
Be	18.2	154.6	218.1						
B	25.1	38.2	258.9	340.4					
C	24.4	48.1	64.2	392.4	494.3				
N	29.6	46.8	77.2	98.0	550.7	667.8			
O	35.1	55.1	77.2	114.0	137.9	741.5	871.6		
F	34.9	62.9	87.2	114.0	157.0	184.8	954.0	1097.0	
Ne	41.1	64.2	97.1	126.2	159.1	206.8	238.1	1188.1	1357.2
Na	47.3	72.0	98.9	138.8	172.1	208.1	264.1	299.7	1461.3
Mg	15.0	80.2	109.3	141.4	186.9	225.5	266.7		
Al	18.8	28.5	120.1	153.5	190.4	240.7	285.3		
Si	16.3	33.5	45.2	166.1	203.8	245.0	301.4		
P	19.7	30.2	51.4	65.0	223.3	268.4	316.1		
S	23.4	35.1	47.1	72.0	88.0	281.4	329.5		
Cl	23.8	39.9	53.5	67.8	97.1	114.5	346.9		
Ar	27.6								
K	31.8	45.5	60.6	82.8	101.0	120.1	155.2		
Ca	11.9	51.0	67.0	84.1	111.0	127.0	151.1		
Sc	12.8	24.8	73.5	91.1	110.6	140.9	157.8		
Ti	13.6	27.6	43.4	99.7	118.8	140.3	176.0		
V	14.7	26.5	48.1	64.7	128.4	150.0	172.6		
Cr	16.5	32.0	51.0	72.0	89.8	160.4	183.9		
Mn	15.7	34.0	52.9	75.9	101.0	119.2	195.1		
Fe	16.2	30.0	55.9	78.9	104.9	133.1	150.9		
Co	17.0	34.0	52.9	82.0	109.3	137.9	170.0		
Ni	18.1	36.0	55.9	78.9	112.7	143.1	176.0		
Cu	20.3	37.9	59.0	82.8	109.3	148.3	181.7		
Zn	18.0	40.0	62.0	85.9	114.0	144.0	187.8		
Ga	20.5	30.8	63.7	90.2	117.9	148.7	183.0		

Element	I_2	I_3	I_4	I_5	I_6	I_7	I_8	I_9	I_{10}
Ge	15.9	34.2	45.7	93.7	123.1	154.8	189.1		
As	18.6	28.3	50.0	62.6	127.5	160.0	196.0		
Se	21.5	34.0	42.9	72.8	81.5	166.1	202.1		
Br	21.6	35.6	50.2	60.0	86.9	104.1	210.3		
Kr	24.5								

* For I_1 values see table of first ionization potentials.

Electron Affinities of Some Elements

Electron affinity ($\mathcal{E}$) is the energy released by the atom of an element due to capture of an electron of zero kinetic energy.

Element	H	C	O	F	S	Cl	Br	I
Electron Affinity $\mathcal{E}$ in e.v.	0.747	1.25	1.47	3.45	2.07	3.61	3.36	3.06

IV.4. Valency and Chemical Binding

IV.4.A. Glossary Glossary of a few commonly used terms for discussing valency and chemical binding are given below.

Alternant and Non-Alternant Hydrocarbons (AH and NAH):

Alternant hydrocarbons (AH) are planar conjugated hydrocarbons having only even-membered rings. In these systems if one marks alternate carbon positions by a "star" it is found that each starred atom has only unstarred carbon atoms as neighbors. If the number of starred atoms is equal to unstarred atoms the system is an even-alternant hydrocarbon. If the number of starred and unstarred positions differ by one we have an odd alternant hydrocarbon. In non-alternant hydrocarbons (NAH) all starred atoms do not have unstarred atoms as neighbors.
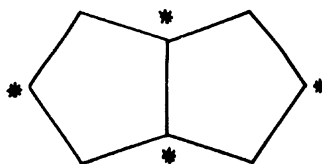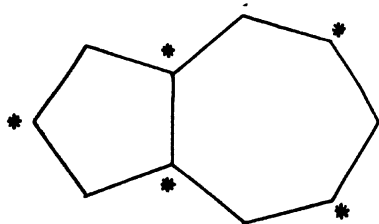
Atomic orbitals (AO): Probability distribution for an electron in atoms. AO's are classified as s, p, d .... depending on the angular momentum quantum number 0, 1, 2 .... respectively. These quantum numbers refer to the angular momentum (units of $\hbar$) along a chosen axis.

Antibonding Molecular Orbital (ABMO): A molecular orbital whose energy value is higher than the value corresponding to the individual energy values of the atomic orbitals used in the linear combination process.

Bond energy: This refers to the molecular binding energy in the case of a diatomic molecule and in a polyatomic molecule the bond energy of a bond A-B is the contribution of this bond to the total molecular binding energy.

Bonding Molecular Orbital (BMO): A molecular orbital whose energy value is lower than the value corresponding to the individual energy values of the atomic orbitals used in the linear combination process.

Bond Order: A number which refers to the nature of a bond as to whether it is single, double, triple etc. (bond order 1,2,3 etc. respectively). This number thus refers in valence bond theory to the number of pairs of electrons (with opposite spins) involved in a bond. In molecular orbital theory it is defined as below.

$$\text{Bond order} = \tfrac{1}{2}\left[\begin{array}{cc}\text{Number of electrons} & \text{Number of electrons} \\ \text{in bonding m.o's} & \text{in antibonding m.o.'s}\end{array}\right]$$

Born-Oppenheimer approximation: The total wave function of a molecule is assumed to be separable into electronic and nuclear parts. $\Psi = \Psi$ (electronic) . Ψ (nuclear) . This assumption can be justified in many cases especially those where the electronic wave function varies slowly with nuclear co-ordinates. However, if the system has degeneracy or near-degeneracy of electronic wave functions this approximation may break down.

Charge-Transfer Complexes: These are complexes formed by the interaction between an electron donor (D) and an electron acceptor (A) as for example, $BF_3 \longleftarrow NH_3$. Iodine-benzene is another such case. **Mulliken** has given a quantum-mechanical picture of these complexes. According to this if $\Psi(D,A)$ is the wave function of the separated D, A systems (no-bond case) and $\Psi(D^+A^-)$ is the wave function for the ionic case involving transfer of the charge then linear combination of these wave functions yields two wave functions Ψ_+ and Ψ_- for the charge transfer complex. One of these corresponds to an energy value lower than that of $\Psi(D,A)$ or $\Psi(D^+A^-)$. The transition between Ψ_+ and Ψ_- levels gives rise to a **charge-transfer band** since charge is transferred from D to A in this process. Valence bond theory is suitable for weak complexes while molecular orbital theory is better for strong complexes.

Configuration Interaction (C.I.): Different electronic configurations of a system may be described by appropriate linear combination of wave functions (Ψ). Due to the presence of the electron repulsion term in the Hamiltonian H of a many electron system the wave functions Ψ_i, Ψ_j, ... of these various configurations may yield non-zero values for integrals of the type $\int \Psi_i H \Psi_j \cdot d\tau$. Such configurations are then said to interact. A linear combination of the wave functions Ψ_i, Ψ_j, ... yields a lower energy value (configuration interaction).

Correlation Diagrams: The variation of molecular orbital energies with internuclear distance in homonuclear and heteronuclear molecules can be represented schematically by diagrams in which on one side we represent the energy values

of separated atomic orbitals ($r = \infty$) and on the other those of the united atom ($r = 0$) (united atom is the atom which is isoelectronic with the molecule in question) with the molecular orbitals in between. Lines are then drawn to show how the atomic orbitals on linear combination yield corresponding m.o.'s which in turn go over to the various united a.o.'s at $r = 0$.

<u>Coulomb Integral</u> (α): A quantity used in molecular orbital theory. $\alpha_A = \int \varphi_A H \varphi_A \, d\tau$ where φ_A is the atomic orbital on A. In the Hückel molecular orbital theory H is an effective one-electron Hamiltonian.

<u>Coulomb Repulsion Integral</u> (J):

$$J = \iint \varphi_A(1) \, \varphi_B(2) \, e^2/r_{12} \, \varphi_A(1) \, \varphi_B(2) \, d\tau_1 \, d\tau_2;$$ r_{12} is the

distance between electrons 1 and 2. In some instances the coulomb integral (J) is defined as follows.

$$J = \iint \varphi_A(1) \, \varphi_B(2) \, H' \, \varphi_A(1) \, \varphi_B(2) \, d\tau_1 \, d\tau_2$$

where H' is an interaction Hamiltonian appropriate to the situation. The symbol Q is also used for this quantity.

<u>Covalent Bond</u>: A bond between two atoms formed by the sharing of a pair of electrons of opposite spin, each atom contributing one electron of the shared-pair. The concept was originally introduced by <u>G.N. Lewis</u>.

<u>Delocalization energy</u> (D.E.): This is the extra bonding energy that results in allowing electrons to delocalize in a molecule as compared to the localized case. The energy of the conventional chemical formula structure is taken usually as reference (localized case). M.O. Calculations of delocalization energy (D.E.) provide useful information regarding stability of systems.

<u>Directed Orbitals</u>: These are atomic orbitals which are highly directional and are oriented so as to yield maximum probability of finding the electron of this orbital in a specified direction (usually towards the atomic orbital of another atom). Directed orbitals may be pure p, d, f... orbitals or hybrid orbitals which are formed by linear combination of atomic orbitals on the given atom.

<u>Dissociation energy</u> (D): Energy required to dissociate a molecule into its constituent atoms.

<u>Electronegativity</u> (χ): A property which serves as a measure of the power of an atom in a molecule to hold electrons to itself. For a bond A-B formed by two atoms with electronegativity values χ_A and χ_B, <u>Pauling</u> uses the relation:

$$\chi_A - \chi_B = \left[D(A-B) - \tfrac{1}{2} \left(D(A-A) + D(B-B) \right) \right]^{\frac{1}{2}} /23$$

where D(A-B) is the experimental bond energy of A-B. $\tfrac{1}{2} \left[\left(D(A-A) + B(B-B) \right) \right]$ is the covalent bond energy of A-B. <u>Mulliken</u> defines electronegativity as $\tfrac{1}{2}(I + \mathcal{E})$ where I and $\mathcal{E}$ are the ionization potential and electron affinity

of the atom. The Pauling and Mulliken scales are related approximately.
$X(Mulliken) \approx 2.78 \; X \; (Pauling)$.

Equivalent Orbitals: Linear combination of orbitals which can be converted
into one another by appropriate symmetry operations of the molecule and
thus showing equivalence. In a sense, they can be said to be the molecular
counter part of atomic hybrid orbitals.

Exchange Integral (K):

$$K = \iint \varphi_A(1) \; \varphi_B(2) \; \frac{e^2}{r_{12}} \; \varphi_A(2) \; \varphi_B(1) \; d\tau_1 \, d\tau_2$$

r_{12} is the distance between electrons 1 and 2. K is also sometimes defined
as below

$$K = \iint \varphi_A(1) \; \varphi_B(2) \quad H' \; \varphi_A(2) \; \varphi_B(1) \; d\tau_1 \, d\tau_2$$

where H' is an interaction Hamiltonian including e^2/r_{12} and nuclear –electron
attraction terms. Some authors use the symbols J and K^2 for this quantity.

Hybridization: The process of making a linear combination of atomic orbitals
on a given atom.

Hydrogen bond: A bond between two atoms of fairly high electronegativity
due to a hydrogen atom in between(hydrogen bridge). Hydrogen bond energy
values are usually of the order of 6 k.cal/mole. The bond is represented
as A–H...B. Such bonds may occur between atoms on separate molecules
(intermolecular hydrogen bonding) or between atoms in the same molecule
(intramolecular hydrogen bonding). In some crystals hydrogen bonding may be
extensive and of structural importance (ex: ice). Hydrogen bond plays an
extremely important role in the structure and properties of biologically
important molecules (ex: DNA–deoxyribonuclei acid). Other well-known
examples are $(F....H....F)^-$ ion in KHF_2
and formic acid dimer.

$$H - C \overset{\displaystyle O- - - - -H - O}{\underset{\displaystyle O - H - - - - -O}{\diagdown \diagup}} C - H$$
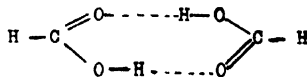
Hyperconjugation: A methyl group attached to a conjugated system exhibits
properties that are analogous to a group having π-electrons and thus
conjugation is extended to the methyl group. This phenomenon has been termed
hyperconjugation (Mulliken). Any group which has orbitals having the same
symmetry as the π-orbitals can thus exhibit extended conjugation.

Ionic Bond: A bond between two atoms due to electrostatic force arising
out of charges on the atoms. A simple model for such a bond is one where
an atom A parts with its valence electron to another more electronegative
atom to yield $A^+ B^-$. The energy of such a bond is calculated from the
Born-Mayer expression

$$E(r) = - \frac{e^2}{r} + b \; exp - (\alpha \; r)$$

b and α are empirical constants determined from other experimental data such
as compressibility data on the ionic solid. Another expression for the energy
of such a bond is

$$E(A^+ B^-) = \mathcal{E}_B - I_A + \frac{e^2}{r_0} \left(1 - \frac{1}{n} \right)$$

$\mathcal{E}_B$ = electron affinity of B; I_A = ionization potential of A and n is a parameter. (value around 9).

Ionic character: Ionic character of a bond A-B is a measure of the extent to which the bond may be described as a polar bond $A^+ - B^-$. Dipole moments and electronegativity values as well as many other physical properties of a bond can be correlated to this quantity.

Ionic-Covalent Resonance: The wave functions of a molecule or bond may be written as a linear combination of the purely covalent and purely ionic wave functions. Such a linear combination can yield an energy value which is lower than that of either E(cov.) or E(ionic). This feature is termed ionic-covalent resonance and is employed in valence bond theory.

Jahn-Teller Effect: If a non-linear molecule possesses an orbitally-dege-nerate state the system will distort itself so as to remove the degeneracy. This is known as Jahn-Teller distortion. This effect is thought to play an important role in determining the structure of several inorganic complexes.

LCAO-MO: Linear combination of atomic orbitals molecular orbital, that is a molecular orbital built up by linear combination of a.o.'s.

$$\Psi = \sum_j c_j \varphi_j \quad ; \ (\ \Psi = \text{LCAO-MO}; \quad \varphi_j = \text{j-th AO and } c_j = \text{linear coefficient})$$

Molecular binding energy: Difference in the energy value of a molecule in its equilibrium configuration and with its constituent atoms removed from one another to infinite distance.

Molecular Orbitals (M.O.) : Probability distribution for an electron in a molecule. M.O.'s are classified as σ, π, δ ..... depending on the angular momentum quantum number being 0, 1, 2......respectively. These quantum numbers refer to the angular momentum (in units of $\hbar$) measured along the bond axis. M.O's built by linear combination of atomic orbitals are referred to as LCAO-M.O.'s.

Non-bonding Molecular Orbital (NBMO): A molecular orbital whose energy value is equal to the energy value of atomic orbitals used in the linear combination process, (overlap between atomic orbitals is effectively zero).

One-electron Bond: A bond between two atoms due to the sharing of a single electron (unlike the more common shared electron pair bonds). The role of such bonds is emphasized in valence bond theory. Example: H_2^+ as $H_A^+ H_B$ and $H_A H_B^+$.

Overlap integral (S): $S_{AB} = \int \varphi_A \ \varphi_B \ d\tau$ where φ_A and φ_B are two wave functions. This integral provides a measure of the overlap charge clouds $\int \varphi_A^2 d\tau$ and $\int \varphi_B^2 d\tau$. If φ_A and φ_B are the atomic orbitals involved in the bond A-B the larger the value of S_{AB} the stronger the bond is. A

generalization of this statement in molecules goes under the name of "criterion of maximum overlap".

P-P-P method: Also known as the P-method is an extension the Hückel molecular orbital theory of π-electron systems in which electron repulsion terms are included and self-consistent field procedures employed. The method derives its name from the names of the originators R.Pariser, R.G. Parr and J.A. Pople.

Perfect - Pairing Approximation: If a single structure for a molecular system is assumed with all atomic orbitals paired off using electrons of opposite spins such a valence bond structure is said to be a perfectly-paired structure. The wave function of the molecule may be assumed to be the one corresponding to this structure alone and this is known as the perfect-pairing approximation.

Pi-bond (π-bond): A bond between two atoms due to the "side-wise" overlapping of π-orbitals. Unlike the σ-bond the electron distribution in this bond is not cylindrically symmetric with respect to the internuclear axis.

Resonance: A concept used in valence bond theory. The total wave function of some molecules cannot be adequately represented in the perfect pairing approximation and it is then necessary to introduce other valence bond wave functions corresponding to various structures. However, none of these structures is individually able to explain the properties of the molecular system while a linear combination of all these wave functions is more satisfactory. The molecule is then said to "resonate" amongst these structures and the concept is termed resonance. It must be emphasized that the feature is a purely mathematical one and a mental construct.

Resonance Energy: The difference between the observed energy of a molecular system and the energy corresponding to the most stable valence-bond structure (perfect-paired structure). Since the experimental data are obtained with great difficulty several empirical approaches (like additivity of bond energies to yield total molecular energy) are employed. In conjugated hydrocarbon systems heats of hydrogenation are employed to determine empirical resonance energy values.

Resonance integral (β): $\beta_{AB} = \int \varphi_A H \varphi_B d\tau$; used extensively in Hückel molecular orbital theory and H in this context refers to the appropriate one-electron Hamiltonian.

Sandwich Compounds: Compounds in which a transition metal bonds symmetrically to two conjugated hydrocarbon systems; ex. ferrocene (iron bis-cyclopentadienyl).

Secular determinant: The determinant involved in energy calculations using the linear variational method where the linear coefficients are varied to minimize energy. For example, a typical 2 x 2 secular determinant appears as follows:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$H_{11} = \int \varphi_1 H \varphi_1 d\tau$ and $S = \int \varphi_1 \varphi_2 d\tau$ etc.   In most atomic and molecular problems $H_{ij} = H_{ji}$. E is the energy value which is a root of the secular determinant. In general for a n x n secular determinant n roots are possible although not all of them may be distinct. If two roots are identical they are said to be <u>degenerate</u>. The determinant may be also written as a set of <u>secular equations</u> with the coefficients appearing.

<u>"Tau"- bond</u> (τ -bond): A bond between two atoms with the bonding atomic orbitals overlapping neither "end-wise" nor "side-wise", the orbitals not being either directed towards the other nucleus or perpendicular to the internuclear axis. Such a bond is also called a "bent" bond or a "banana" bond. The bonding between carbon atoms in cyclopropane is believed to involve such bonds.

<u>Three-electron bond</u>: Similar to the one-electron bond in valence bond theory. An example is provided by He_2^+ involving resonance structures $He_A^+ \cdot : He_B$ and $He_A : \cdot^+ He_B$.

<u>Three-Center Bond</u>: A "common" bond involving three nuclei. Such a bond has been postulated for the B_2H_6 structure with B-H-B present. The orbitals of the two boron atoms and the hydrogen atom overlap forming one bonding M.O., one antibonding M.O. and one non-bonding M.O. Since <u>two</u> electrons can go into the bonding M.O. and only one in the non-bonding <u>M.O.</u> a stable bond results with a lesser number of electrons than in conventional bonds. Such bonds are postulated in explaining the stability of some electron-deficient molecules, especially in boron chemistry.

<u>Valence-Bond Structure</u>: This refers to a particular way of pairing electrons of various atomic orbitals in a molecule. The wave function corresponding to this pairing scheme is also sometimes referred to as the valence-bond structure, since each set of paired orbitals with electrons of opposite spin corresponds to a bond.

IV.4.B. <u>Valence Bond Theory</u>

* <u>Valence Bond Function for a Bond A-B</u>

$$\Psi (A-B) = c_0 \Psi_{cov.} + \sum_i c_i \Psi_{ion}^i$$

$$\Psi_{cov.} = \left[\varphi_A(1) \varphi_B(2) + \varphi_A(2) \varphi_B(1) \right]$$

$$\Psi_{ion}^1 = \varphi_A(1) \varphi_A(2)$$

$$\Psi_{ion}^2 = \varphi_B(1) \varphi_B(2)$$

φ's are atomic orbitals.

* <u>Pauli Exclusion Principle and V.B. Functions</u>

Since the total wave function has to be antisymmetric a symmetric V.B. space function has to be combined with an antisymmetric spin function. $\left[\varphi_A(1) \varphi_B(2) + \varphi_A(2) \varphi_B(1) \right]$ goes with the spin function $\left[\alpha(1)\beta(2) - \alpha(2)\beta(1) \right]$ where $\alpha(1)$ refers to the spin function of electron 1 in orbital A with $m_s = + 1/2$. Similarly $\left[\varphi_A(1) \varphi_B(2) - \varphi_A(2) \varphi_B(1) \right]$ goes with the spin functions $\alpha(1)\alpha(2)$, $\left[\alpha(1)\beta(2) + \alpha(2)\beta(1) \right]$ and $\beta(1)\beta(2)$

<u>Orbital Function</u>	<u>Spin Functions</u>
$\varphi_A(1) \varphi_B(2) + \varphi_A(2) \varphi_B(1)$	$\alpha(1)\beta(2) - \alpha(2)\beta(1)$ <u>Singlet</u>
$\varphi_A(1) \varphi_B(2) - \varphi_A(2) \varphi_B(1)$	$\alpha(1)\alpha(2), \left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right]$ <u>Triplet</u> and $\beta(1)\beta(2)$

* <u>H.L.S.P. (Heitler-London-Slater-Pauling) Function for Polyatomic Molecules</u>

Consider a polyatomic molecule with ground state as $^1\Sigma$ and each atomic orbital involved in bonding as singly occupied. Neglecting ionic structures the H.L.S.P. wave function is

$$\Psi = \frac{1}{2^{N/2}} \sum_R (-1)^R \mathcal{R} \left[\frac{1}{[(2n)!]^{1/2}} \sum_P (-1)^P \mathcal{P} \varphi(1) \varphi(2) \cdots \cdots \varphi_{2n}(2n) \right]$$

n=number of bonds, $\mathcal{P}$ and $\mathcal{R}$ are permutation and reversal operators, P and R are number of permutations and reversals. Permutation is of electrons between orbitals while reversal changes spins α and β. φ_i is a space orbital for i with spin function α while φ_i is that space orbital with spin function β. The total valence bond function of a molecule can be expressed as a linear combination of the wave functions Ψ_j for the various valence bond structures. $\Psi_{V.B.} = \sum_j c_j \Psi_j$. <u>Rumer</u> and <u>Pauling</u> have outlined methods for obtaining various matrix elements $\langle \Psi_i | H | \Psi_j \rangle$ in order to set up the secular determinant. For this purpose one sets up a <u>Rumer diagram</u> with the orbitals arranged in a circle and the structures drawn indicating which orbitals are paired (line between orbitals). Structures in which the lines do not cross are called

canonical structures. (Number of such canonical structures is $(2n)!/[n!(n+1)!]$ where n = number of bonds). Coefficients of matrix elements for coulomb (Q) and exchange (A) terms are obtained by superposing diagrams corresponding to these structures. (For details see Pauling, J. Chem. Phys. 1, 280 (1953). Generally only single exchange integrals are considered and ionic structures omitted. Further only near-neighbor exchange interactions are considered.

* Some V.B. Results:

Hydrogen molecule: The two energy levels are

$$E_1 = 2E_H + (Q+A)/(1+S^2) \; ; \; E_2 = 2E_H + (Q-A)/(1-S^2)$$

Π-electron calculations: (energy values)

Butadiene   : $Q \pm \sqrt{3} A$; Resonance energy (R.E) = 0.232 A

Cyclobutadiene: $Q \pm A$; R.E. = 1.0 A

Benzene   : Q ; $Q -2 A$ (degenerate); $Q-(1\pm\sqrt{13})A$

                R.E. = 1.1056 A

IV.4.C. Molecular Orbital Theory

* Molecular Orbital Function for a Bond A-B

$$\Psi_{M.O.} = c_1 \varphi_A + c_2 \varphi_B$$

φ_A and φ_B are atomic orbitals combining to yield the M.O. c_1 and c_2 are coefficients. For the case of H_2 molecule we have $c_1 = \pm c_2$ and $\varphi_A = \varphi_B = \varphi_{1s}$. The M.O. $\varphi_{1s}^A + \varphi_{1s}^B$ has a total angular momentum value equal to zero and hence is a σ orbital. The other combination $\varphi_{1s}^A - \varphi_{1s}^B$ is a non-bonding σ orbital, usually designated as σ^*. Thus, we have in general, σ, π, δ ...as well as $\sigma^*, \pi^* \delta^*$...etc. molecular orbitals. It is customary to refer to a σ M.O. formed from 1s orbitals as $\sigma 1s$ or $1s\sigma$ and similarly $\sigma 2p$ or $2p\sigma$ and so on.

* For homo-nuclear diatomic molecules formed from atoms in the first row of the Periodic Table the M.O. energy level scheme is schematically illustrated here. The level notations are also given.

	Mulliken Notation		Serial Notation
σ^*2p		$u\sigma$	6σ
π_y^*2p	π_z^*2p	$v\pi$	$2\pi_y, 2\pi_z$
$\pi_y 2p$	$\pi_z 2p$	$w\pi$	$1\pi_y, 1\pi_z$
σ^-2p		$x\sigma$	5σ
σ^*2s		$y\sigma$	4σ
σ^-2s		$z\sigma$	3σ
σ^*1s		KK	2σ
σ^-1s			1σ

Energy ↑

* g and u Classification·

If the molecule has a center of symmetry the g and u symbols denote that the wave function either does not change its sign (g) or does (u) after the inversion operation. In the H_2 molecule, for ex., the M.O. $\varphi_{1s}^A + \varphi_{1s}^B$ does not change sign on inversion.

A   B

+   +

A   B

+   −

Centre of Symmetry

(σ^-1s) (σ^*1s)
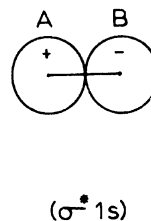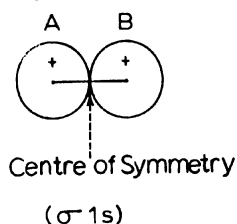
Therefore $\sigma 1s$ is of g-type. On the other hand $\varphi_{1s}^A - \varphi_{1s}^B$ changes sign upon inversion and hence is of u-type. $\pi 2p$ is of the u-type while π^*2p is of g-type.

Z axis ↑

+   +

−   −

Z axis ↑

+   −

−   +

Centre of Symmetry

$(\pi\, 2p_z)$ (π^*2p_z)
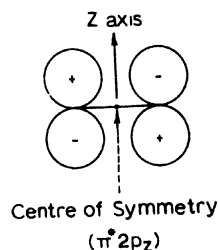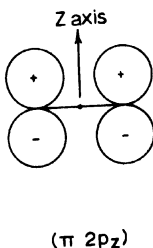
* **For heteronuclear diatomic molecules** g and u classification does not hold since there is no center of symmetry. The m.o.'s are generally

classified following Mulliken notation or the serial notation.

United Atom   M O   Separated Atoms
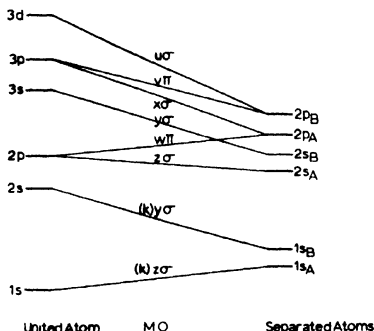
Molecular orbitals and Correlation Diagram
for heteronuclear diatomic molecules

* __Molecular Orbital Function for a Polyatomic Molecule__

$$\Psi_{M.O.} = \sum_{i} c_i \varphi_i$$

where φ_i's are the atomic orbitals and c_i's are coefficients that minimize the energy of the M.O.

* __Hückel M.O. Theory__

If the φ_i's are restricted to those atomic orbitals which have their axis of symmetry __not lying__ in the molecular plane and further if these atomic orbitals overlap side-wise we have the Ψ(M.O.) which corresponds to the Hückel type. Thus for the six $2p_z$ carbon orbitals of benzene whose axis of symmetry is perpendicular to the molecular plane we may write $\Psi = \sum_{i=1}^{6} c_i \varphi_i$, The orbitals are shown below:
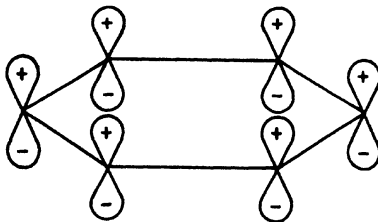
The coefficients c_i's are to be determined from the energy minimization process (Variational Method). In the Hückel procedure one usually neglects the overlap integral and all two electron operators are absorbed into an equivalent __one-electron__ Hamiltonian. The secular determinant is a 6 x 6 and appears as follows. α and β are coulomb and exchange integrals.

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

The values for the energy levels are: $\alpha+2\beta$, $\alpha+\beta$, $\alpha+\beta$, α, $\alpha-\beta$, $\alpha-\beta$ and $\alpha-2\beta$. Since β is a negative quantity $\alpha+2\beta$ corresponds to the lowest energy M.O. ($\beta \approx 18$ K·cal./mole for benzene).

* **Hückel Energy Levels in Planar Monocyclic π-Conjugated (Carbon Ring) Systems.**

| Cyclobutadiene | Cyclopentadiene | Benzene |
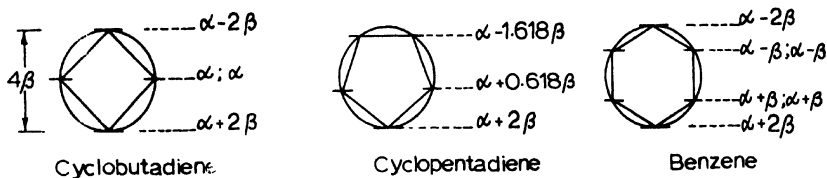
The radius of the circle in which the polygon is inscribed with one apex at the bottom is equivalent to 2β and energy levels are measured off with this scale.

* **Hückel Energy Levels for Other Systems**

        The π-electron energy levels of a straight chain conjugated polyene containing n carbon atoms are given by the expression $\alpha -2\beta \cos\left[a\pi/(n+1)\right]$ with a = 1,2...n. For a ring of n conjugated carbon atoms the energy values are given by $\alpha -2\beta \cos(2b\pi/n)$, with b = 1,2...n. For conjugated systems containing carbon atoms as well as other atoms (hetero atoms) the Hückel parameters α and β are to be chosen carefully. For hetero atoms the relations $\alpha_i = \alpha_0 + h\beta$ and $\beta_{ij} = k\beta_{c-c}$ are used where h and k are parameters. Modifications of the Hückel theory have been made. These include the Pariser-Parr-Pople method and ω-technique. Some simple procedures are also available for calculation of energies. (Dewar's R-S technique). For further details see Streitwieser, "Molecular Orbital Theory for Organic Chemists", John Wiley, New York, (1961); Roberts, "Notes on Molecular Orbital Calculations", Benjamin, New York, (1962) and other books listed in the bibliography at the end of this section.

* **Free Electron Model**

        For a linear conjugated polyene ($C_{2k}H_{2k+2}$) the π-electron energy

levels are given by $E_n = 2 \sum\limits_{n=1}^{k} n^2 h^2/(8ma^2)$ (number of π-electrons is $2k$;
number of filled levels is k). The energy expression is based on the one-dimensional box-model (box dimension = a). For a circular box model
$E_n = (2m)^{-1} \hbar^2 n^2 R^{-2}$ (R = radius of circle; $n = 0, \pm 1, \pm 2, \ldots \pm \infty$). One
can apply the above model to benzene with a value of $R = 1.39$ Å. The six
π-electrons are filled in the $n = 0, \pm 1$ levels. The free-electron model
provides a simple way of calculating energy differences, $E(n_1) - E(n_2)$, which
correspond to spectral transition frequencies. For further details see:
Bayliss, J. Chem. Phys., 16, 287 (1948); Kuhn, Helv. Chim. Acta, 31, 144 (1948);
32, 2247 (1949); Z. Elektrochem., 55, 220 (1957); Platt, J. Chem. Phys., 17,
484 (1949); Rudenberg and Parr, J. Chem. Phys., 19, 1268 (1957); Rudenberg and
Scherr, J. Chem. Phys., 21, 1565 (1953); and Simpson, J. Chem. Phys., 16, 1124
(1948).

IV.4.D. Ligand Field Theory

The energy levels of an ion subjected to an electrical field are different
from those of the free ion due to Stark effect. Under suitable conditions,
some orbitals of this ion which have the same energy (degeneracy) in the
absence of the electric field may have different energy values in the presence
of the electric field. This "lifting" of degeneracy may take place for an ion
surrounded by other oppositely charged ions as in a crystal. This is known as
crystal-field splitting. The removal of the degeneracy in the case of d- or f-
orbitals is of common interest. The details and extent of splitting depend
on the symmetry and the strength of the crystalline electric field. Crystal
field theory assumes that the neighboring ions do not overlap with the central
ion under consideration. However, in reality, appreciable overlapping may be
present with the surrounding ligands and the general theory to deal with such
situations is called the ligand field theory. The presence of covalent bond-
ing between the ion and the ligands which may be ions, or molecular dipoles,
or certain other molecular systems can also be taken into account.

The ions of interest are those of the iron group (3d), palladium group
(4d) rare-earth group (4f), platinum group (5d) and actinide group (6d and 5f).
The valence orbitals are indicated in parenthesis. The theory deals with
three broad categories: a) crystal field V is less than the spin-orbit ($\underline{l \cdot s}$)
coupling b) crystal field is of intermediate strength in comparison to spin-
orbit and electron repulsion terms (e^2/r_{ij}) and c) crystal field strength
is greater than electron repulsion terms. Complexes of rare earths belong to
category a) while complexes of the first transition group and "covalent"
complexes belong to categories b) and c) respectively.

For illustration we consider an ion with a single d electron subjected
to an external electric field (crystal field) of octahedral symmetry. The
energy level scheme in the new situation is illustrated here.

$$d \Big< \begin{array}{l} d_{x^2-y^2}, d_{z^2} \quad (e_g) \quad E(e_g) = 6\,Dq \\[2em] \\ d_{xy}, d_{xz}, d_{yz} \quad (t_{2g}) \quad E(t_{2g}) = -4\,Dq \end{array}$$

$\Delta = 10\,Dq$

Free ion   Octahedral field
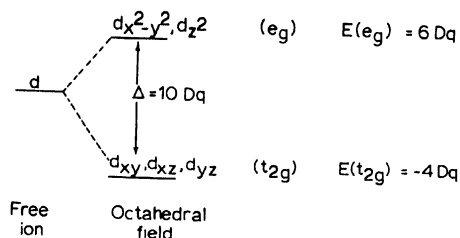
The $d_{x^2-y^2}$ and d_{z^2} orbitals transform as the e_g representation and d_{xy} d_{xz} and d_{yz} transform as the t_{2g} representation under the point group O_h. The level is said to "split" into e_g and t_{2g} with t_{2g} as the lower energy level. The energy values are given in terms of the crystal field parameters D and q. The level separation Δ between e_g and t_{2g} is 10Dq. If the field has tetrahedral symmetry the e_g level has lower energy, in other words the situation is just the reverse. These are some of the elementary results of the theory.

The Δ values can be correlated with electronic transitions and the crystal filed parameters can be obtained from spectroscopic measurements. Magnetic susceptibility (χ) measurements can also be related to the energy level separations. The g-value from electron paramagnetic reso- nance (e.p.r.) measurements also serve a similar purpose. The hyperfine interaction observed sometimes in the e.p.r. spectra can be interpreted on the basis of the magnetic interactions between the nucleus of the paramagnetic ion of interest as well as nuclei in the neighbouring ligands. Such results have provided excellent confirmation of the theory.

Bibliography (Ligand Field Theory and Related Topics)

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Parr, "Quantum Theory of Molecular Electronic Structure", Benjamin, New York (1964).

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Syrkin and Dyatkina, "Structure of Molecules and the Chemical Bond", Dover, New York (1964).

IV.5 Bond and Molecular Properties   ----

* Hückel M.O. Delocalisation Energies and Empirical Resonance Energies of Some Aromatic Hydrocarbons

Hydrocarbon	H.M.O. Delocalization Energy in units of β	Empirical Resonance Energy in units of k-cal/mole
Benzene	2.000	36.0
Naphthalene	3.683	61.0
Anthracene	5.314	83.5
Phenanthrene	5.448	91.3
Pyrene	6.506	108.9
Tetracene	6.932	110.0
1,2-Benzanthracene	7.101	111.6
3,4-Bensphenanthrene	7.187	109.6
Chrysene	7.190	116.5
Triphenylene	7.275	117.7
Perylene	8.245	126.3

Average value of β = -16 k. cal/mole

For details concerning M.O. results in several organic molecules see:

Coulson and Daudel, "Dictionary of Values of Molecular Constants", Centre de chimie Theorique de France, Paris (1955).

Coulson and Streitwieser, "Dictionary of Molecular Orbital Calculations",
    Pergamon, (1960)

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    New York (1961).

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    Pergamon (1962).

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* Average Bond Energies (B.E.) in K cal/mole

Bond	B.E.	Bond	B.E.	Bond	B.E.	Bond	B.E.
H–H	104.2	C=C	146.8	N=N	100	Cl–Cl	57.9
H–F	135.0	C≡C	200.6	N≡N	225.8	Br–Br	46.1
H–Cl	103.1	C–O	85.5	N–Cl	48	I–I	36.1
H–Br	87.4	O=O	178.0	O–H	110.6	S–S	51
H–I	71.4	C–Cl	78	O–O	33	Cl–F	60.6
H–S	81	C–Br	66	O=O	119.1	Br–Cl	52.3
C–H	98.8	N–H	93	O–F	44	I–Cl	50.3
C–C	83.2	N–N	38	F–F	37.0	I–Br	42.5

References: Pauling, "Nature of the Chemical Bond", Cornell Univ. Press,
                   Ithaca (1960).

              Cottrell, "The Strengths of Chemical Bonds", Butterworths,
                   London (1958).

* Average Bond Lengths (R) in Å

Bond	R	Bond	R	Bond	R	Bond	R
H–H	0.74	C≡C	1.20	C–Br	1.94	F–F	1.42
H–F	0.92	C–N	1.47	C–I	2.12	Cl–Cl	1.99
H–Cl	1.28	C=N	1.29	C–S	1.81	Br–Br	2.28
H–Br	1.41	C≡N	1.16	N–H	1.00	I–I	2.67
H–I	1.60	C–O	1.43	N≡N	1.09	C–H(methane)	1.095
C–H	1.08	C=O	1.22	O–H	0.97	C–H(ethylene)	1.080
C–C	1.54	C–F	1.38	S–H	1.33	C–H(acetylene)	1.065
C=C	1.34	C–Cl	1.77	O=O	1.21		

For bibliography on bond lengths see the section on "Shapes of Molecules
and Ions". (See IV.6.B)

* Covalent Radii of Some Atoms

Atom	Single-Bond Radius (Å)	Double-Bond Radius (Å)	Triple-Bond Radius (Å)
C	0.772	0.667	0.603
Si	1.17	1.07	1.00
P	1.10	1.00	0.93
S	1.04	0.94	0.87
Cl	0.99	0.89	
Ge	1.22	1.12	
As	1.21	1.11	
Se	1.17	1.07	
Br	1.14	1.04	
Sn	1.40	1.30	
Sb	1.41	1.31	
Te	1.37	1.27	
I	1.33	1.23	

* Pauling Electronegativity Values (X)

Atom	H	He	Li	Be	B	C	N	O	F	Ne
X	2.1		1.0	1.5	2.0	2.5	3.0	3.5	4.0	

Atom	Na	Mg	Al	Si	P	S	Sl	Ar
X	0.9	1.2	1.5	1.8	2.1	2.5	3.0	

Atom	K	Ca	Sc	TI	V	Cr	Mn	Fe[a]	Co	Ni	Cu[a]
X	0.8	1.0	1.3	1.5	1.6	1.6	1.5	1.8-1.9	1.8	1.8	1.9--2.0

Atom	Zn	Ga	Ge	As	Se	Br	Kr
X	1.6	1.8	1.8	2.0	2.4	2.8	

Atom	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
X	0.8	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2

Atom	Ag	Cd	In	Sn	Sb	Te	I	Xe
X	1.9	1.7	1.7	1.8-1.9	1.9	2.1	2.5	

Atom	Cs	Ba	La to Lu*	Hf	Ta	W	Re	Os	Ir	Pt
X	0.7	0.9	1.1-1.2	1.3	1.5	1.7	1.9	2.2	2.2	2.2

Pauling Electronegativity Values (X) (contd.)							
Atom	Au	Hg	Tl	Pb	Bi	Po	At	Rn
X	2.4	1.9	1.8	1.8	1.9	2.0	2.2	
Atom	Br	Ra	Ac – Lw#					
X	0.7	0.9	Ac 1.1; Th 1.3; Pa: 1.5; U: 1.7; Np – Lw: 1.3.					

(a)   Electronegativity values appear to vary with the oxidation number
(see also Gordy and Orville-Thomas, J. Chem. Phys. 24 439 (1956)).

* Lanthanide Series; # Actinide Series

For further discussion on electronegativity see: Little and Jones,
J. Chem. Ed., 37, 231, (1961); Pauling, "Nature of the Chemical Bond",
Cornell Univ. Press, Ithaca (1961); Pritchard and Skinner, Chem.
Rev., 55, 745 (1955).

* Relations Between Bond Order and Bond Distance for Carbon-carbon
Bonds

a) $r = r_s - \left[(r_s - r_d)/ 1 + kp(1-p))\right]$

r_s = "natural" single – bond distance in $\overset{o}{A}$; r_d = double-bond
distance in $\overset{o}{A}$; p = bond order; k = a parameter whose value is
1.05 for carbon sp^2-sp^2 hybrids. (See Coulson, Proc. Roy. Soc.
(London), A169, 413 (1959).

b) $r = 1.517 - 0.18p$

This relationship is obtained by using appropriate carbon-carbon
distances ($\overset{o}{A}$) and a k value of 1.0 in Coulson's equation (see a
above)

(See Coulson and Golebiewski, Proc. Phys. Soc. (London), 78 1310
(1961); Skancke Acta Chem. Scand. 18, 1671 (1964); Cruickshank and
Sparks (Proc. Roy. Soc. (Lond), A258, 270 (1960)) give

the relation $r = 1.567 - 0.267p$ for benzenoid hyrocarbons
p = Huckel bond order)

c) $r = r_s - 0.71 \log p$

(Pauling, "Nature of the Chemical Bond", Cornell Univ. Press,
Ithaca, 1960).

* Schomaker-Stevenson Equation for Bond Distance (J. Amer. Chem.
Soc., 63, 37 (1941); See also Gordy, J. Chem. Phys., 15, 81 (1947) and
Pauling, loc. cit.)

$$r(A-B) = r_A + r_B + C , \left| X_A - X_B \right|$$

r_A and r_B are covalent radii of atoms A and B in $\overset{o}{A}$; X_A and X_B are electro-
negativities of atoms A and B; r(A-B) is the bond distance between A and B

in $\overset{\circ}{A}$; C = Schomaker-Stevenson coefficient (in $\overset{\circ}{A}$ units)

* Table of Schomaker-Stevenson Coefficients

Description of Bond A-B	C (in $\overset{\circ}{A}$)
Either A or B or both A and B belong to first row in the periodic table	0.08
A = Si, P or S and B is an atom whose electro-negativity value is greater than A	0.06
A = Ge, As or Se and B is an atom whose electronegativity value is greater than A	0.04
A = Sn, Sb or Te and B is an atom whose electronegativity value is greater than A	0.02
A = Carbon and B is an atom in the fifth, sixth or seventh group (not in the first row)	0

* Pauling Electronegativity and Percent Ionic Character of Single Bonds

$$\text{Percentage Ionic Character (\% I.C)} = 100 \left\{ 1 - \exp\left[-0.25(X_A - X_B)^2 \right] \right\}$$

Note: This formula is of an approximate nature and is especially not valid for large $X_A - X_B = \Delta X$ values.

ΔX	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
% I.C.	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47
ΔX	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0		
% I.C.	51	55	59	63	67	70	74	76	79	82	84	86	88	89		

* Hannay-Smyth Expression for % I.C. (J. Amer. Chem. Soc., **68**, 171(1946))

$$\% \text{ I.C.} = 100 \cdot \left\{ 0.16 \left| (X_A - X_B) \right| + 0.035 (X_A - X_B)^2 \right\}$$

* Percent Double Bond Character of Bonds (Pauling)

$$\% \text{ Double bond character} - p; \quad p = \left[(r_s - r) / (r_s + 2r - 3r_d) \right] \cdot 100$$

r = observed bond length ($\overset{\circ}{A}$); r_s = "pure" single bond distance ($\overset{\circ}{A}$);
r_d = "pure" double bond distance ($\overset{\circ}{A}$).

Example: Graphite r = 1.42 $\overset{\circ}{A}$; r_s (carbon-carbon) = 1.54 $\overset{\circ}{A}$; r_d (carbon-carbon) = 1.34 $\overset{\circ}{A}$; p = $33\frac{1}{3}$%

"Pure" single and double bond distances can be obtained from the table of covalent radii.

* **Dipole Moments**

Dipole Moment = charge x distance ; Unit = debye = 10^{-18} e.s.u. (d)
Debye equation for electrical polarisation: Total poplarization = Polarization due to induced moments + polarization due to permanent moments.

$$P_M = \frac{\epsilon-1}{\epsilon+2} \frac{M}{d} = \frac{4}{3}\pi N\left(\alpha + \mu^2/3kT\right)$$

P_M = molar polarization; ϵ = dielectric constant; M = Mol. wt.; d = density;

N = Avogadro number; α = polarizability; μ = dipole moment; k = Boltzmann
constant. In the above equation $(4\pi N\alpha)/3$ refers to both electronic and
atomic polarizations. The term $4\pi N\mu^2/3kT$ is referred to as the orientation
polarization due to the orientation of molecular dipoles in an applied field.
Dipole moments are generally measured from dielectric constant data of vapors
(gas phase method) or solutions of polar molecules in non-polar solvents
(solution method). It is also possible to obtain dipole moments from die-
lectric constant data of pure polar liquids. However, the equations used
for pure polar liquids are believed to be less reliable. Microwave spectros-
copy provides accurate dipole moment data using Stark effect. Molecular beam
investigations also yield reliable data (Electric resonance method).

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(1963).

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Smyth, "Dielectric Behaviour and Structure", McGraw-Hill, New York (1955).

* **Dipole Moments (μ) of a few Molecules in Vapor Phase**

Molecule	(d)	Molecule	(d)	Molecule	(d)
HF	1.91	PF_3	1.025	CH_3Cl	1.86
HCl	1.03	PCl_3	0.80	CH_3Br	1.79
HBr	0.79	PBr_3	0.61	CH_3I	1.64
HI	0.38	PI_3	0	CH_3CN	3.94
HCN	2.93	AsH_3	0.15	CH_3NH_2	1.28
H_2O	1.84	AsF_3	2.815	CH_3NO_2	3.54
H_2O_2	2.13	$AsCl_3$	2.1	CH_3OH	1.69
H_2S	0.93	$AsBr_3$	1.7	CH_3CHO	2.72
CO	0.11	AsI_3	0.96	CH_2F_2	1.96
OCS	0.72	SbH_3	0.12	CH_2Cl_2	1.62
NH_3	1.44	$SbCl_3$	3.9	CH_2Br_2	1.43

Dipole Moments

Molecule	(d)	Molecule	(d)	Molecule	(d)
$N(CH_3)_3$	0.64	$SbBr_3$	2.8	CHF_3	1.64
NF_3	0.234	SbI_3	1.58	$CHBr_3$	1.06
NO	0.16	KF	8.62	$CHCl_3$	1.05
N_2O	0.17	KCl	10.6	CHF_2Cl	1.40
O_3	0.52	KBr	10.85	$CHCl_2F$	1.29
FCl	0.88	KI	11.05	CF_2Cl_2	0.51
FBr	1.29	$RbBr$	10	CF_2Br_2	0.66
$BrCl$	0.57	CsF	7.9	$CFCl_3$	0.45
ICl	0.65	$CsCl$	10.46	CF_3Cl	0.46
$ClCN$	2.80	CsI	12.1	CF_3Br	0.65
SO_2	1.61	$HCHO$	2.27	CF_3I	0.92
PH_3	0.55	CH_3F	1.81	$CH_3.CH_2.F$	1.92
$CH_3.CH_2.Cl$	2.05	$n-C_3H_7I$	1.97	$H_2C=CHBr$	1.41
$CH_3.CH_2.Br$	2.01	$n-C_3H_7CN$	4.05	$H_2C=CHI$	1.26
$CH_3.CH_2.I$	1.87	$n-C_3H_7NO_2$	3.58	$H_2C=CHCN$	3.88
$CH_3.CH_2.CN$	4.04	$n-C_3H_7OH$	1.66	$H_2C=CH.CHO$	3.04
$CH_3.CH_2.NO_2$	3.58	$n-C_3H_7CHO$	2.72	$H_2C=CH.CH_3$	0.35
$CH_3.CH_2.NH_2$	0.99	$iso-C_3H_7Cl$	2.15	$H_2C=CH.CH_2Cl$	2.01
$CH_3.CH_2.OH$	1.67	$iso-C_3H_7Br$	2.19	$H_3C.HC=CHCl(cis)$	1.71
$CH_3.CH_2.CHO$	2.73	$iso-C_3H_7NO_2$	3.37	$H_3C.HC=CHCl(trans)$	1.91
$CH_3.CH.F_2$	2.24	$iso-C_3H_7OH$	1.65	$H_3C.HC=CHCN(trans)$	4.50
$CH_3.CH.Cl_2$	2.07	$(CH_3)_2CCl_2$	2.25	$H_3C.HC=CHO(trans)$	3.67
$(CH_3)_2O$	1.29	$n-C_4H_9Cl$	2.11	$H_3C\equiv C.Cl$	0.44
$CH_3.CF_3$	2.35	$n-C_4H_9Br$	2.15	$H_3C\equiv C.Br$	0
$CH_3.CF_2Cl$	2.14	$n-C_4H_9I$	2.08	$H_3C\equiv C-CH_3$	0.20
$CH_3.CCl_3$	1.78	$n-C_4H_9CN$	4.09	C_6H_5F	1.57
$CHCl_2.CCl_3$	0.92	$n-C_4H_9NO_2$	3.35	C_6H_5Cl	1.70
$CHF_2.CF_3$	1.54	$n-C_4H_9OH$	1.63	C_6H_5Br	1.71
$CF_3.CF_2Cl$	0.52	$sec-C_4H_9Cl$	2.12	C_6H_5CN	4.39
$(CH_3)_2CO$	2.85-3.02	$iso-C_4H_9Cl$	2.04	$C_6H_5NH_2$	1.48
$n-C_3H_7Cl$	2.10	$tert-C_4H_9Cl$	2.13	$C_6H_5NO_2$	4.20
$n-C_3H_7Br$	2.15	$H_2C=CHCl$	1.44	$C_6H_5CH_3$	0.37

* Bond Moments and Group Moments #

Bond	$(d)^{(a)}$	Bond/Group	$(d)^{(a)}$	Angle between μ and bond axis $C \overset{\alpha}{\rightarrow} X$
$O-H^{(b)}$	1.5; (1.5)	$C-F^{(c)}$	1.57	
$S-H^{(b)}$	0.7; (0.7)	$C-Cl^{(c)}$	1.69	
$N-H^{(b)}$	1.3; (1.3)	$C-Br^{(c)}$	1.71	
$P-H^{(b)}$	0.4; (0.4)	$C-I^{(c)}$	1.7	
$C-N^{(b)}$	0.45	$C-NO_2$	4.23	$0°$
$C-P^{(b)}$	1.4; (2.1)	$C-NH_2^{(c)}$	1.48	$142°$
$C-Cl^{(b)}$	1.5; (2.3)	$C-CN^{(c)}$	4.39	$0°$
$C-Br^{(b)}$	1.5; (2.2)	$C-CH_3^{(c)}$	0.37	$180°$
$C-I^{(b)}$	1.3; (2.0)	$C-CF_3^{(c)}$	2.86	$0°$
$N-O^{(b)}$	0.5; (0.5)	$C-OH^{(c)}$	1.40	$62°$
$C=O^{(b)}$	2.4; (3.1)	$C-OCH_3^{(c)}$	1.32	$57°$
$C-O^{(b)}$(alcohols)	1.0; (1.7)	$C-CHO^{(c)}$	(3.1)	$55°$
$C-O^{(b)}$(ethers)	0.8; (1.5)			

\# These values are necessarily of an approximate nature.

(a) Values calculated with C^--H^+ bond moment of 0.4d; values in parentheses are those corresponding to C^+-H^- bond moment of 0.3d.

(b) Values in aliphatic molecules.

(c) Values in aromatic molecules.

* Polarizability: $\vec{\mu}$(induced) $= \underline{\underline{\alpha}} . \vec{E}$; $\underline{\underline{\alpha}}$ = polarizability tensor; μ(induced) = induced electric dipole moment; $\vec{E}$ = intensity of electric field. Polarizability tensor in the general form is as follows.

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

In the principal axis system

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

For free atoms and their ions $\underline{\underline{\alpha}}$ is isotropic. However, for molecules $\underline{\underline{\alpha}}$ may by anisotropic. We refer to average polarizability as $(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 = \alpha$. Notation $\alpha_{xx} = \alpha_1$; $\alpha_{yy} = \alpha_2$; $\alpha_{zz} = \alpha_3$.

α_1 is generally along the molecular symmetry axis while α_2 and α_3 are perpendicular to it. For a tetrahedrally symmetric or spherically symmetric molecule $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$. For molecules with $\alpha_2 = \alpha_3$, the following notation is also used: $\alpha_1 = \alpha_{||}$; $\alpha_2 = \alpha_3 = \alpha_\perp$.

The <u>Lorents-Lorenz</u> relation is usually employed for obtaining polarisability values from molar (atomic) refraction data

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \frac{4}{3}\pi N \alpha = 2.54 \times 10^{24} \alpha$$

n = refractive index; M = mol. (at.) wt.; d = density and N = Avogadro number. The refractive index values are those extrapolated to very large wave lengths. (For further details refer: Stuart, "Molekulstruktur", Springer Verlag, Berlin, 1934.)

* <u>Polarizability of Some Atoms</u> (values in units 10^{-24} cc)

Atom	H	He	Li	Ne	Ar	K	Kr	I	Xe	Cs
α	0.67	0.20	12	0.40	1.66	34	2.54	4.96	4.15	42

* <u>Polarizability of Some Ions</u> (values in units of 10^{-24} cc)

Ion	H^-	Li^+	Be^{2+}	O^{2-}	F^-	Na^+	Mg^{2+}	S^{2-}	Cl^-	K^+	Ca^{2+}	Se^{2-}
α	10.18	0.03	0.008	2.74	0.96	0.19	0.10	8.94	3.60	0.89	0.55	11.4

Ion	Br^-	Rb^+	Sr^{2+}	Te^{2-}	I^-	Cs^+	Ba^{2+}
α	5.0	1.50	1.02	16.1	7.60	2.60	1.86

* <u>Molecular Polarisabilities</u> (units: 10^{-24} cc)

Molecule	α	α_1	α_2	α_3
H_2	0.79	0.93	0.71	0.71
HF	2.46	-	-	-
HCl	2.63	3.13	2.39	2.39
HBr	3.61	4.22	3.31	3.31
HI	5.44	6.58	4.89	4.89
HCN	2.59	3.92	1.92	1.92
N_2	1.76	2.38	1.45	1.45
O_2	1.60	2.35	1.21	1.21
Cl_2	4.61	6.60	3.62	3.62
CO	1.95	2.60	1.625	1.625
CO_2	2.65	4.10	1.93	1.93

Molecule	α	α_1	α_2	α_3
SO_2	3.72	5.49	2.72	3.49
H_2S	3.78	4.04	3.44	4.01
CS_2	8.74	15.14	5.54	5.54
NH_3	2.26	2.42	2.18	2.18
CH_4	2.60	2.60	2.60	2.60
C_2H_6	4.47	5.48	3.97	3.97
C_3H_8	6.29	5.01	6.93	6.93
$H_2C=CH_2$	4.26	5.61	3.59	3.59
$HC≡CH$	3.33	5.12	2.43	2.43
C_6H_6 (Benzene)	10.32	6.35	12.31	12.31
CH_3Cl	4.56	5.42	4.14	4.14
CH_2Cl_2	6.48	5.02	8.47	5.96
$CHCl_3$	8.23	6.68	9.01	9.01
CCl_4	10.5	10.5	10.5	10.5
$SnCl_4$	13.77	13.77	13.77	13.77

* Bond Polarizabilities

Bond Polarizability tensor - γ

Bond axis - x; y and z axes perpendicular to the bond axis; Longitudinal polarizability γ_{xx}; Transverse polarizabilities γ_{yy} and γ_{zz}; (units: 10^{-24}cc).

Bond	γ_{xx}	$\gamma_{yy}=\gamma_{zz}$
C-H	0.79	0.58
C-C	1.88	0.02
$C_{ar}-C_{ar}$	2.25	0.48
C=C	2.86	1.06
C≡C	3.54	1.27
C-N	0.86	-
C≡N	3.1	1.4
C-O	0.84	-
C=O	1.99	0.75
C-P	0.96	-
C=S	7.57	2.77
C-Cl	3.67	2.08
C-Br	5.04	2.88

Bond	γ_{xx}	$\gamma_{yy} = \gamma_{zz}$
C-I	8.09	-
N-H	0.58	0.84
N≡N	2.43	1.43
S-H	2.30	1.72

An estimate of γ_{xx} can be obtained from the approximate relation $\gamma_{xx} = 1.4\,\overline{\gamma}$ where $\overline{\gamma}$ is the mean polarizability of a bond: $\overline{\gamma} = (\gamma_{xx} + \gamma_{yy} + \gamma_{zz})/3$. $\overline{\gamma}$ values may be obtained from refractivity data of various molecules. The molecular polarizability is assumed to be a sum of bond contributions and thus the bond polarizabilities can be obtained. For additional details see Denbigh, Trans. Faraday Soc., 36, 936 (1940).

IV. 6. Molecular Structure

IV.6.A. Directed Hybrid Orbitals

* ### Some Equivalent Hybrid Orbitals Using s, p and d Orbitals

Digonal (sp)

$$\Psi_1(\text{digonal}) = \frac{1}{\sqrt{2}}\,\varphi_s + \frac{1}{\sqrt{2}}\varphi_{p_x}$$

$$\Psi_2(\text{digonal}) = \frac{1}{\sqrt{2}}\,\varphi_s - \frac{1}{\sqrt{2}}\varphi_{p_x}$$

Digonal Hybrid

Trigonal Hybrid
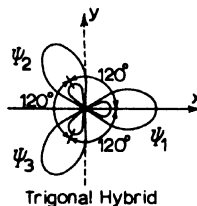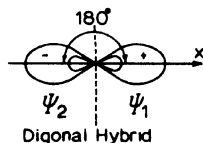
Trigonal (sp²)

$$\Psi_1(\text{trigonal}) = \frac{1}{\sqrt{3}}\,\varphi_s + \frac{\sqrt{2}}{\sqrt{3}}\,\varphi_{p_x}$$

$$\Psi_2(\text{trigonal}) = \frac{1}{\sqrt{3}}\,\varphi_s - \frac{1}{\sqrt{6}}\,\varphi_{p_x} + \frac{1}{\sqrt{2}}\varphi_{p_y}$$

$$\Psi_3(\text{trigonal}) = \frac{1}{\sqrt{3}}\,\varphi_s - \frac{1}{\sqrt{6}}\,\varphi_{p_x} - \frac{1}{\sqrt{2}}\varphi_{p_y}$$

Tetrahedral (sp^3)

$$\Psi_1(\text{tetrahedral}) = \tfrac{1}{2}\varphi_s + \tfrac{\sqrt{3}}{2}\varphi_{p_x}$$

$$\Psi_2(\quad " \quad) = \tfrac{1}{2}\varphi_s - \tfrac{1}{2\sqrt{3}}\varphi_{p_x} + \tfrac{\sqrt{2}}{\sqrt{3}}\varphi_{p_z}$$

$$\Psi_3(\quad " \quad) = \tfrac{1}{2}\varphi_s - \tfrac{1}{2\sqrt{3}}\varphi_{p_x} + \tfrac{1}{2}\varphi_{p_y} - \tfrac{1}{\sqrt{6}}\varphi_{p_z}$$

$$\Psi_4(\quad " \quad) = \tfrac{1}{2}\varphi_s - \tfrac{1}{2\sqrt{3}}\varphi_{p_x} - \tfrac{1}{\sqrt{2}}\varphi_{p_y} - \tfrac{1}{\sqrt{6}}\varphi_{p_z}$$

The four hybrids are directed towards the corners of a regular tetrahederon from the body center where the nucleus for the atomic orbitals is located. All the angles between hybrid orbitals equal 109°28′

Octahedral (d^{2}sp^3)

$$\Psi_1(\text{octahedral}) = \tfrac{1}{\sqrt{6}}\varphi_s + \tfrac{1}{\sqrt{2}}\varphi_{p_z} + \tfrac{1}{\sqrt{3}}\varphi_{d_{z^2}}$$

$$\Psi_2(\quad " \quad) = \tfrac{1}{\sqrt{6}}\varphi_s - \tfrac{1}{\sqrt{2}}\varphi_{p_z} + \tfrac{1}{\sqrt{3}}\varphi_{d_{z^2}}$$

$$\Psi_3(\quad " \quad) = \tfrac{1}{\sqrt{6}}\varphi_s + \tfrac{1}{\sqrt{2}}\varphi_{p_x} + \tfrac{1}{\sqrt{12}}\varphi_{d_{z^2}} + \tfrac{1}{2}\varphi_{d_{x^2-y^2}}$$

$$\Psi_4(\quad " \quad) = \tfrac{1}{\sqrt{6}}\varphi_s - \tfrac{1}{\sqrt{2}}\varphi_{p_x} + \tfrac{1}{\sqrt{12}}\varphi_{d_{z^2}} + \tfrac{1}{2}\varphi_{d_{x^2-y^2}}$$

$$\Psi_5(\quad " \quad) = \tfrac{1}{\sqrt{6}}\varphi_s + \tfrac{1}{\sqrt{2}}\varphi_{p_y} + \tfrac{1}{\sqrt{12}}\varphi_{d_{z^2}} - \tfrac{1}{2}\varphi_{d_{x^2-y^2}}$$

$$\Psi_6(\quad " \quad) = \tfrac{1}{\sqrt{6}}\varphi_s - \tfrac{1}{\sqrt{2}}\varphi_{p_y} + \tfrac{1}{\sqrt{12}}\varphi_{d_{z^2}} - \tfrac{1}{2}\varphi_{d_{x^2-y^2}}.$$

The six hybrids are directed towards the corners of a regular octahedron with the nucleus containing the atomic orbitals at the body center.

Square (dsp^2)

$$\Psi_1(\text{Square}) = \tfrac{1}{2}\varphi_s + \tfrac{1}{\sqrt{2}}\varphi_{p_x} + \tfrac{1}{2}\varphi_{d_{xy}}$$

$$\Psi_2(\quad " \quad) = \tfrac{1}{2}\varphi_s - \tfrac{1}{\sqrt{2}}\varphi_{p_x} + \tfrac{1}{2}\varphi_{d_{xy}}$$

$$\Psi_3(\quad " \quad) = \tfrac{1}{2}\varphi_s + \tfrac{1}{\sqrt{2}}\varphi_{p_y} - \tfrac{1}{2}\varphi_{d_{xy}}$$

$$\Psi_4(\quad " \quad) = \tfrac{1}{2}\varphi_s - \tfrac{1}{\sqrt{2}}\varphi_{p_y} - \tfrac{1}{2}\varphi_{d_{xy}}$$

All the four hybrids lie in a plane and are directed towards the four corners of a square with the nucleus containing the atomic orbitals at the center.

Shapes of sp and sp^2-hybrids.

Ψ_2 Ψ_1
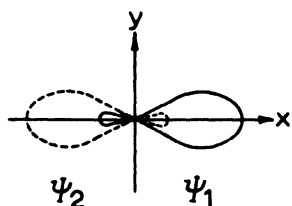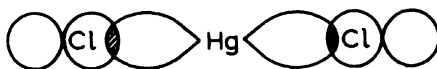
sp-hybrids

HgCl$_2$: sp-hybrids on Hg
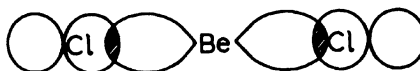
BeCl$_2$: sp-hybrid on Be
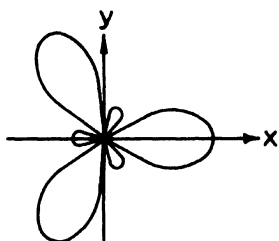
sp^2- hybrids
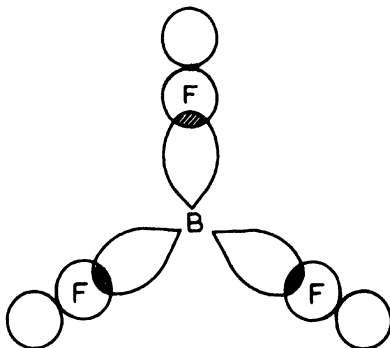
BF$_3$: sp^2- hybrids on B
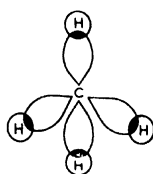
P 239

CH$_4$ sp^3-hybrids on C
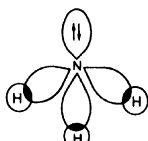
NH$_3$ sp^3 hybrids on N with
a lone-pair of electrons
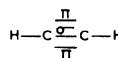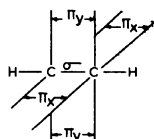
Acetylene Two π bonds due to overlap of
p$_x$ and p$_y$ orbitals on C

Two lone-pair
orbitals
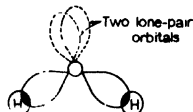
H$_2$O sp^3-hybrids on O with two lone-
pair orbitals
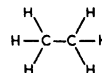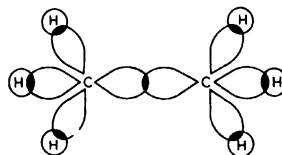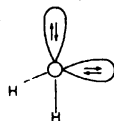
Ethane sp^3 hybrids on both carbons
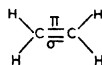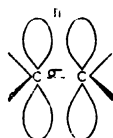
Ethylene π - bonding due to overlap of
p orbitals on carbon , the σ-bonds are
formed by sp^2 hybrids on C
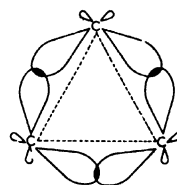
Cyclopropane Carbon-Carbon bonds
are "bent" bonds or T - bonds

* Atomic Orbitals Involved in σ and π Bonds for Various Arrangements Around a Central Atom

Coordination number	Arrangement of σ-orbitals	σ-Orbitals	Strong π-bond orbitals	Weak π-bond orbitals
2	Linear	sp,dp	p^2d^2	–
	Angular	$\Big(\ p^2$ $\Big(\ ds$	dp,d_2^2 dp,d^2	ds,d_2^2 sp,p^3,dp
3	Trigonal plane	$\big(\ sp^2,dp^2$ $\big(\ d^2s,d^3$	pd^2 pd^2	d^2 p^2
	Unsymmetrical plane	dsp	pd^2	pd,d^2
	Trigonal pyramid	$\big(\ p^3$ $\big(\ d^2p$	– –	d^4s,d^5 sp^2d^2,p^2d^3
4	Tetrahedral	$\big(\ sp^3$ $\big(\ d^3s$	d^2 d^2	d^3 p^3
	Irregular tetrahedron	$\big(\ d^2sp$ $\big(\ dp^3,d^3p$	– –	d s
	Tetragonal plane	dsp^2,d^2p^2	d^3p	–
	Tetragonal pyramid	d^4	d	sp,p^2
5	Bipyramid	$\big(\ dsp^3$ $\big(\ d^3sp$	d^2 d^2	d^2 p^2
	Tetragonal bipyramid	$\big(\ d^2sp^2$ $\big(\ d^4s$ $\big(\ d^2p^3$ $\big(\ d^4p$	d d d d	pd^2 p^3 sd^2 sp^2
	Pentagonal pyramid	d^5	–	sp^2,p^3
	Pentagonal plane	d^3p^2	pd^2	–
6	Octahedron	d^2sp^3	d^3	–
	Trigonal prism	$\big(\ d^4sp$ $\big(\ d^5p$	– –	p^2d p^2s
	Trigonal antiprism	d^3p^3	–	sd
7	Octahedron (face centered with central atom at body center)	$\big(\ d^3sp^3$ $\big(\ d^5sp$	– –	d^2 p^2
	Trigonal prism (with extra atom at center of one square face)	$\big(\ d^4sp^2$ $\big(\ d^4sp^3$ $\big(\ d^5p^2$	– – –	dp ds ps

Atomic Orbitals Involved in σ and π Bonds   (contd.)

Coord. No.	Arrangement of σ- -orbitals	σ- Orbitals	Strong π- bond orbitals	Weak π-bond orbitals
8	Dodecahedron	d^4sp^3	d	-
↕	Antiprism	d^5p^3	-	s
	Face-centered prism (with only two square faces occupied)	d^5sp^2	p	-

For further details refer: Van Vleck and Sherman, Rev. Mod. Phys. **7**, 174
                          (1935); Kimball, J. Chem. Phys. **8**, 188 (1940)

IV.6.B. <u>Shapes of Some Molecules and Ions</u>   (See illustrations on page 243)

      a) <u>Linear</u>:   Example: $HgCl_2$; other examples: OCO, SCS, HCN,

                    ClHgHgCl, HCCH, NCCN, NNO, $\left[I_3\right]^-$, $\left[N_3\right]^-$

     b) <u>Bent</u>:   Example: H_2O; Other examples are listed below:

Molecule	Bond Angle (α)	Molecule	Bond Angle (α)
ONO	134°18'	HSH	93°18'
ONCl	125°	OSO	119°30'
HOH	104°30'	ClSCl	100°18'
O_3	116°50'	OClO	116°30'
FOF	100°	$\left[OClO\right]^-$	110°30'
ClOCl	115°	HSeH	91°
$(CH_3)O(CH_3)$	111°		

      c) <u>Pyramidal</u>   Example: NH_3; Other examples are listed below.

Molecule	Bond angle (α)	Molecule	Bond angle (α)
NH_3	107°18'	$\left[SO_3\right]^{2-}$	111°
$N(CH_3)_3$	180°	$\left[ClO_3\right]^-$	107°
NF_3	102°6'	ClF_3	89°
PH_3	93°18'	AsF_3	102°
$P(CH_3)_3$	100°	$AsCl_3$	98°24'
PF_3	104°	$SbCl_3$	99°30'
PCl_3	101°	$SbBr_3$	96°
PBr_3	100°	$BiCl_3$	100°
PI_3	98°	$BiBr_3$	100°

d) <u>Trigonal-planar</u> Example: BF_3 ; other examples:

BCl_3, BBr_3, [structure: O=C with H, H], Br [structure: O=C with Br, Br], F [structure: O=C with F, F], $\left[CO_3\right]^{2-}$, $\left[NO_3\right]^{-}$.
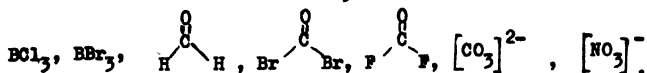
e) 'T-shaped': Examples: ClF_3, BrF_3

f) <u>Tetrahedral</u> Example: CH_4

Other examples: $\left[BeF_4\right]^{2-}$, $\left[BH_4\right]^{-}$, $\left[BF_4\right]^{-}$, CF_4, CCl_4, CBr_4, CI_4, $\left[NH_4\right]^{+}$,

$\left[AlCl_4\right]^{-}$, SiH_4, SiF_4, $SiCl_4$, $SiBr_4$, SiI_4, $\left[PH_4\right]^{+}$, $\left[H_2PO_2\right]^{-}$, $\left[HPO_3\right]^{2-}$,

$\left[PO_4\right]^{3-}$ $POCl_3$, $\left[PCl_4\right]^{+}$, $\left[SO_4\right]^{2-}$, $\left[ClO_4\right]^{2-}$, $TiBr_4$, $\left[CrO_4\right]^{-}$, $Ni(CO)_4$, $TiCl_4$,

$\left[Cu(CN)_4\right]^{3-}$, $\left[Zn(CN)_4\right]^{2-}$, $\left[AsO_4\right]^{3-}$, $\left[SeO_4\right]^{2-}$, $ZrCl_4$, $SnCl_4$, $SnBr_4$,

SnI_4, $\left[IO_4\right]^{-}$, $PbCl_4$.
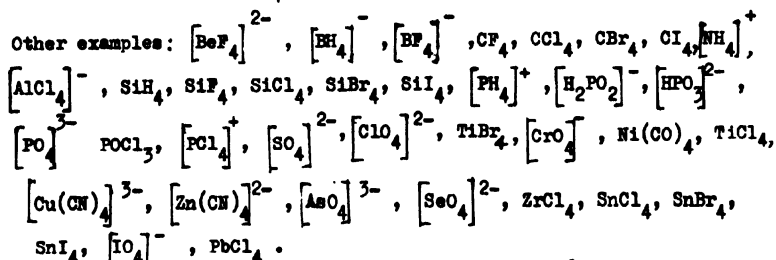
g) <u>Square</u>: Example: XeF_4; Other examples: $\left[Ni(CN_4)_4\right]^{2-}$, $\left[BrF_4\right]^{-}$,

$\left[PdCl_4\right]^{2-}$, $\left[ICl_4\right]^{-}$, $\left[Pt(NH_3)_4\right]^{2-}$, $\left[AuCl_4\right]^{-}$.

h) <u>Square pyramid</u>: Example: BrF_5; Other examples: IF_5, $\left[SbF_5\right]^{2-}$.

i) <u>Trigonal bipyramid</u>: Example: PCl_5; other examples: PF_5, AsF_5, $SbCl_5$.

j) <u>Octahedral</u>: Example: SF_6; other examples: $\left[BiCl_6\right]^{-}$, $\left[PF_6\right]^{-}$, $\left[PCl_6\right]^{-}$,

$\left[AsF_6\right]^{-}$, SoF_6, MoF_6, $\left[SbCl_6\right]^{-}$, TeF_6, WCl_6, UF_6.

Several metal complexes with coordination number 6 for the metal
atom exhibit octahedral arrangement.

k) <u>Pentagonal-bipyramid</u>: Example: IF_7; other examples: $\left[ZrF_7\right]^{3-}$,

$\left[UF_7\right]^{3-}$, $\left[UO_2F_5\right]^{3-}$.

l) <u>Dodecahedral</u> Example: $\left[MO(CN)_8\right]^{4-}$ (The eight CN groups are arranged
                                                    around MO as shown in the
                                                    accompanying figure.)

m) <u>Square-antiprismatic</u>: <u>Example</u>: $\left[TaF_8\right]^{3-}$

n) "Sandwich" structure: Example: (C_5H_5) Fe (C_5H_5) (Ferrocene)

<u>Bibliography</u>: For data on inter-bond distances and angles for various
molecules see:

Robertson, "Organic Crystals and Molecular Structure", Cornell Univ.
    Press, Ithaca, (1953).

(a) Linear   (b) Bent   (c) Pyramidal
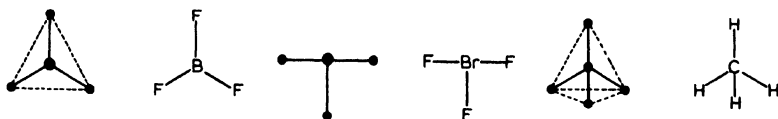
(d) Trigonal planar   (e) T-shaped   (f) Tetrahedral
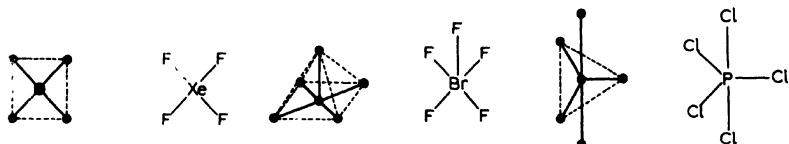
(g) Square   (h) Square pyramid   (i) Trigonal bipyramid
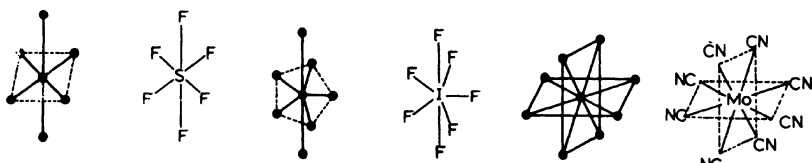
(j) Octahedral   (k) Pentagonal bipyramid   (l) Dodecahedral
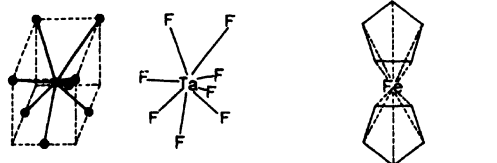
(m) Square-antiprismatic   (n) "Sandwich" structure

Sutton (Editor) "Tables of Inter-atomic Distances", Chem. Soc. Spl. Publ. (1958); see also "Supplement to Tables of Inter-atomic Distances (1964),

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IV.6.C. Symmetry Point Groups and Character Tables

E = identity operation

C_n = rotation about an axis of symmetry through an angle $2\pi/n$.

C_2', C_2'' = rotation through 180° about the two axes perpendicular to C_n.

σ_v = reflection in a plane of symmetry which contains the principal axis, i.e. the axis which has the largest n value in C_n.

σ_d = reflection in a plane of symmetry which contains the principal axis, and which bisects the angle between C_2' and C_2''.

σ_h = reflection in a plane perpendicular to the principal axis.

i = inversion in a center of symmetry

S_n = rotation about an axis by $2\pi/n$ followed by reflection in a plane perpendicular to the axis of rotation.

(Note: $\sigma_d^2 = \sigma_d \cdot \sigma_d$; $C_n^3 = C_n \cdot C_n \cdot C_n$ etc.)

A large number of problems in physics and chemistry require the use of character tables to simplify their solution. Perhaps the most common use is in finding the number of various irreducible representations. The number of times (a_i) an irreducible representation occurs in a reducible representation is given by the formula

$$a_i = \frac{1}{h} \sum_R \chi_i (R) \chi (R)$$

where $\chi_i (R)$ is the character for the operation R in the irreducible representation Γ_i; $\chi(R)$ the corresponding character in the reducible representation and h is the order of the group. The order of the group is easily found from the tables since $\sum_i \left[\chi_i (E)\right]^2 = h$. The sum is performed over all the irreducible representations.

The following character tables give information concerning the irreducible representations of the rotational (R) and translational (T) coordinates in addition to the x, y, z coordinates. This information can be used in classifying infrared, Raman or electronic transitions also. The symbols for the various irreducible representations appear in the first column while the top left refers to the point group symmetry.

* Character Tables for Some Symmetry Point Groups

1. C_s, C_i and C_n (n = 1,2,3,4,5,6) Groups

1. C_s, C_i and C_n (n = 1,2,3,4,5,6) Groups

$C_s \equiv C_{1h}$	E	σ_h		
A'	1	1	T_x, T_y, R_z	x^2, y^2, z^2, xy
A"	1	-1	T_z, R_x, R_y	xz, yz

$C_i \equiv S_2$	E	i		
A_g	1	1	R_x, R_y, R_z	x^2, y^2, z^2, xy, xz, yz
A_u	1	-1	T_x, T_y, T_z	

C_1	E
A	1

C_2	E	C_2		
A	1	1	T_z, R_z	x^2, y^2, z^2, xy
B	1	-1	T_x, T_y, R_x, R_y	xz, yz

C_3	E	C_3	C_3^2			w = exp $(2\pi i/3)$
A	1	1	1	T_z, R_z		$x^2+y^2+z^2$
E	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} w \\ w^2 \end{matrix}$	$\begin{matrix} w^2 \\ w \end{matrix}$	$(T_x, T_y)(R_x, R_y)$		$(x^2-y^2, xy)(xz, yz)$

C_4	E	C_2	C_4	C_4^3		
A	1	1	1	1	T_z, R_z	x^2+y^2, z^2
B	1	1	-1	-1		x^2-y^2, xy
E	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} -1 \\ -1 \end{matrix}$	$\begin{matrix} i \\ -i \end{matrix}$	$\begin{matrix} -i \\ i \end{matrix}$	$(T_x, T_y)(R_x, R_y)$	(xz, yz)

C_5	E	C_5	C_5^2	C_5^3	C_5^4		w=exp $(2\pi i/5)$
A	1	1	1	1	1	T_z, R_z	x^2+y^2, z^2
E'	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} w \\ w^4 \end{matrix}$	$\begin{matrix} w^2 \\ w^3 \end{matrix}$	$\begin{matrix} w^3 \\ w^2 \end{matrix}$	$\begin{matrix} w^4 \\ w \end{matrix}$	$(T_x, T_y)(R_x, R_y)$	(xz, yz)
E"	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} w^2 \\ w^3 \end{matrix}$	$\begin{matrix} w^4 \\ w \end{matrix}$	$\begin{matrix} w \\ w^4 \end{matrix}$	$\begin{matrix} w^3 \\ w^2 \end{matrix}$		(x^2-y^2, xy)

1'. C_s, C_i and C_n (n= 1,2,3,4,5,6) Groups (contd.)

C_6	E	C_6	C_3	C_2	C^2	C_6^5			w=exp($2\pi i/6$)
A	1	1	1	1	1	1	T_z, R_z		x^2+y^2, z^2
B	1	-1	1	-1	1	-1			
E'	$\begin{cases}1 \\ 1\end{cases}$	$\begin{matrix}w \\ w^5\end{matrix}$	$\begin{matrix}w^2 \\ w^4\end{matrix}$	$\begin{matrix}w^3 \\ w^3\end{matrix}$	$\begin{matrix}w^4 \\ w^2\end{matrix}$	$\begin{matrix}w^5 \\ w\end{matrix}$	(T_x,T_y) (R_x,R_y)		(xz, yz)
E"	$\begin{cases}1 \\ 1\end{cases}$	$\begin{matrix}w^2 \\ w^4\end{matrix}$	$\begin{matrix}w^4 \\ w^2\end{matrix}$	$\begin{matrix}1 \\ 1\end{matrix}$	$\begin{matrix}w^2 \\ w^4\end{matrix}$	$\begin{matrix}w^4 \\ w^2\end{matrix}$			(x^2-y^2, xy)

2. C_{nv}(n = 2, 3, 4, 5, 6) Groups

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	T_z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	T_x, R_y	xz
B_2	1	-1	-1	1	T_y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	T_z	x^2+y^2, z^2
A_2	1	1	-1	R_z	(x^2-y^2, xy)
E	2	-1	0	$(T_x,T_y)(R_x,R_y)$	(xz, yz)

C_{4v}	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	1	-1	1	-1		x^2-y^2
B_2	1	1	-1	-1	1		xy
E	2	-2	0	0	0	$(T_x,T_y)(R_x,R_y)$	(xz, yz)

2. C_{nv} (n = 2,3,4,5,6) Groups (contd.)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$		
A_1	1	1	1	1	T_z	x^2+y^2, z^2
A_2	1	1	1	-1	R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(T_x,T_y)(R_x,R_y)$	(xz, yz)
E_2	2	2 cos 144°	2 cos 72°	0		(x^2-y^2, xy)

C_{6v}	E	C_2	$2C_3$	$2C_6$	$3\sigma_6$	$3\sigma_v$		
A_1	1	1	1	1	1	1	T_z	x^2+y^2, z^2
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	-1	1		
B_2	1	-1	1	-1	1	-1		
E_1	2	-2	-1	1	0	0	$(T_x,T_y)(R_x,R_y)$	(xz, yz)
E_2	2	2	-1	-1	0	0		(x^2-y^2, xy)

3. C_{nh} (n = 1,2,3,4,5,6) Groups

$C_{1h} \equiv C_s$

C_{2h}	E	C_2	σ_h	i		
A_g	1	1	1	1	R_{zz}	x^2, y^2, z^2, xy
A_u	1	1	-1	-1	T_z	
B_g	1	-1	-1	1	R_x, R_y	xz, yz
B_u	1	-1	1	-1	T_x, T_y	

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5		$w = exp(2\pi i/3)$
A'	1	1	1	1	1	1	R_z	$x^2 + y^2$, z^2
A''	1	1	1	-1	-1	-1	T_z	
E'	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} w \\ w^2 \end{matrix}$	$\begin{matrix} w^2 \\ w \end{matrix}$	$\begin{matrix} 1 \\ 1 \end{matrix}$	$\begin{matrix} w \\ w^2 \end{matrix}$	$\begin{matrix} w^2 \\ w \end{matrix}$	(T_x,T_y)	(x^2-y^2, xy)
E''	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} w \\ w^2 \end{matrix}$	$\begin{matrix} w^2 \\ w \end{matrix}$	$\begin{matrix} -1 \\ -1 \end{matrix}$	$\begin{matrix} -w \\ -w^2 \end{matrix}$	$\begin{matrix} -w^2 \\ -w \end{matrix}$	(R_x,R_y)	(xz, yz)

$C_{4h} = C_4 \times i$; $C_{5h} = C_5 \times \sigma_h$; $C_{6h} = C_6 \times i$

4. <u>S_n (n = 2, 4, 6) Groups</u>

   $S_2 \equiv C_i$

S_4	E	C_2	S_4	S_4^3		
A	1	1	1	1	R_z	x^2+y^2, z^2
B	1	1	-1	-1	T_z	
E	$\begin{cases} 1 \\ 1 \end{cases}$	$\begin{matrix} -1 \\ -1 \end{matrix}$	$\begin{matrix} i \\ -1 \end{matrix}$	$\begin{matrix} -1 \\ i \end{matrix}$	$(T_x,T_y)(R_x,R_y)$	(xz, yz) (x^2-y^2, xy)

   $S_6 = C_3 \times i$.

5. <u>D_n (n = 2,3,4,5,6) Groups</u>

$D_2 \equiv$ V	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A_1	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	T_z, R_z	xy
B_2	1	-1	1	-1	T_y, R_y	xz
B_3	1	-1	-1	1	T_x, R_x	yz

D_3	E	$2C_3$	$3C_2'$		
A_1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	T_z, R_z	
E	2	-1	0	$(T_x,T_y)(R_x,R_y)$	$(xz, yz)(x^2-y^2,xy)$

D_4	E	C_2	$2C_4$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	T_z, R_z	
B_1	1	1	-1	1	-1		
B_2	1	1	-1	-1	1		
E	2	-2	0	0	0	$(T_x,T_y)(R_x,R_y)$	$(xz, yz)(x^2-y^2,xy)$

5. D_n (n = 2,3,4,5,6) Groups (contd.)

D_5	E	$2C_5$	$2C_5^2$	$5C_2$		
A_1	1	1	1	1		x^2+y^2 , z^2
A_2	1	1	1	-1	T_z, R_z	
E_1	2	2 cos 72°	2 cos 144°	0	$(T_x,T_y)(R_x,R_y)$	$(xz,\ yz)$
E_2	2	2 cos 144°	2 cos 72°	0		$(x^2-y^2,\ xy)$

D_6	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$		
A_1	1	1	1	1	1	1		x^2+y^2 , z^2
A_2	1	1	1	1	-1	-1	T_z, R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	-2	-1	1	0	0	$(T_x,T_y)(R_xR_y)$	$(xz,\ yz)$
E_2	2	2	-1	-1	0	0		(x^2-y^2,xy)

6. $\underline{D_{nd}}$ (n = 2,3) Groups

D_{2d}	E	C_2	$2S_4$	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		x^2+y^2 , z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	1	-1	1	-1		$x^2 - y^2$
B_2	1	1	-1	-1	1	T_z	xy
E	2	-2	0	0	0	$(T_x,T_y)(R_x,R_y)$	$(xz,\ yz)$

$D_{3d} = D_3 \times i$

7. $\underline{D_{nh}}$ (n = 2,3,4,5,6) Groups

$D_{2h} = D_2 \times i$; $D_{3h} = D_3 \times \sigma_h$; $D_{4h} = D_4 \times i$; $D_{5h} = D_5 \times \sigma_h$; $D_{6h} = D_6 \times i$

8. Cubic Groups

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2,x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x,R_y,R_z)	
T_2	3	0	-1	-1	1	(T_x,T_y,T_z)	

8. Cubic Goups (contd.)

O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2,\ x^2-y^2)$
T_1	3	0	-1	1	-1	(T_x,T_y,T_z)	
						(R_x,R_y,R_z)	
T_2	3	0	-1	-1	1		$(xy,\ xz,\ yz)$

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	-1	1		
E_g	2	-1	2	0	0	2	-1	2	0	0		$(2z^2-x^2-y^2,x^2-y^2)$
E_u	2	-1	2	0	0	-2	1	-2	0	0		
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x,R_y,R_z)	
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		$(xy,\ xz,\ yz)$
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(T_x,T_y,T_z)	
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

9. $C_{\infty v}$ and $D_{\infty h}$ Groups

$C_{\infty v}$	E	$2C_\varphi$	.....	$\infty\sigma_v$			
A_1	1	1	....	1	T_z		$x^2+y^2+z^2$
A_2	1	1	....	-1	R_z		
E_1	2	$2\cos\varphi$	....	0	$(T_x,T_y);(R_x,R_y)$	$(xz,\ yz)$	$(x^2-y^2,\ xy)$
E_2	2	$2\cos 2\varphi$	..	0			
..	..		...	. ...			

$D_{\infty h}$	E	$2C_\varphi$	...	∞_v	i	$2S_\varphi$	...	∞C_2		
A_{1g}	1	1	....	1	1	1	.....	1		$x^2+y^2;\ z^2$
A_{2g}	1	1	....	-1	1	1	.....-1		R_z	
E_{1g}	2	$2\cos\varphi$	.....	0	2	$-2\cos\varphi$	. 0		(R_x,R_y)	$(zz,\ yz)$
E_{2g}	2	$2\cos 2\varphi$	...	0	2	$2\cos 2\varphi$	.0			$(x^2-y^2,\ xy)$
...	..	...	....							
A_{1u}	1	1	......	1	-1	-1	.....-1		T_z	

9. $C_{\infty v}$ and $D_{\infty h}$ Groups   (contd.)

$D_{\infty h}$	E	$2C_\varphi$	...	∞_v	i	$2S_\varphi$	...∞C_2		
A_{2u}	1	1	...	-1	-1	-1	... -1		
E_{1u}	2	$2\cos\varphi$	...	0	-2	$2\cos\varphi$	... 0	(T_x, T_y)	
E_{2u}	2	$2\cos 2\varphi$	...	0	-2	$-2\cos 2\varphi$	... 0		
...	..	...	...	..	...	...	... .		

*   **Some Examples of Molecules Belonging to Various Symmetry Point Groups**

C_{2v} : H_2O, H_2S, SO_2 Cl$\diagdown$C=C$\diagup$Cl with H and H

C_{3v} : NH_3, CH_3Br, PCl_3

C_{2h} :   Cl$\diagdown$C=C$\diagup$H with H and Cl

D_{2d} : $H_2C=C=CH_2$ (allene)

D_{3d} :   "Staggered" form of ethane

D_{5d} :   Ferrocene

D_{3h} :   "eclipsed" form of ethane, PCl_5-(Trigonal bipyramid)

D_{4h} : $\left[AuCl_4\right]^-$ - (square)

D_{5h} :   Ruthenocene: $(C_5H_5)Ru(C_5H_5)$ (Pentagonal bipyramid)

D_{6h} :   Benzene (hexagonal)

T_d :   methane(tetrahedral)

O_h : SF_6(octahedral)

$C_{\infty v}$: CO_2, HCl,$HgCl_2$(linear)

$D_{\infty h}$: H_2, O_2, CO_2, H-C≡C-H (linear)

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IV.7. <u>Molecular Spectroscopy</u>

* <u>Introduction</u>: Molecules may absorb energy from electromagnetic
radiation of suitable frequency resulting in electronic excitation (visible
and ultraviolet) or molecular rotational/vibrational excitations (infrared
and microwave). The experimental arrangement for investigating such absorp-
tion phenomena consists of a source of radiation and a monochromator (in the
case of microwaves the sources themselves provide usually monochromatic
radiation) a sample cell containing the molecules under investigation and a
detector to measure the intensity of transmitted radiation. Radiation from
a source, after being scattered by the sample, can also be examined to yield
information on vibrational and rotational energy levels through changes in
the frequency of the scattered radiation (<u>Raman Effect</u>).Emission spectroscopy
in which the sample serves as the source, although not commonly employed,
is complementary to absorption studies.

Magnetic nuclei as well as unpaired electrons, if present in the
molecular system may give rise to <u>resonant absorption</u> of electromagnetic
radiation when the sample is placed in a magnetic field (<u>nuclear and electron
paramagnetic resonance</u>). The experimental set-up here consists of a source
for monochromatic radiation (generally in the radio frequency region), a
sample holder arrangement such that the sample can be placed in a uniform
magnetic field and simultaneously irradiated with the r.f. radiation and a
detector to measure the resonant power absorption by the sample. Nuclei
with quadrupole moments may be present in molecules and such nuclei in solids
resonantly absorb energy even without the presence of a magnetic field (<u>pure
quadrupole resonance</u>).

The wave-length of the radiation absorbed ranges from a few thousand
(10^3) cm^{-1} in the case of u.v. spectroscopy to a few hundredths (10^{-2}) cm^{-1}
in the case of nuclear-electron paramagnetic and pure quadrupole resonance.

IV.7.A <u>Visible and Ultraviolet Spectroscopy</u>

* <u>General</u>: Transitions between electronic energy levels in molecular
systems are of interest from the point of view of elucidation of their
structure and related properties. Such transitions $(\nu = E_2-E_1/h)$ usually
fall in the range 2000 Å – 8000 Å of the electromagnetic spectrum. Since
electronic transitions are very rapid compared with nuclear motions the
former occur generally without changes in internuclear distance. (<u>Franck-
Condon principle</u>). Under high resolution the vibrational structure in these
transitions can be seen and due to the operation of the Franck-Condon
principle the vibrational quantum numbers of the two levels between which
electronic transitions take place may differ.

The absorption spectrum is usually studied by monitoring the
intensities of the incident (I_0) and transmitted (I) radiation. If c is the
molar concentration of the absorbing species in a layer of thickness
(path length in cms) according to <u>Beer's law</u> Log $I_0/I= \epsilon$ lc = A where ϵ is
the absorptivity (molar extinction coefficient) and A is the absorbance.
(I/I_0) 100 is the <u>percentage transmittance</u>. A correlation can be made
between chemical structure and visible and u.v. spectra with the help of
λ max and ϵ max values for the various absorption maxima. Quantitative
analysis of a homogeneous mixture containing different absorbing species

can be also made.

* **Instrumentation**

Sources: Tungsten filament lamps (visible), hydrogen discharge
lamps (visible and u.v.), xenon discharge lamps (u.v.), mercury arcs (u.v.)

Monochromators: Glass prisms (visible), fused silica or quartz
prisms (visible and u.v.) or reflection gratings.

Detectors: Photocells or photomultipliers and barrier-layer
photovoltaic cells. Photoconductive cells permit operation down to 1μ
(near infrared). Conventional electronic amplification methods are used
to amplify photo signals. In recording instruments chopping or beam
switching produces periodically varying detector output which is synchronous-
ly detected and recorded.

Sample Preparation and Cells: Some of the solvents for the region
include heptane (or any saturated hydrocarbon), ethyl or methyl alcohol,
diethyl ether, dioxane, and water. Cells (cuvettes) are generally of 1cm
thickness and "effective thickness" (optical thickness) is changed by
changing concentration. For visible region cells made of glass and for
u.v. region cells made of quartz are employed. Solid samples can be examined
as thin films (cast or painted or evaporated), KBr pellets or "Nujol" mulls.
Reflectance studies are also made on solids. Weak bands and vibrational
structure studies are best carried out at low temperatures using specially
designed cells. Some well-known manufacturers of commercial u.v. and visible
spectrometers are: Adam-Hilger Ltd. (U.K.), Beckman Instruments Inc. (U.S.A.)
Carl Zeiss (East Germany), Coleman Instruments (U.S.A.), Applied Physics
Corp. (U.S.A.) and Perkin-Elmer Corpn.(U.S.A.) Since atmospheric oxygen
u.v. absorption starts $\sim$195mμ(Schumann-Range band system) most spectrometers
are limited to this wave length limit. In order to overcome this problem
the spectrometer system is best evacuated (vacuum u.v. spectroscopy).

* **Interpretation of Spectra**

Electronic transitions of molecules in the visible and u.v. region
can be classified as follows: σ-σ*, n-σ* , n-π* and π-π* (usual order of
decreasing energy). σ-σ* transitions for most hydrocarbons have $\lambda_{max}\sim$135m
In comparison, n-σ* transitions occur at longer wavelengths (ex: methyl
alcohol $\sim$183 mμ, ϵ_{max} 150). n-π* and π-π* transitions occur at compara-
tively longer wavelengths.

Schematic energy level diagram showing various electronic transitions

1 - σ - σ^* transition
2 - n - σ^* "
3 - π - π^* "
4 - n - π^* "
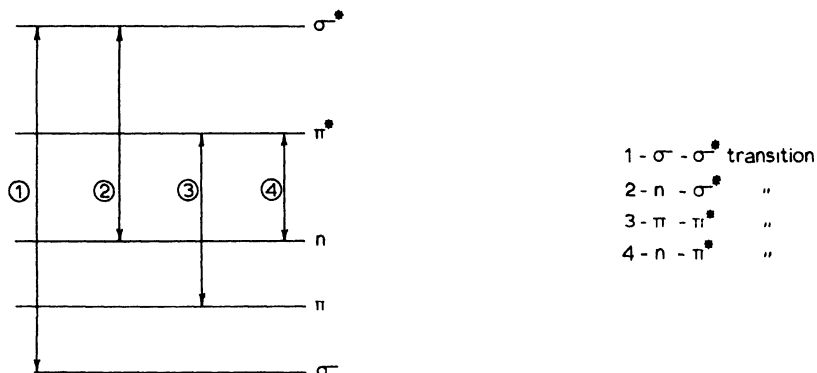
The π-π^* transitions in conjugated carbon systems are of particular chemical interest. For simple molecules the M.O. theory provides a convenient method of studying their electronic energy levels and transitions between these levels and hence the M.O. method is useful in interpretation of spectra. The molar extinction coefficient is a measure of the strength of the electric dipole transition involved. "Oscillator strengths" or f-values can be obtained from careful studies of the absorption intensities. $f = 4.32 \times 10^{-9}$ $\int \epsilon \, d\bar{\nu}$; the integral is of the molar absorptivity as a function of wavelength which is expressed in cm^{-1}. For symmetric absorption lines $f \sim 4.60 \times 10^{-9} \epsilon_{max} \Delta \bar{\nu}_{1/2}$ where $\Delta \bar{\nu}_{1/2}$ is the band width at half maximum intensity .

    Interpretation of spectra of complex molecules is done on the basis of functional groups (not in conjunction with other groups) which have characteristic absorptions in visible and u.v. regions. These groups are called chromophores. For conjugated groups empirical corrections are used. λ_{max} values for extended conjugated systems can be predicted on the basis of the free-electron model. Hindered rotation in extended conjugated systems alters the λ_{max} values since the π -electron energy levels are affected.

    Changes in spectra are clearly seen in many cases where protonation of a functional group is involved. pH affects the spectrum in such cases. Solvent affects are useful in identifying the nature of the transitions. The n-π^* solvent effects associated with the interaction of the lone pair electrons in oxygen-or nitrogen-containing systems in polar solvents is a case in point. The shifts of absorption bonds and their intensity changes are generally described in the literature using the following terminology.

Bathochromic Shift: A shift of λ_{max} to longer wave lengths (also called the red shift); Hypsochromic Shift: A shift of λ_{max} to shorter wavelengths (also called the blue shift); Hyperchromic Effect: Increase in intensity of an absorption band, usually with reference to the value of ϵ_{max} ;

Hypochromic Effect: Decrease in intensity of an absorption band usually with reference to the value of ϵ_{max}.

The λ_{max} and ϵ_{max} values of a few chromophores and systems are given in the accompanying tables.

λ_{max} and ϵ_{max} values for Some Functional Groups

	λ_{max} (mμ)	ϵ_{max}	Example
$C=C$	171	15,530	ethylene (vapor)
$-C\equiv C-$	178	10,000	
	196	2,100	2-octyne[a]
	223	160	
$C=0$	160	20,000	
	180	10,000	acetaldehyde (vapor)
	290	17	acetaldehyde[b]
	166	16,000	acetone (vapor)
	189	900	acetone[b]
	279	15	
$-COCl$	220	100	acetyl chloride[b]
$-CO_2H$	208	32	acetic acid[c]
$-CONH_2$	178	9,500	acetamide[b]
	220	63	acetamide[d]
	211	57	acetamide[c]
$-CO_2R$	211	57	ethyl acetate[c]
$-NO_2$	201	5,000	nitromethane[e]
	274	17	
$-ONO_2$	270	17	butyl nitrate[c]
$-ONO$	220	14,500	butyl nitrate[b]
	356	87	
$-NO$	300	100	Nitrosobutane[f]
	665	·20	
$C-N$	235	100	amines[c]
$-C\equiv N$	167	?	acetonitrile (vapor)
$-N_3$	285	20	azadoacetic ester[c]
$=N_2$	~410	3	diazomethane (vapor)
$-N=N-$	338	4	azomethane[c]

(a) in heptane, (b) in hexane, (c) in ethanol, (d) in water, (e) in methanol, (f) in ether.

λ_{max} and ϵ_{max} Values for Some Conjugated Groups			
	$\lambda_{max}(m\mu)$	ϵ_{max}	Example
$O=\overset{\mid}{C}-\overset{\mid}{C}=O$	195	25	glyoxal[a]
	280	3	
	463	4	
$\diagdown C=\overset{\mid}{C}-\overset{\mid}{C}=O$	218	18,000	crotonaldehyde[b]
	320	30	
$\diagdown C\equiv C-\overset{\mid}{C}=O$	214	4,500	1-hexyn- 3 one[b]
	308	20	
$\diagdown C=\overset{\mid}{C}-CO_2H$	206	13,500	cis-crotonic acid[b]
	242	250	
$-C\equiv C-CO_2H$	210	6,000	n-butylpropionic acid[b]
$C=\overset{\mid}{C}-\overset{\mid}{C}=N-$	219	25,000	N-n-butylcrotonaldimine[a]
$\diagdown C=\overset{\mid}{C}-C\equiv N$	215	680	methacrylonitrile[b]
$\diagdown C=\overset{\mid}{C}-NO_2$	229	9,400	1 nitro-1-propene[b]
	235	9,800	
$\diagdown C=\overset{\mid}{C}-C\equiv C-$	219	7,600	Vinylacetylene[a]
	228	7,800	
$\diagdown C=\overset{\mid}{C}-\overset{\mid}{C}=C\diagup$	217	20,900	Butadiene[a]

(a) Solvent, hexane (b) Solvent, ethanol.

λ_{max} and ϵ_{max} Values for Some Monosubstituted Benzenes

C_6H_5-X*	$\lambda_{max}(m\mu)$	ϵ_{max}
-H	203.5	7,400
	254	204
-CH$_3$	206.5	7,000
	261	225
-Cl	209.5	7,400
	263.5	190
-Br	210	7,900
	261	192
-I	207	7,000
	257·	7000
-OH	210.5	6,200
	270	1,450
-OCH$_3$	217	6,400
	269	1,480
-CN	224	13,000
	271	1,000
-CO$_2$H	230	11,600
	273	970
-CO$_2^-$	224	8,700
	268	550

C_6H_5 -X*	λ max (mμ)	ϵ max
-NH$_2$	230	8,600
	280	1,430
-NHCOCH$_3$	238	10,500
-NO$_2$	268.5	7,800
-CHO	249.5	11,400
-COCH$_3$	245.5	9,800

* Solvent-water.

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IV.7B. Infrared Spectroscopy

* <u>General</u>: The feature of characteristic absorption of radiation
by many molecules in the infrared (IR) region has provided physicists and
chemists with an extremely elegant and powerful tool for the elucidation
of molecular structure. Near infrared, 0.8 to 2.5μ(12,500 to 4000 cm^{-1});
Infrared, 2.5 to 15μ(4000 to 167 cm^{-1}); Far infrared: 15 to 200μ(667 to
50 cm^{-1}).

Vibrational and rotational-vibrational motion of molecules are res-
ponsible for absorption of energy. The rotational-vibrational absorption
bands are usually found in gases. The change ($\triangle J$) in the total quantum
number gives rise to P, Q and R branches ($\triangle J$ = -1 for P; $\triangle J$ = 0 for Q;
$\triangle J$ = +1 for R). Since the rotational frequencies depend on the moments
of inertia of the molecule in question the rotational-vibrational spectra
are of help in the study of molecular structure. In condensed gases,
liquids and solids one generally observes only the vibrational bands in
this region.

* <u>Diatomic Molecules</u>: The vibrations of a diatomic molecule (only
one degree of vibrational freedom) can be understood in terms of the harmo-
nic oscillator model (see sec. IV.1). ($V = \frac{1}{2} k x^2$ with $x = r-r_e$ where V
is the potential, r is the internuclear distance, r_e = equilibrium inter-
nuclear distance and k = force constant). A better potential function which
can explain the observation of overtones is the <u>Morse function</u> for which
$V = hcD_e\left\{1-\exp\left[-\beta(r-r_e)\right]\right\}^2$ (D_e= dissociation energy, β is a constant).
If the Morse function is expanded and cubic and higher order terms neglected
we get $\beta = \left[2\pi^2\mu/(D_e hc)\right]\frac{1}{2}\nu_e$, where μ= reduced mass.

Empirical relations between internuclear distance and the force
constants have been suggested. The most commonly used relation is <u>Badger's</u>
rule $k_e(r_e -d_{ij})^3$ = C where k_e = force constant r_e = equilibrium inter-
nuclear distance, d_{ij} is a constant depending on atoms i and j and C is
an empirical constant.

* <u>Polyatomic molecules</u>: For a molecule containing N atoms we have in
general 3N degrees of freedom. For a linear molecule 3N-5 and for a non-
linear molecule 3N-6 of the total 3N degrees of freedom correspond to
vibrational degrees of freedom. The vibrational motions need not be only
stretching of bonds. They can be bond bendings as well. If q is the
co-ordinate for the motion and $\underline{m}$ the dipole moment then $\partial\underline{m}/\partial q$ should be
non-zero for <u>infrared activity</u>. The intensity of IR absorption is pro-
portional to $\left|\int\Psi_i\,\partial\underline{m}/\partial q\,\Psi_j\,d\tau\right|^2$ where Ψ_i and Ψ_j, are wave functions for the
two vibrational energy levels between which the transition takes place.
Experimental determination of integrated IR band intensities can provide
one with $\partial\underline{m}/\partial q$ values which in turn can be correlated to electronic
structure of molecules. The question whether a particular vibrational
transition is allowed or not is determined by molecular symmetry. The
frequency of a given vibration is determined by the masses of nuclei involv-
ed and the nature of the potential function which, of course, is expressed

in terms of the various force constants. In most cases an empirical corre-
lation between the frequency and the nature of the vibration mode of a
functional group in the molecule can be given.

    * Instrumentation:

<u>Sources:</u> Globar (heated silicon carbide); Nernst glower (molded rod con-
taining a mixture of zirconium oxide, yttrium oxide and erbium oxide heated
electrically around 1500°C); heated nichrome wire, heated alumina tube or
Welshbach mantle (good for λ below 400 cm^{-1}). Tunable laser sources hold
promise.

<u>Monochromators:</u> Prisms of suitable materials as well as gratings are used.
A combination of prism and grating is also used. Gratings are especially
useful for higher resolution.

<u>Ranges of Different Prisms:</u> LiF, 0.6 -6μ; CaF$_2$, 0.2 - 8.5μ; NaCl, 2-15μ;
KBr, 10 - 25 μ; TlBr-TlI(KRS-5), 2-40μ; and CsI, upto~50μ.

<u>Detectors:</u> Thermocouples and photoconductive cells (PbS, PbTe and semi-
conductor types). Other sensitive detectors include bolometers and pneu-
matic detectors <u>(Golay cells)</u>.

<u>Sample Cells and Sample Preparation:</u> Gases can be studied in suitable gas-
cells usually made of glass with "windows". Cell path lengths vary from
few centimeters to meters. For gases under high pressure metal cells are
used. Liquid samples are held between plates of suitable window material
(for ex: NaCl for non-aqueous samples and AgCl for aqueous samples).
Commonly employed liquid film thickness values: 0.025 mm; 0.1 mm; 0.5 mm.
In some cell designs liquid thickness (ath length) can be adjusted.
Solvents most often are CCl$_4$, CS$_2$ or CHCl$_3$. Samples should be dry since
water absorbs strongly~3710 cm^{-1} and ~1630 cm^{-1}. Solid specimens can be
examined in alkali halide pellets or as a mull. (most commonly in nujol).

<u>Calibration:</u> Spectra can be calibrated using well-known standards.
(CH$_4$, H$_2$O, CO$_2$ and NH$_3$). Polystyrene (3.509 μ; 6.238 μ; 11.035 μ)
is commonly used. Other standards include indene, toluene and some subs-
tituted benzenes.

<u>Near Infrared Region:</u> This region can be studied by many instruments that
are commonly used for u.v. and visible spectroscopic work.

<u>Commercial Instruments:</u> A variety of instruments are commercially available
for infrared spectroscopic work. Some instruments use large prisms or
multi-pass, multi-prism or prism-grating arrangements. Both single beam
and double beam (one beam for reference) versions are available. Most
modern instruments are of the automatic scanning and recording type with
output from the recorder appearing on precalibrated (wave length) charts
in some cases. The beam is chopped or switched between reference and
sample cells in a periodic manner to provide a periodically varying detector
output which is then synchronously detected. Some of the well-known
manufacturers of IR spectrometers are - U.S.A: Baird-Atomic Inc., Cambridge,
Mass., Beckman Instruments Inc., Fullerton, California and Perkin-Elmer Corp.
Norwalk, Conn.; U.K.: Unicam Instruments Ltd., Cambridge, Grubb-Parsons Ltd.
New Castle-upon Tyne, and Hilger and Watts.; East Germany: Carl Zeiss, Jena.

* <u>Interpretation of IR Spectra:</u> The complete analysis of the IR spectrum of a complex molecule in terms of its geometry, nuclear masses and molecular potential function is extremely difficult since the mathematical problem of calculation of the fundamental modes of vibration is quite involved. (see books by <u>Herzberg</u> and <u>Wilson</u> <u>et al.</u> referred to in the bibliography at the end of this section). Although such analyses provide one with a set of valuable force constants and help classify the vibrational transitions on the basis of symmetry the more common approach is to empirically correlate the observed features of the IR spectra to functional groups and thus to molecular structure.

The various absorption bands of functional groups are assigned to the fundamental modes of vibrations like stretching (symmetric and anti-symmetric) and bending or deformation (scissoring, wagging, twisting, rocking) vibrations. Others can be assigned to overtones or combinations (sum and difference) of fundamentals. If two bonds of same symmetry are located closely within the molecule coupling effects can be seen in vibrational transitions. For such situations vibrational assignments may need some corection. Also, in some cases coupling between a fundamental vibration and an overtone or combination whose frequency is near that of the fundamental may take place if the symmetry character of these vibrations is the same. The intensity of the overtone or combination band shows anomalous increase or even exhibits a splitting and the phenomenon is called <u>Fermi Resonance</u>. Relative intensities of bands are qualitatively noted as S, M, W, etc. to indicate strong, medium,weak etc. intensities. Dependence of X-H stretching frequency (x = C, O, N, F) on <u>hydrogen bonding</u> have been investigated in detail and it is found that the stretching frequency decreases while the bending frequency increases with hydrogen bonding. A similar result holds for $>C=O$ frequency in carboxylic acids. If D is substituted for H in the X-H the stretching frequency is reduced. An approximate expression for the frequency of such a fragment is $\nu\,(cm^{-1}) = (2\pi c)^{-1}\,\left[k/\mu\right]^{1/2}$ where μ is the reduced mass and k is the force constant. Stretching frequency can be also related to <u>bond order</u>. Thus the frequency is higher for a triple bond as compared to a double bond and so on. The overtones or combinations of stretching vibrations due to C-H, O-H, N-H etc. are observed generally in the near infra-red region. Hindered rotation in molecules may give rise to interesting temperature and solvent dependence of IR spectra. From such studies one can obtain useful information on barrier height to rotation.

The stretching frequencies of polar groups of molecules in non-polar solvents depend on the dielectric constant ϵ of the solvent. If ν_0 is the frequency in vapor phase and ν_s in solution,

$$(\nu_0 - \nu_s)/\nu_0 = K(\epsilon - 1)/(2\epsilon + 1)$$

(<u>Kirkwood-Bauer-Magat equation</u>) where K is a proportionality factor.

The IR spectrum of a molecule can be said to be its "fingerprint" since it is characteristic of the molecule. In this regard, the IR spectrum in the region 1300-650 cm^{-1} is of importance and is known as the <u>fingerprint</u> region. The bending frequencies of most bonds as well as stretching frequencies of bonds like C-C, C-N, C-O, C-X (X = halogens) fall in this region.

Chart of IR characteristic frequencies compiled by N. Colthup has been
extensively referred to in the literature. The characteristic frequencies
of many functional groups are given in the accompanying tables.

* Characteristic IR Frequencies in cm^{-1} (Correlation Table)

C-H Stretching				
paraffins	2850–2965 (m–s)		aromatics	3000–3100 (v)
alkenes	3010–3100 (m)		aldehydes	2820–2900 (w)
				2700–2775 (w)
C-H Bending				
C-H alkane	1340 (w)		trans–disubst.	1295–1310 (m)
–CH₂–alkane	1445–1485 (m)		alkene	960– 970 (s)
–CH₃–alkane	1430–1470 (m)		Gem-disbsti-	
	1370–1380 (s)		alkene	1410–1420 (s)
gem–dimethyl	1380–1385 (s)			885–895 (s)
	1365–1370 (s)		trisubst.alkene	790–840 (s)
t-butyl	1385–1395 (m)		alkyne	630 (s)
	1365 (s)		Benzenes	
vinylalkane	1410–1420 (s)		one adjacent H	880 (v)
	985– 995 (s)		2 adjacent H	830 (v)
	905– 915 (s)		3 adjacent H	780 (v)
			4 adjacent H	750 (v)
cis – disubst.	690 (s)		5 adjacent H	750 (v)
alkene				
C=C stretching				
alkenes	1620–1670 (m)		benzenes	1600 (v)
dienes	1600–1650 (w)		(skeletal	1580 (v)
alkynes	2100–2260 (v)		vibrations)	500 (v)
allenes	~1960~1060 (m)			1400 (v)

C=O stretching				
satd. ketones (K)	1705–1725 (s)		aryl ketones	1680–1700 (s)
cyclic 4–K	~1780 (s)		diaryl ketones	1660–1670 (s)
5–K	1740–1750 (s)		α –diketones	1710–1730 (s)
6–K	1705–1725 (s)		β –diketones	1540–1640 (s)
α,β–unsat. ketones			ketene	2150 (s)
acyclic	1665–1685 (s)		satd. aldehydes	1720–1740 (s)
5-mem.Cyclic	1705–1725 (s·)		α,β–unsat. aldehydes	1680–1705 (s)
6-mem.Cyclic	1665–1685 (s)		aryl aldehydes	1695–1715 (s)
Esters				
satd. acyclic	1730–1750 (s)		carbonates	1740–1780 (s)
β–lactones	~1820 (s)		sat. RCOOH	1700–1725 (s)
γ –lactones	~1770 (s)		α,β –unsat. RCOOH	1690–1715 (s)
δ –lactones	~1747 (s)		(COO)⁻	1550–1610 (s)
vinyl	1770–1800 (s)			1300–1400 (m)
α,β–unsat & aryl	1715–1730 (s)		α,β–unsat. and	1740–1800 (s)
α –keto–	1740–1755 (s)		aryl anhyd.	1720–1770 (s)
β–keto–	1650 (s)			

Characteristic IR Frequencies in cm^{-1} (contd.)

O-H and C-O stretching and related vibrations			
free OH	3590-3650 (v)	OH bend alcohols	1260-1410 (s)
intermol HB	3450-3550 (v)	phenols	1310-1410 (s)
HB polymer	3200-3400 (s,b)	C-O stretch alcohols	1050-1200 (s)
intramol HB (chelate)	2500-3200 (w,b)	C-O-C (ethers)	1050-1275 (s)
(HB=hydrogen bonded)			1060-1150 (m)

N-H stretching			
free primary amines	~3500 (m),~3400	free primary amides	~3500 (m),~3400
free secondary amines	3310-3500 (m)	bonded primary amides	~3350 (m), 3180
imines (=N-H)	3300-3400 (m)	free secondary amides	~3430 (m)
amine salts	3030-3130	bonded secondary	3140-3320 (m)

N-H bending			
primary amines	1500-1650 (s-m)	Primary amides	
secondary amines	1550-1650 (w)	(dil. solns).	1590-1620 (s)
amine salts	1575-1600 (s)	secondary amides	
	~1500	(dil. soln.).	1510-1550 (s)

C-N stretching			
aromatic amines	1250-1340 (s)	aliphatic amines	1020-1220 (w)

>C=N stretching			
alkyl amines, oximes	1640-1690 (v)	α, β unstd. oximes	1630-1660 (v)

C≡N stretching			
alkyl nitriles	2240-2260 (m)	Isocyanates	2240-2275 (m)
Unsatd. and aryl nitriles	2215-2245 (v)	Isocyanides	2070-2220 (m)

-N=N stretching (azo)	1575-1630 (v)	-N=C=N-stretching	2130-2155 (s)

-N₃ stretching	2120-2160 (s)		
	1180-1340 (w)		

C-X stretching			
C-F	1000-1400 (s)	C-Br	500-600 (s)
C-Cl	600-800 (s)	C-I	~500 (s)

S=O stretching			
sulfoxides	1030-1070 (s)	sulfonyl chlorides	1165-1185 (s)
sulfones	1140-1160 (s)		1340-1370 (s)
	1300-1350 (s)	sulfonamides	1140-1180 (s)
sulfites	1150-1230 (s)		1300-1350 (s)
	1350-1430 (s)	sulfonic acids	1150-1210 (s)
			1030-1060 (s)
			~650

Characteristic IR Frequencies in cm^{-1} (contd.)

Others			
S-H stretching	2550-2600 (w)	O-NO$_2$ in nitrates	1600-1650 (s)
			1250-1300 (s)
C-S stretching (mer-captans, sulfoxides)	600-800 (w)	C-NO in nitroso compounds	1500-1600 (s)
C=S stretching	1050-1200 (s)		
C-NO$_2$ in aromatic nitro compounds	1500-1570 (s)	O-NO in nitrites	1650-1680 (s)
	1300-1370 (s)		1610-1625 (s)
C-NO$_2$ in aliphatic nitro compounds	1550-1570 (s)	P-H stretching	2350-2440 (m)
	1370-1380 (s)	P=O stretching	1250-1300 (s)

Inorganic Ions			
CO$_3^{--}$	1410-1450 (v.s.)	NH$_4^+$	3030-3300 (v.s.)
	860- 880 (m)		1390-1430 (w)
SO$_4^{--}$	1080-1130 (v.s.)	PO$_4^{3-}$, HPO$_4^{2-}$, H$_2$PO$_4^-$	1000-1100 (s)
	610- 680 (m)		
NO$_3^-$	1350-1380 (v.s.)	CN$^-$, SCN$^-$, OCN$^-$	2000-2200 (s)
	815- 846 (m)		
NO$_2^-$	1320-1380	Silicates	900-1100 (s)
	1230-1250 (v.s.)		
	800- 840 (w)		

v.s. = very strong; s = strong; m = medium ; w = weak; v = variable; These refer to intensity of bands. b-broad.

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IV.7.C. Microwave Spectroscopy

* General: Absorption of electromagnetic energy due to molecular rotational transitions occur in the microwave region in general (0.2 to 200 cm^{-1}; cm and mm wave region). The necessary condition for absorption in this region is the presence of a molecular electric dipole moment and hence homonuclear diatomic molecules as well as molecules with high degree of symmetry (spherical tops for which the moments of inertia in the three principal molecular axes are equal) do not give rise to microwave absorption. Non-linear molecules with permanent electric dipole moment can be classified on the basis of the moments of inertia along the principal molecular axes. We thus have symmetric tops and asymmetric tops. The symmetric tops may be further classified as prolate ($I_a < I_b = I_c$) or oblate ($I_a = I_b < I_c$). For the asymmetric tops, $I_a \neq I_b \neq I_c$. For a diatomic molecule, transition between two rotational levels (quantum numbers J' and J") has the energy

$$E = B_o h \left[J'(J'+1) - J''(J''+1) \right] (\text{in } cm^{-1}) \text{ where } B_o = h / (8\pi^2 I_o), \text{ is the}$$

rotational constant. The value of I_o is μr_o^2 where μ is the reduced mass and r_o the internuclear distance. Thus, bond lengths can be accurately determined. The principle can be extended to linear polyatomic molecules as well and in order to derive the various bond distances additional experimental data are required and these are provided by isotopic substitution studies. Similarly, rotational energy expressions can be obtained for symmetric tops and the experimental data can be analyzed with the help of these expressions to yield bond angles and bond distances. Here again isotopic substitution studies are employed to get complete information on molecular geometry. Accurate data on molecular dipole moments can be obtained by employing the Stark effect. The widths of microwave absorption lines can be related to the molecular quadrupole moment. Zeeman studies are useful in the determination of molecular rotational magnetic moments and nuclear interactions. Hyperfine structure in the rotational spectra observed in this region have provided valuable information on nuclear magnetic and quadrupole interactions in molecules and these have been supplementary to magnetic resonance investigations.

Instrumentation:

Source: Reflex klystrons have been extensively used as sources. These provide highly monochromatic radiation. The region is usually covered in several bands, from 22 kMc/s to 60 kMc/s. Harmonic generators are used to provide the higher frequencies. The frequency of the klystrons is stabilized by an arrangement due to Pound which "locks" the klystron to a high Q-cavity.

Cells: Wave guides with mica windows are used as cells. Samples of gases or vapors are used since these show discrete lines.

Modulation: 100 kc/s modulation (Stark modulation) is generally employed.

Detection: Crystal detectors are used to provide the 100 kc/s output which is then amplified and passed through a phase-sensitive receiver recorder arrangement.

Frequency Measurement: The frequencies of microwave absorption lines are measured with respect to a standard source. Since the usual sources are of lower frequency (r.f. region) multipliers are used to provide harmonics in the klystron frequency range. These harmonics can be superposed on the absorption spectrum as "markers".

The dielectric absorption of polar liquids and solids can also be studied in this region and these studies relate to dielectric relaxation. Hindered rotation of molecules in liquids and solids has been examined by such dielectric methods.

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IV.7.D. Nuclear Magnetic Resonance Spectroscopy

* The Resonance Phenomenon

Magnetic Moment of nucleus = μ ; (Nuclear Spin number = I. $\mu \neq 0$ if I $\neq 0$; Nuclear spin angular momentum = $\sqrt{I(I+1)}\,\hbar$. However, measureable components of the angular momentum vector are $m\hbar$ where m is the magnetic quantum number. m can have $2I + 1$ values I, I-1,.... -(I-1), -I. Energy of a magnetic nucleus in an external uniform field (H_o) is $- \mu \cdot H_o$ =

$-\hbar \mu H_o \cos\theta = -\hbar \mu H_o \frac{m}{I} = -\gamma \hbar H_o m$ where γ = magnetogyric ratio (also called gyromagnetic ratio). These energy values corresponding to different m values are the Zeeman levels. The difference in the energy values for such Zeeman levels having quantum numbers   m and m' (m=m' $\pm$ 1) is

$\triangle E = \gamma \hbar H_o = h\nu$. Hence $2\pi\nu = \omega = \gamma H_o$. Transitions can be induced by a radio frequency field (circularly polarized or linearly polarized with circular components) of frequency ν and the resonant absorption of r.f. energy in the presence of an external uniform magnetic field is referred to as nuclear magnetic resonance (NMR). The magnetic nuclei process around H_o with an angular frequency ω = γHo (Larmor precession) and if the r.f. field has a circular component of the same frequency and phase as the precessing nuclei it can reorient them. NMR frequency depends on γ and H_o values. Since γ depends on the nucleus, for a given nucleus one can either fix H_o and vary frequency or fix frequency and vary H_o to obtain resonance. For a proton with H_o = 10,000 gauss r.f. frequency for resonance is about 42 Mc/s.

* Boltzmann Distribution and Relaxation: The population of magnetic nuclei in the Zeeman levels is governed by Boltzmann distribution (more nuclei in lower energy levels) if the nuclear spins are in equilibrium with the surroundings (lattice). The spin system comes to equilibrium by means of

two relaxation processes: <u>spin-lattice relaxation</u> (time constant T_1) and
<u>spin-spin relaxation</u> (time constant T_2). T_1 and T_2 also referred to as the
longitudinal and transverse relaxation times. The difference in population
between two levels in the presence of a r.f. field inducing transitions is
different from that in the absence of the field. The population difference
is reduced by the r.f. field and if the populations become equal the two
levels are said to be <u>saturated</u>.

* <u>Instrumentation:</u> The bridge method and crossed - coil (induction method)
have been widely used. The source of r.f. is usually a crystal controlled
oscillator and the magnetic field is lowly varied. If the resonance line
widths are large, the r.f. source need not be crystal-controlled. Receivers of
high sensitivity are generally used with suitable preamplifiers. The magnetic
field is modulated at audio frequencies and output detected by phase-
sensitive detectors. (This set-up is common in broad line or wide-line
NMR spectroscopy of nuclei in solids). Nuclei in liquids exhibit very
narrow resonances and it is necessary to have highly stable oscillators and
magnetic fields. The fields should be highly uniform. A few commercial
instruments have been manufactured by Varian Associates, Palo Alto, Calif.
U.S.A., Japan Electron Optics Laboratory Co. Ltd., Tokyo, Japan and others.
R.F. pulses can also cause transitions and the nuclear magnets can be orient-
ed in specific directions. During the "off-period" of the pulses the precess-
ing nuclei can induce a voltage in a coil. (echo). Spin-echo method is used
largely for the study of relaxation phenomena.

* <u>Wide-Line NMR Spectroscopy</u>: The study of NMR in solids can yield useful
information like the distance between magnetic nuclei. The magnetic dipole
interaction causes a broadening of the line (line widths are of the order
of a few gauss) while exchange interaction ($\underline{I_1}.\underline{I_2}$) between unlike nuclei also
causes broadening. However, exchange interaction between <u>like</u> nuclei can lead
to narrowing (<u>exchange narrowing</u>). The analysis of the resonance spectra
is done using <u>Van Vleck's moment method</u> which then yields the internuclear
distances. Internal rotation in solids can also be thus studied. An often-
used procedure, especially in single crystal study, is the orientation
dependence of fine structure in the spectra. <u>Pake's method</u> is employed to
determine the orientation and length of internuclear distance vectors. Such
studies have been made extensively to determine positions of protons in
solids. If there are nuclei present with $I > 1/2$ and thus having nuclear
quadrupole moment additional fine structure may be observed.

* <u>High Resolution NMR Spectroscopy</u>: In fluids the dipolar interaction
betwen magnetic nuclei vanishes and the resonance lines are observed to
be usually quite narrow. A study of these narrow lines (widths of the
order of milli gauss) requires highly homogeneous magnetic fields and
sample spinning. The most interesting and useful phenomenon in high reso-
lution NMR is the modification of the resonance frequency of a nucleus by
the surrounding electron cloud. Thus not all like-nuclei may have the same
resonance frequency at a given field if their electronic surroundings are
different, as for example, in different chemical environments. The field
at the site of the nucleus is modified to a value $H_N = (1 - \sigma)H_o$ where σ is
the <u>shielding constant</u>. The proton of an aldehyde group resonates at a
different frequency compared to the proton of a methyl group and so on.

If the r.f. oscillator frequency is fixed then the magnetic field values
for resonance are different for different environments. These differences
are known as the chemical shifts. Values of chemical shift (δ) are measur-
ed with respect to a standard. For protons the commonly used standard is
tetramethylsilane (TMS). Chemical shifts can be measured by producing side-
bands using an audio-oscillator (side-band technique) which modulates the
magnetic field and thus the spectrum can be recorded with the side-bands
serving the purpose of frequency scale calibration. If the difference in
frequency between the resonance lines of the nucleus in the reference
compound and the sample is $\Delta\nu$ cps then

$$\delta = \frac{\Delta\nu \times 10^6}{\text{oscillator frequency (cps)}}.$$

If TMS is used as a standard the chemical shift values are referred in τ
scale, $\tau = 10 - \delta$ with $\tau = 10$ for protons in TMS. δ and τ values are
independent of spectrometer frequency although $\Delta\nu$ is not. In fact $\Delta\nu$
is proportional to the field (frequency) for a given nucleus.

   τ or δ values are very useful in chemical applications of NMR
spectroscopy. Since values of τ near 10 for a proton suggest a situation
similar to that of TMS one can infer the presence of a methyl group. Protons
in such groups are said to be shielded and the resonance line appears at the
high field side when frequency is fixed and field is varied. On the other
hand protons in benzene resonate at lower fields (2.73 τ) and are deshielded.
The π -electrons of benzene may be thought of as precessing around the
ring and thus give rise to a ring current which causes the deshielding.
Magnetic anisotropy of bonds or groups can cause shielding or deshielding
depending on orientation. A table of τ values for protons in functional
groups of molecules of known structure can be used to identify similar
groups in molecules of unknown structure. A similar procedure is possible
for other nuclei like F^{19}, C^{13} etc. However, the shifts in these cases
are extremely large in comparison with proton chemical shifts.

Spin Coupling: In the spectra of many molecules under high resolution, multiple
structure is observed due to electron-coupled nuclear spin interactions.
The methyl proton in acetaldehyde appears as a doublet due to interaction
with the single aldehyde proton. The two spin states of this single proton
give rise to two lines in the methyl group resonance. Similarly the three
methyl protons have spin states with $\sum m = 3/2, + 1/2 - 1/2$ and $-3/2$ values
(sum of m values for 3 protons). Thus four lines are observed for the
aldehyde. The separations within the multiplet are equal and is designated
J(c.p.s.). The intensities of the lines are related to the statistical
probaility of these states which follow the binomial distribution (here it
is 1:3:3:1). If n equivalent nuclei each with spin I couple to a given
spin/s the number of spin multiplets expected (in first order approximation)
is 2(nI) + 1. If the internal chemical shift between the groups of spin i
and j are comparable to J_{ij} the spin coupling between them then complex
spectra result. The problem has to be analyzed by means of the Hamiltonian.

$$\mathcal{H} = \sum_i \gamma \hbar I_i (1-\sigma_i) H_0 + \sum_{i<j} J_{ij} \underline{I_i} \cdot \underline{I_j}$$

Since the spin-spin interaction is through intra-molecular mechanisms it is independent of the external field strength and thus spin-split lines can be distinguished from chemical shifts by recording spectra at different fields. While proton-proton interactions are of the order of a few cps such interactions involving other nuclei may be quite large. Proton J values depend on the number of intervening bonds, orientation of bonds, hybridization on attached atoms and electronegativity. Karplus has shown how the J value of an ethane fragment (vicinal coupling) depends on the dihedral angle. This relation has been applied extensively in conformational studies.

The analysis of complex NMR spectra of several molecules is by no means trivial and thus chemical shift (τ) and coupling constant (J) data are not obtainable as a matter of routine in many cases. However, empirical assignments are usually quite reliable especially if the spectra of a few closely related systems are available. It is possible in a few cases to simplify interpretation of experimental NMR spectra by using the double resonance method in which a second radio frequency field is used to "de-couple" spin interacting nuclei.

Samples for high resolution NMR work are liquids or solutions (usually in $CDCl_3$, $AsCl_3$ for proton NMR). Deoxygenated samples give better resonance lines since paramagnetic relaxation effects due to oxygen are then absent. Sample tube diameter $\sim$ 5 mm. Microcells can be used if availability of material is limited (1-3 mg; volume $\sim$ 25 μ litre).

Magnetic Properties of Some Nuclei of Interest
in NMR Spectroscopy

Nucleus	Spin(I)	% National abundance	Magnetic Moment*	NMR frequency (Mc/s) (H_o=14,092 gauss)
H^1	1/2	99.9844	2.79268	60.000
H^2	1	0.0156	0.857386	9.211
B^{10}	3	18.83	1.8005	6.447
B^{11}	3/2	81.17	2.6880	19.250
C^{13}	1/2	1.108	0.70220	15.085
N^{14}	1	99.635	0.40358	4.335
N^{15}	1/2	0.365	-0.28304	6.081
O^{17}	5/2	0.037	-1.8930	8.134
F^{19}	1/2	100.0	2.6273	56.446
P^{31}	1/2	100.0	1.1305	24.288
Cl^{35}	3/2	75.4	0.82091	5.879
Cl^{37}	3/2	24.6	0.68330	4.893
Co^{59}	7/2	100.0	4.6388	14.237
Br^{79}	3/2	50.57	2.0990	15.203
Br^{81}	3/2	49.43	2.2626	16.203
I^{127}	5/2	100.0	2.7937	12.005

* Units of nuclear magneton $\beta_N = e\hbar/2Mc$, M = mass of proton.
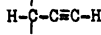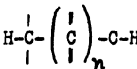
Table of τ-values (TMS = 10.0)

Group	τ	Group	τ
-CH₂-(cyclopropane)	9.78	>C=C<H (acyclic conjugated)	3.5-4.0
CH₄(methane)	9.767	O=C-N<H	1.5-4.5
CH₃-C-(satd.)	9.05-9.15*	Ar-H (benzenoid)	2.0-3.4*
CH₃-C-C-X(X=Cl,Br,I)	8.90-9.10	Ar-H(non-benzenoid)	1.4-3.8*
-CH₂- (satd.)	8.65-8.80	N-C<(=O)H	1.9-2.1
RSH	8.5-8.9 or	O=C-H (O<)	1.8-2.0
-C-H (satd.)	8.35-8.60		
CH₃-C-X(X=F, Cl, Br, I)	8.1-8.8*	>C-N<OH	-0.2-1.2ᵃ
CH₃-C=C<	8.1-8.4	RCHO (aliphatic unsatd)	0.35-0.50
CH₃-C=O	7.4-7.9*	RCHO (aliphatic)	0.2-0.3
Ar-CH₃	7.5-7.75	Ar CHO	0.0-0.3*
CH₃-S-	7.2-7.9	-SO₂H	0.0-0.3*
CH₃-N<	7.0-7.9	RCO₂H (dimer in non polar solvents)	-2.2 to -1.0
-C≡C-H (non-conjugated)	7.35-7.55	Fnols	-6 to -5
-C≡C-H (conjugated)	6.9-7.2		
Ar SH	6.0-7.0 or		
CH₃-O-	6.2-6.5*		
Ar NH₂;(Ar)₂NH	6.0-6.6*		
Ar NHR	6.0-6.6*		
>C=CH₂ (non conjugated)	5.0-5.4		
>C=C<H (acyclic non conjugated)	4.3-4.8*		
>C=C<H (cyclic non conjugated)	4.3-4.8		
>C=CH₂ (conjugated)	4.3-4.7+		
>C=C<H (conjugated)	3.3-4.3*		

* The spread may be larger in some cases.

+ Spread towards lower regions some cases.

(a) -OH groups generally show concentration dependence. The monomers resonate at high values, as in the case of R-OH.

J values for protons			
J			**J**
H_2	280 cps	Ortho	7-10 cps
CH_4	12.4 cps	meta	1-3 cps
C⟨H H	12-15 cps	para	0-1 cps
H-C-C-H	2.9 cps	$J_{23}=$	1.6-2.0 cps
CH_3-CH_2-X	6.5-7.5 cps	$J_{24}=$	0.6-1.0 cps
=C⟨H H	0.5-3 cps	$J_{25}=$	1.3-1.8 cps
H-C=C-H (cis)	6-14 cps	$J_{34}=$	3.2-3.8 cps
H-C=C-H (trans)	11-18 cps	$J_{23}=$	4.6-5.8 cps
H-C≡C-H	9.1 cps	$J_{24}=$	1.0-1.8 cps
H-C-C≡C-H	2-3 cps	$J_{25}=$	2.1-3.3 cps
H-C-C⟨H O	1-3 cps	$J_{34}=$	3.0-4.2 cps
-C=C⟨CH H	4-10 cps	$H-C-\left(\begin{array}{c} C \end{array}\right)_n-C-H$	0.
C=C⟨CH H	0.5-2 cps		
-C=CH-CH=C-	10-13 cps		
CH⟨CH_3 CH_3	5.7-6.8		

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IV.7.E. Electron Paramagnetic Resonance

* General: Systems containing an unpaired electron ($S=\frac{1}{2}$) when placed in
a magnetic field have energy levels (Zeeman levels) between which transi-
tions can be induced in a manner similar to that in NMR spectroscopy. For a
field of 3,500 gauss the electron spin resonance (ESR) or electron paramag-
netic resonance (EPR) frequency is of the order of 10KMC/S and such radio
frequencies are usually produced by klystrons. As in NMR, the resonancy
frequency satisfies the relation $\hbar\omega_0 = g\beta H_0$ where g is the "g-factor" which
is a tensor in the general case and β is the Bohr magneton ($e\hbar/2\,mc$).
Magnetic energy levels may be affected by orbital contributions and spin-
orbit coupling effects. Since frequency and field value can be very accu-
rately determined g values can be determined with great precision. These
are then interpreted in terms of electronic structure. For a free electron
$g = 2.00232$. Differences from this g-value are called "g-shifts". Para-
magnetic samples may be in the form of crystals or powders. g-values of
paramagnetic complexes yield information on their bonding and structure.
Most systems of chemical interest are examined in solution form. Free
radicals in solution are easily produced by chemical methods. Other methods
include X-irradiation, flash photolysis, etc.

* Hyperfine Interaction: Of the several interaction terms for an unpaired
electron the hyperfine interaction terms are important dipolar and contact
types. The interaction between a magnetic nucleus and the spin of the odd-
electron gives rise to splittings in the ESR spectra. In solids these may
arise from the interaction with the magnetic nucleus of a paramagnetic ion

itself and between the unpaired electron and a nucleus on another atom
(super hyperfine interaction). A complete analysis of the spectra of
solids using a spin Hamiltoman yields the magnitudes of various interactions
including the hyperfine interaction. For free radicals in solution the
dipolar part of the hyperfine interaction averages out to zero and only
the contact term $(\underline{I}.\underline{S})$ remains and this results in rather sharp lines
(splittings) in the ESR spectra. The splitting constants (a_N) yield data
on the spin densities of the unpaired electron at the various positions
in the molecular framework. Molecular orbital and valence bond theories
have been used in the calculation of spin densities in free radicals.

* Instrumentation: Klystron frequencies around 10 KMC/S and 35 KMC/S
are commonly used. The sample is held in a microwave cavity and field
modulation usually employed. In order to prevent frequency drift auto-
matic frequency control (AFC) systems are employed. The AFC system due
to Pound which "locks" the klystron to the frequency for which Q-factor
is maximum for the cavity is generally used. Bridge method is usually
employed in the detection scheme with a crystal detector. Phase sensitive
detection results in the recorder presentation of the first derivative of
the absorption spectrum. Superheterodyne method is also used, especially
for lines which are quite narrow. Commercial instruments are available
from Varian Associates, Palo Alto, Calif. U.S.A., Japan Electron Optics
Laboratory, Tokyo, Japan, Microspin, London, U.K. and others.

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V. INORGANIC AND ANALYTICAL CHEMISTRY

V.1 Properties of the Elements

A.No. = atomic number; A.W. = atomic weight, ^{12}C = 12 exactly; d. = density, g ml^{-1} at 20°C; m.p. = melting point, °C; b.p. = boiling point, °C

Stable isotopes only are listed: figures underlined are isotopes forming more than 20% of the naturally occurring element.

Element		A.No.	A.W.	d.	m.p.	b.p.	isotopes
Actinium	Ac	89	(227)		1050		
Aluminium	Al	13	26.98	2.70	660	2450	27
Americium	Am	95	(243)	11.7			
Antimony	Sb	51	121.75	6.62	631	1380	121, 123
Argon	Ar	18	39.95		-189	-186	36, 38, 40
Arsenic	As	33	74.92	5.72	817	sub.	75
Astatine	At	85	(210)		(302)		
Barium	Ba	56	137.34	3.50	714	1640	130, 132, 135, 136, 137, 138
Berkelium	Bk	97	(247)				
Beryllium	Be	4	9.012	1.85	1280	2770	9
Bismuth	Bi	83	208.98	9.8	271	1560	209
Boron	B	5	10.81	2.34	(2030)		10, 11
Bromine	Br	35	79.91	3.12	-7	58	79, 81
Cadmium	Cd	48	112.40	8.65	321	765	106, 108, 110, 111, 112, 113, 114, 116
Caesium	Cs	55	132.91	1.90	29	690	133
Calcium	Ca	20	40.08	1.55	838	1440	40, 42, 43 44, 46
Californium	Cf	98	(251)				
Carbon	C	6	12.01	2.26	3730	4830	12, 13
Cerium	Ce	58	140.12	6.67	795	3470	136, 138, 140, 142
Chlorine	Cl	17	35.45	1.56 (1.)	-101	-35	35, 37
Chromium	Cr	24	52.00	7.19	1870	2660	50, 52, 53, 54
Cobalt	Co	27	58.93	8.90	1490	2900	59
Copper	Cu	29	63.54	8.96	1083	2600	63, 65

Properties of Elements

Element		A.No.	A.W.	d.	m.p.	b.p.	isotopes
Curium	Cm	96	(247)				
Dysprosium	Dy	66	162.50	8.54	1410	2600	156, 158, 160, 161, 162, 163 164
Einsteinium	Es	99	(254)				162, 164, 166, 167, 168, 170
Erbium	Er	68	167.26	9.05	1500	2900	
Europium	Eu	63	151.96	5.26	826	1440	151, 153
Fermium	Fm	100	(253)				
Fluorine	F	9	19.00		-220	-188	19
Francium	Fr	87	(223)		(27)		
Gadolinium	Gd	64	157.25	7.89	1310	3000	152, 154 155, 156, 157, 158, 160
Gallium	Ga	31	69.72	5.91	30	2240	69, 71
Germanium	Ge	32	72.59	5.32	937	2830	70, 72, 73, 74, 76
Gold	Au	79	196.97	19.3	1063	2970	197
Hafnium	Hf	72	178.49	13.1	2220	5400	174, 176, 177, 178, 179, 180
Helium	He	2	4.003		-270	-269	3, 4
Holmium	Ho	67	164.93	8.80	1460	2600	165
Hydrogen	H	1	1.008		-259	-253	1, 2
Indium	In	49	114.82	7.31	156	2000	113, 115
Iodine	I	53	126.90	4.94	114	183	127
Iridium	Ir	77	192.2	22.5	2450	5300	191, 193
Iron	Fe	26	55.85	7.86	1540	3000	54, 56, 57, 58
Krypton	Kr	36	83.80		-157	-152	78, 80, 82 84, 86
Lanthanium	La	57	138.91	6.17	920	3470	138, 139
Lawrencium	Lw	103	(257)				
Lead	Pb	82	207.19	11.4	327	1730	204, 206, 207, 208
Lithium	Li	3	6.94	0.53	180	1330	6, 7
Lutecium	Lu	71	174.97	9.84	1650	3330	175, 176
Magnesium	Mg	12	24.31	1.74	650	1110	24, 25, 26

Element		A.No.	A.W.	d.	m.p.	b.p.	isotopes
Manganese	Mn	25	54.94	7.43	1250	2150	55
Mendelevium	Md	101	(256)				
Mercury	Hg	80	200.59	13.6	-38	357	196, 198, 199, 200, 201, 202 204
Molybdenum	Mo	42	95.94	10.2	2610	5560	92, 94, 96, 97, 98, 100
Neodymium	Nd	60	144.24	7.00	1020	3030	142, 145, 146, 143, 144, 148, 150
Neon	Ne	10	20.18		-249	-246	20, 21, 22
Neptunium	Np	93	(237)	19.5	637		
Nickel	Ni	28	58.71	8.90	1450	2730	58, 60, 61, 62, 64
Niobium	Nb	41	92.91	8.40	2420	3300	93
Nitrogen	N	7	14.007		-210	-196	14, 15
Nobelium	No	102	(254)				
Osmium	Os	76	190.2	22.6	2700	5500	184, 186, 187, 188, 189, 190, 192
Oxygen	O	8	16.00		-219	-183	16, 17, 18
Palladium	Pd	46	106.4	12.0	1550	3980	102, 104 105, 106, 108, 110
Phosphorus	P	15	30.97	1.82	44	280	31
Platinum	Pt	78	195.09	21.4	1770	4530	190, 192, 194, 195, 196, 198
Plutonium	Pu	94	(242)		640	3230	
Polonium	Po	84	(210)	9.2	254		
Potassium	K	19	39.10	0.86	64	760	39, 41
Praeseodymium	Pr	59	140.91	6.77	935	3130	141
Promethium	Pm	61	(147)		(1030)		
Protoactinium	Pa	91	(231)	15.4	(1230)		
Radium	Ra	88	(226)	5.0	700		
Radon	Rn	86	(222)		-71	-62	
Rhenium	Re	75	186.2	21.0	3180	5900	185, 187
Rhodium	Rh	45	102.91	21.4	1970	4500	103
Rubidium	Rb	37	85.47	1.53	39	688	85, 87

Properties of Elements

Element		A.No	A.W.	d.	m.p.	b.p.	isotopes
Ruthenium	Ru	44	101.07	12.2	2500	4900	96, 98, 99, 100, 101, 102, 104
Samarium	Sm	62	150.35	7.54	1070	1900	144, 147, 148, 149, 150, 152, 154
Scandium	Sc	21	44.96	3.0	1540	2730	45
Selenium	Se	34	78.96	4.79	217	685	74, 76, 77, 78, 80, 82
Silicon	Si	14	28.09	2.33	1410	2680	28, 29, 30
Silver	Ag	47	107.87	10.5	961	2210	107, 109
Sodium	Na	11	22.99	0.97	98	892	23
Strontium	Sr	38	87.62	2.6	768	1380	84, 86, 87, 88
Sulphur	S	16	32.06	2.07	119	445	32, 33, 34, 36
Tantalum	Ta	73	180.95	16.6	3000	5430	181
Technetium	Tc	43	(99)	11.5	2200		
Tellurium	Te	52	127.60	6.24	450	990	120, 122, 123, 124, 125, 126, 128, 130
Terbium	Tb	65	158.92	8.27	1360	2800	159
Thallium	Tl	81	204.37	11.85	303	1460	203, 205
Thorium	Th	90	232.04	11.7	1750	3850	
Thulium	Tm	69	168.93	9.33	1550	1730	169
Tin	Sn	50	118.69	7.30	232	2270	112, 114, 116, 117, 118, 119, 120, 122, 124
Titanium	Ti	22	47.90	4.51	1670	3260	46, 47, 48, 49, 50
Tungsten	W	74	183.85	19.3	3410	5930	180, 182, 183, 184, 186
Uranium	U	92	238.04	19.07	1130	3820	
Vanadium	V	23	50.94	6.1	1900	3450	50, 51

Element		A.No	A.W.	d.	m.p.	b.p.	isotopes
Xenon	Xe	54	131.30		-112	-108	124, 126, 128, 129, 130, 131, 132, 134, 136
Ytterbium	Yb	70	173.04	6.98	824	1430	168, 170, 171, 172, 173, 174, 176
Yttrium	Y	39	88.91	4.47	1510	2930	89
Zinc	Zn	30	65.37	7.14	419	906	64, 66, 67 68, 70
Zirconium	Zr	40	91.22	6.49	1850	3580	90, 91, 92 94, 96

V.2 Allotropic Forms of Common Elements

Element	Allotrope	Structure	d.	m.p.	b.p.
Arsenic	grey	rhombohedral	5.73	817	sub.
	black	amorphous	4.71	dec.	
	yellow	cubic	2.03	dec.	
Carbon	diamond	cubic	3.51	——	——
	graphite	hexagonal	2.26	3730	4830
Oxygen	oxygen	O_2 molecules	——	-219	-183
	ozone	O_3 molecules	——	-251	-111
Phosphorus	yellow	P_4 molecules	1.82	44	280
	red	polymeric	2.35	590	sub.417
Selenium	red	Se_8 molecules	4.50	——	——
	grey	chains	4.79	217	685
Sulphur	rhombic α	S_8 molecules	2.07	113	——
	monoclinic β	S_8 molecules	1.96	119	445
Tin	grey	diamond	5.76	——	——
	white	metal	7.30	232	2270

V.3 Properties of Inorganic Compounds

col.= colour; r = red; p = pink; bk = black; o = orange; y = yellow;
bn = brown; g = green; b = blue; gy = grey; v = violet; w = white or (colourless

d = density, g ml^{-1} at 20°C; m.p. = melting point, °C, b.p. = boiling point,
°C; dec = decomposition; sol. = solubility in g anhydrous compound per 100g
water at 20°C; s = soluble; sp.s = sparingly soluble; hyd. = hydrolysed
compound;

After the formula, the structure of some solids is indicated:

M = molecular; 1 = NaCl; 2 = CsCl; 3= Zinc blende; 4 = wurtzite;
5 = nickel arsenide; 6 = fluorite (or antifluorite); 7 = rutile;
8 = layer; 9 = chain and 10 = structure other than 1-9.

Compound	Formula		col.	d.	m.p.	b.p.	sol.
Aluminium							
bromide	$AlBr_3$ dimer	M	w	3.0	97	265	hyd.
chloride	$AlCl_3$	8	w	2.4	190	180	46
fluoride	AlF_3	10	w	3.1	1040		0.5
hydroxide	$Al(OH)_3$		w	2.4	dec.		sp.s
iodide	AlI_3 dimer		bn	4.0	191	386	hyd.
nitrate	$Al(NO_3)_3$		w		dec.		67
oxide	Al_2O_3	10	w	4.0	2045	3000	sp.s
phosphate	$AlPO_4$		w	2.6	1500		sp.s
sulphate	$Al_2(SO_4)_3$		w	2.7	dec.		38
ammonium	$NH_4Al(SO_4)_2$		w		dec.		6.6
potassium	$KAl(SO_4)_2$		w				6.3
Ammonium							
acetate	$NH_4O_2CCH_3$		w	1.1	114	dec.	69
bromide	NH_4Br		w	2.3	dec.		75
carbonate, hydrogen	NH_4HCO_3		w	1.6	sub.	107	12
chloride	NH_4Cl		w	1.5	dec.		37
fluoride	NH_4F		w		dec.		8
iodide	NH_4I		w	2.6	dec.		172
molybdate	$(NH_4)_2MoO_4$		w	2.3	dec.		8
nitrate	NH_4NO_3		w	1.7	170	dec.	192
oxalate	$(NH_4)_2C_2O_4$		w		dec.		4.4
phosphate, hydrogen	$(NH_4)_2HPO_4$		w	1.6	dec.		65
sulphate	$(NH_4)_2SO_4$		w	1.8	dec.		75
thiocyanate	NH_4SCN		w	1.3	146	dec.	163
vanadate, meta	NH_4VO_3		w	2.3	dec.		0.6
Antimony							
bromide(III)	$SbBr_3$	M	Y	4.2	97	280	hyd.

Compound	Formula		col.	d.	m.p.	b.p.	sol.
chloride(III)	$SbCl_3$	M	w	3.1	73	219	hyd.
chloride(V)	$SbCl_3$	M	y	2.3	4	dec.	hyd.
fluoride(III)	SbF_3	M	w	4.4	292		hyd.
fluoride(V)	SbF_5		w	3.0	7	150	hyd.
iodide(III)	SbI_3	8	r	4.8	167	401	hyd.
oxide(III)	Sb_2O_3	9	w	5.7	655	1425	.002
oxide, tetra-	SbO_2	10	w	4.1	1060		hyd.
oxide(V)	Sb_2O_5		w	3.8	450	1060	0.3
sulphide(III)	Sb_2S_3	9	o,bk	4.6	546		.00017
Arsenic							
acid, arsenic	H_3AsO_4		w				s
bromide(III)	$AsBr_3$	M	y	3.5	31	221	hyd.
chloride(III)	$AsCl_3$	M	w	2.2(1)	-16	122	hyd.
chloride(V)	$AsCl_5$		w		-40	dec.	hyd.
iodide(III)	AsI_3	8	o	4.4	146	403	6.0
oxide(III)	As_4O_6	M,8	w	3.7	sub.	218	1.84
oxide(V)	As_4O_{10}		w	4.2	315	dec.	67
sulphide(III)	As_4S_6		y	3.4	300	700	.00005
sulphide(V)	As_2S_5		y		sub.		.0002
Barium							
carbonate	$BaCO_3$		w	4.4	1740	dec.	.002
chloride	$BaCl_2$	10	w	3.1	960		36
chromate	$BaCrO_4$		y	5.0			.0004
fluoride	BaF_2	6	w	4.8	1287	1400	0.16
hydroxide	$Ba(OH)_2$		w	2.1	dec.		3.9
iodide	BaI_2	10	w	5.1	dec.		205
nitrate	$Ba(NO_3)_2$		w	3.2	585	dec.	9.0
oxide	BaO	1	w	5.7	1920		hyd.
peroxide	BaO_2		w	5.0	dec.		
sulphate	$BaSO_4$		w	4.5	1350		.00024
Beryllium							
chloride	$BeCl_2$	9	w	1.9	405	487	73
fluoride	BeF_2	10	w	2.1	800		s
hydroxide	$Be(OH)_2$		w		dec		.0001

Compound	Formula		col.	d.	m.p.	b.p.	sol.
oxide	BeO	4	w	3.0	2400	3900	sp.s
Bismuth							
bromide	$BiBr_3$	M	y	5.7	218	461	hyd.
chloride	$BiCl_3$	M	w	4.7	224	441	hyd.
hydroxide	$Bi(OH)_3$		w	4.4	dec.		.00014.
iodide	BiI_3	8	bk	5.7	439	dec.	hyd.
nitrate	$Bi(NO_3)_3$		w		dec.		hyd.
oxide	Bi_2O_3	10	y	8.9	817	1900	sp.s
sulphide	Bi_2S_3	9	bn	7.4	747		.00002
Boron							
acid, boric	H_3BO_3		w	1.4	185		4.9
chloride	BCl_3	M	w	1.4(1)	-107	12	hyd.
fluoride	BF_3	M	w		-128	-102	hyd.
hydride	B_2H_6	M	w		-169	-88	
oxide	B_2O_3	10	w	1.8	577		hyd.
Bromine							
chloride	BrCl		o			10,dec.	hyd.
fluoride(III)	BrF_3		y	2.5	9	135	hyd.
fluoride(V)	BrF_5		w	2.5	-61	40	hyd.
hydride	HBr		w		-87	-67	199
Cadmium							
bromide	$CdBr_2$	8	y	5.2	583	963	98
carbonate	$CdCO_3$		w	4.3	dec.		sp.s
chloride	$CdCl_2$		w		570	967	113
hydroxide	$Cd(OH)_2$		w	4.8	dec.		.00026
iodide	CdI_2	8	bn	5.7	390	800	84
nitrate	$Cd(NO_3)_2$		w		dec.		150
oxide	CdO	1	bn	8.1			hyd.
sulphide	CdS	3,4	y	4.6	1750		sp.s
sulphate	$CdSO_4$		w		dec.		76
Caesium							
bromide	CsBr	2	w	4.4	636	1300	108

Compound	Formula		col.	d.	m.p.	b.p.	sol.
carbonate	Cs_2CO_3		w			dec.	s
chloride	CsCl	2	w	4.0	642	1300	186
fluoride	CsF	1	w	3.6	715	1250	370
iodide	CsI	2	w	4.5	621	1280	79
Calcium							
acetate	$Ca(O_2CCH_3)_2$		w		dec		35
bromide	$CaBr_2$	7	w	3.3	730	810	143
carbide	CaC_2	10	gy	2.2	2300		hyd.
carbonate	$CaCO_3$		w	2.7	1282	dec.	.0014
chloride	$CaCl_2$	7	w	2.1	772		74
fluoride	CaF_2	6	w	3.2	1392		.0016
hydroxide	$Ca(OH)_2$		w	2.3	dec.		0.156
nitrate	$Ca(NO_3)_2$		w		dec.		129
oxalate	CaC_2O_4		w	2.2	dec.		.0007
oxide	CaO	1	w	3.3	2700		hyd.
phosphate	$Ca_3(PO_4)_2$		w	3.1	1670		.0025
sulphate	$CaSO_4$		w	3.0	1300		0.21
Carbon (see "Properties of Organic Compounds")							
acid, hydro- cyanic	HCN		w	0.688	−14	26	misc.
oxy-(phosgene)	$COCl_2$			1.37	−104	8	hyd.
nitride, (cyanogen)	C_2N_2		w		−27	−20	sp.s
oxide, mono-	CO		w		−205	−190	sp.s
oxide, di	CO_2	0	w		sub.	−78	hyd.
Cerium							
oxide(IV)	CeO_2	6	w	7.3	1950		sp.s
sulphate(IV)	$Ce(SO_4)_2$		y	3.9		dec.	dec.
Chlorine							
acid, chloric	$HClO_3$	6	w		dec.		s
perchloric	$HClO_4$		w	1.8(1)	−112	dec.	s
fluoride(I)	ClF		w	1.6(1)	−154	−101	hyd.
fluoride(III)	ClF_3	M	w	1.8(1)	−83	11	hyd.
hydride	HCl		w		−114	−85	72

Compound	Formula		col.	d.	m.p.	b.p.	sol.
oxide, mono-	Cl_2O		y		-20	2	hyd.
oxide, di-	ClO_2		y		-76	11	10.8
oxide, hept-	Cl_2O_7		w		-92	dec.	hyd.
Chromium							
chloride	$CrCl_3$	8	r	2.8	dec.		sp.s
oxide(III)	Cr_2O_3	10	g	5.2	1900		sp.s
oxide(VI)	CrO_3	9	o	2.7	dec.		166
sulphate	$Cr_2(SO_4)_3$		g	3.0			hyd.
Cobalt							
carbonate	$CoCO_3$		bn	4.1	dec.		sp.s
chloride	$CoCl_2$	8	b	3.4	727	1050	64
hydroxide	$Co(OH)_2$		p	3.6	dec.		sp.s
nitrate	$Co(NO_3)_2$						98
oxide	CoO		bk	5.7	1800		sp.s
sulphate	$CoSO_4$		bn	3.7	987		35
sulphide	CoS	5	bk	5.5	1100		.00038
Copper							
acetate(II)	$Cu(O_2CCH_3)_2$		g				7.3
bromide(I)	$CuBr$	3	bn	4.7	504	1355	sp.s
bromide(II)	$CuBr_2$	9	bk		498	dec.	127
carbonate(II)	$CuCO_3$		g		dec.		sp.s
chloride(I)	$CuCl$	3	w	3.5	430	1490	0.1
chloride(II)	$CuCl_2$	9	y	3.1	498	dec.	73
cyanide(I)	$CuCN$		w	2.9	474		.00026
hydroxide(II)	$Cu(OH)_2$		b	3.7	dec.		sp.s
iodide(II)	CuI	3	w	5.6	605	1340	sp.s
nitrate(II)	$Cu(NO_3)_2$		b				122
oxide(I)	Cu_2O	10	r	6.0	1230	1800	.00001
oxide(II)	CuO	10	bk	6.4	dec.		hyd.
sulphate(II)	$CuSO_4$		w	3.6	dec.		20.5
sulphide(I)	Cu_2S	10	bk	5.8	1130		.00005
sulphide(II)	CuS	10	bk	4.6	dec.		.00005
thiocyanate (I)	$CuSCN$		w	2.8	1084		.00044

Compound	Formula		col.	d.	m.p.	b.p.	sol.
Fluorine							
hydride	HF		w	0.99(1)	−83	19	s
oxide	F$_2$O		w		−224	−145	
Gallium							
chloride(III)	Ga$_2$Cl$_6$		w		78	201	s
oxide(III)	Ga$_2$O$_3$	10	w		1740		sp.s
Germanium							
chloride(IV)	GeCl$_4$		w	1.9	−49.5	86.5	hyd.
oxide(IV)	GeO$_2$	7	w	4.7	1086		0.41
sulphide(IV)	GeS$_2$	10	w		800	dec.	0.45
Hydrogen (These compounds are listed under the other elements present)							
Iodine							
acid, iodic	HIO$_3$		w	4.6	dec.		316
chloride(I)	ICl	9	r	3.2	27	97	hyd.
chloride(III)	I$_2$Cl$_6$	M	o	3.2(1)	14	97	hyd.
fluoride(V)	IF$_5$		w	3.5(1)	−8	97	hyd.
fluoride(VII)	IF$_7$	M	w	2.8	sub.	5	hyd.
hydride	HI		w		−51	−35	s
oxide(IV)	IO$_2$		y	4.2	dec.		hyd.
oxide(V)	I$_2$O$_5$		w	4.8	dec.		hyd.
Iron							
bromide(III)	FeBr$_3$	8	r				hyd.
carbonate(II)	FeCO$_3$		bn	3.8	dec.		.006
chloride(II)	FeCl$_2$	8	y	3.0	670	1030	63
hydroxide(II)	Fe(OH)$_2$		g	3.4	dec.		.01
hydroxide(III)	Fe(OH)$_3$		o	3.9	dec.		sp.s
nitrate(III)	Fe(NO$_3$)$_3$		r				82
oxalate(II)	FeC$_2$O$_4$				dec.		.004
oxide(II)	FeO	1	bk	5.7	1380		sp.s
oxide(II/III)	Fe$_3$O$_4$	10	bk	5.2	dec.		sp.s
oxide(III)	Fe$_2$O$_3$	10	o	5.1	dec.		sp.s
phosphate(III)	FePO$_4$		y				sp.s

Compound	Formula		col.	d.	m.p.	b.p.	sol.
sulphate(II)	$FeSO_4$		w	3.1	dec		26.3
ammonium	$Fe(NH_4)_2(SO_4)_2$				dec.		26.4
sulphate(III)	$Fe_2(SO_4)_3$		y	3.1	dec.		hyd.
ammonium	$Fe(NH_4)(SO_4)_2$				dec.		44(25°)
sulphide(II)	FeS	5	bk	4.8	1195		.0006
Lead							
acetate(II)	$Pb(O_2CCH_3)_2$		w	3.2	280	dec.	44.3
acetate(IV)	$Pb(O_2CCH_3)_4$		w	2.2	175		hyd.
carbonate	$PbCO_3$		w	6.6	dec.		.00016
chloride(II)	$PbCl_2$	10	w	5.8	498	954	1.00
chloride(IV)	$PbCl_4$		w	3.2(1)	-15	dec.	hyd.
chromate	$PbCrO_4$		y	6.3	844	dec.	10^{-5}
hydroxide	$Pb(OH)_2$		w	7.6	dec.		.016
iodide	PbI_2	8	y	6.2	412	822	.068
nitrate	$Pb(NO_3)_2$		w	4.5	dec.		55
oxide(II)	PbO	8	y	9.5	890		.002
oxide(II/IV), (red lead)	Pb_3O_4	10	o	9.1	dec.		hyd.
oxide(IV)	PbO_2	7	bn	9.4	dec.		hyd.
sulphate	$PbSO_4$		w	6.2	1087		.004
sulphide	PbS	1	bk	7.5	1114		sp.s
Lithium							
bromide	$LiBr$	1	w	3.5	552	1310	177
carbonate	Li_2CO_3		w	2.1	618	dec.	1.33
chloride	$LiCl$	1	w	2.1	614	1350	83
fluoride	LiF	1	w	2.3	870	1670	0.13
hydride	LiH	1	w	0.8	680		hyd.
hydroxide	$LiOH$		w	2.5	462		13
iodide	LiI	1	w	4.1	440	1171	165
nitrate	$LiNO_3$		w	2.4	250	dec.	70
oxide	Li_2O	6	w	2.0	>1700		hyd.
sulphate	Li_2SO_4		w	2.2	857		35
Magnesium							
bromide	$MgBr_2$	8	w	3.7	711		104

Compound	Formula		col.	d.	m.p.	b.p.	sol.
carbonate	$MgCO_3$		w	3.1	dec.		.01
chloride	$MgCl_2$	8	w	2.3	712	1418	55
fluoride	MgF_2	7	w	3.0	1396		.009
hydroxide	$Mg(OH)_2$		w	2.4	dec.		.0009
iodide	MgI_2	8	w	4.2	dec.		138
nitrate	$Mg(NO_3)_2$		w				70
oxide	MgO	1	w	3.6	2640		sp.s
sulphate	$MgSO_4$		w	2.7	1185		33
Manganese							
acetate(II)	$Mn(O_2CCH_3)_2$		p	1.7			8
carbonate(II)	$MnCO_3$		p	3.1	dec.		.0065
chloride(II)	$MnCl_2$	8	p	3.0	650	1190	74
fluoride(II)	MnF_2	7	p	4.0	856		105
fluoride(III)	MnF_3	10	r	3.5	dec.		sp.s
hydroxide(II)	$Mn(OH)_2$		p	3.3	dec.		sp.s
nitrate(II)	$Mn(NO_3)_2$						138
oxide(II)	MnO	1	gy	5.2	1650		sp.s
oxide(II/III)	Mn_3O_4	10	bk	4.7	dec.		sp.s
oxide(III)	Mn_2O_3	10	bk	4.8	dec.		sp.s
oxide(IV)	MnO_2	7	bk	5.0	dec.		sp.s
oxide(VII)	Mn_2O_7		r	2.4(1)	liq.	dec.	hyd.
sulphate(II)	$MnSO_4$		p	3.2	700		63
Mercury							
acetate(II)	$Hg(O_2CCH_3)_2$		w	3.3	dec.		25
bromide(I)	Hg_2Br_2	M	y	7.3	sub.	345	4×10^{-6}
bromide(II)	$HgBr_2$	M	y	6.1	241	319	0.55
chloride(I)	Hg_2Cl_2	M	w	7.2	302	384	.00004
chloride(II)	$HgCl_2$	M	w	5.4	277	304	6.5
cyanide(II)	$Hg(CN)_2$		w	4.0	dec.		10
iodide(II)	HgI_2	8	o	6.3	250	354	.004
nitrate(I)	$Hg_2(NO_3)_2$		w				hyd.
nitrate(II)	$Hg(NO_3)_2$		w				hyd.
oxide(II)	HgO	9	y or r	11.1	dec.		.005
sulphate(I)	Hg_2SO_4		w	7.6	dec.		0.06

Compound	Formula		col.	d.	m.p.	b.p.	sol.
sulphate(II)	$HgSO_4$		w	6.5	850		hyd.
sulphide(II)	HgS, α	9	r	8.1	sub.	580	sp.s
	β	3	bk	7.7	sub.	446	sp.s
Molybdenum							
fluoride(VI)	MoF_6		w		17	36	hyd.
oxide(VI)	MoO_3	8	y	4.5	785	1150	0.18
sulphide(IV)	MoS_2	8	bk	4.8	118.5		sp.s
Nickel							
carbonate	$NiCO_3$		g		dec.		.009
chloride	$NiCl_2$	8	y	3.5	1000	987	62
hydroxide	$Ni(OH)_2$		g	4.4			.0013
iodide	NiI_2	8	bk	5.8	797		130
nitrate	$Ni(NO_3)_2$						94
oxide	NiO	1	gy	7.4	1990		sp.s
sulphate	$NiSO_4$		y	3.7	dec.		37
sulphide	NiS	5,10	bk	4.6	797		.0004
Nitrogen							
acid, hydra-zoic	HN_3		w		-80	37	s
acid, nitric	HNO_3		w	1.5(1)	-47	86	misc.
ammonia	NH_3	M	w	0.8(1)	-78	-33	53
hydrazine	N_2H_4	M	w	1.0(1)	1	114	s
sulphate	$N_2H_4 \cdot H_2SO_4$		w	1.4	254	dec.	2.8
hydroxyl-amine	NH_2OH		W	1.3	34	56	s
chloride	$NH_2OH \cdot HCl$		w	1.7	151	dec.	83
oxide(I)	N_2O		w		~103	-88	0.12
oxide(II)	NO		w		-164	-152	.0056
oxide(III)	N_2O_3		b		-102	3	hyd.
oxide(IV)	N_2O_4	M	bn		-9	21	hyd.
oxide(V)	N_2O_5	10	w		30	33	hyd.
nitrosyl chloride	$NOCl$		o		-65	-6	hyd.
sulphide	N_4S_4	M	o	2.2	sub.	179	hyd.

Compound	Formula		col.	d.	m.p.	b.p.	sol.
Oxygen							
hydride, (water)	H_2O	M	w	1.0	0	100	
hydrogen peroxide	H_2O_2	M ,	w	1.4	-2	158	misc.
Phosphorus							
acid, phosphoric	H_3PO_4		w	1.8	42	dec.	570
acid, phosphorous	H_3PO_3		w	1.6	74	dec.	s
acid, hypophosphorous	H_3PO_2		w	1.5	17	dec.	s
bromide(III)	PBr_3		w	2.8	-40	173	hyd.
bromide(V)	PBr_5	10	y		sub.	106	hyd.
chloride(III)	PCl_3		w	1.6	-91	74	hyd.
chloride(V)	PCl_5	10	w		148	164	hyd.
chloride, oxy	$POCl_3$		w	1.7	1	105	hyd.
fluoride(III)	PF_3		w		-160	-95	hyd.
fluoride(V)	PF_5		w		-92	-85	hyd.
hydride, (phosphine)	PH_3		w		-133	-88	sp.s
oxide(III)	P_4O_6		w	2.1	24	173	hyd.
oxide(V)	P_4O_{10} M,	10	w	2.4	569	591	hyd.
Potassium							
acetate	KO_2CCH_3		w	1.8	292	dec.	256
bromate	$KBrO_3$		w	3.3	dec		6.9
bromide	**KBr**	**1**	**w**	**2.7**	**742**	**1380**	**65**
carbonate	K_2CO_3		w	2.3	897	dec.	110
hydrogen	$KHCO_3$		w	2.2	dec.		33
chlorate	$KClO_3$		w	2.3	368	dec.	7.3
chloride	KCl	1	w	2.0	770	1407	34
chromate	K_2CrO_4		y	2.7	975	dec.	63
di-	$K_2Cr_2O_7$		o	2.7	398	dec.	12
cyanide	KCN		w	1.5	623		8
ferricyanide	$K_3Fe(CN)_6$		o	1.9	dec.		46
ferrocyanide	$K_4Fe(CN)_6$		y		dec.		28

Compound	Formula		col.	d.	m.p.	b.p.	sol.
fluoride	KF	1	w	2.5	857	1500	95
boro	KBF$_4$		w	2.5	dec.		s
silico-	K$_2$SiF$_6$		w	2.7			0.11
hydride	KH	1	w	0.8	dec.		hyd.
hydroxide	KOH		w	2.0	360	1327	112
iodate	KIO$_3$		w	3.9	560		8.1
iodide	KI	1	w	3.1	682	1324	144
nitrate	KNO$_3$		w	2.1	338	dec.	31.6
nitrite	KNO$_2$		w	1.9	297	dec.	300
oxalate	K$_2$C$_2$O$_4$		w				35
oxide, mono-	K$_2$O	6	w	2.3	dec.		hyd.
oxide, per-	KO$_2$	10	y				hyd.
perchlorate	KClO$_4$		w	2.5	dec.		1.65
perman- ganate	KMnO$_4$		v	2.7	dec.		6.4
periodate	KIO$_4$		w	3.6	582	dec.	0.4
phosphate	K$_3$PO$_4$		w		1340		s
dihydrogen	KH$_2$PO$_4$		w	2.3	96	dec.	23
phyro-	K$_4$P$_2$O$_7$		w	2.3	1090		s
sulphate	K$_2$SO$_4$		w	2.7	1074		11.1
hydrogen	KHSO$_4$		w	2.4	210	dec.	49
pyro-	K$_2$S$_2$O$_7$		w	2.3			s
per-	K$_2$S$_2$O$_8$		w				4.7
sulphide	K$_2$S	6	y	1.8	471		hyd.
thiocyanate	KSCN		w	1.9	179		217

Rubidium

Compound	Formula		col.	d.	m.p.	b.p.	sol.
bromide	RbBr	1	w	3.4	677	1352	110
carbonate	Rb$_2$CO$_3$		w		837	dec.	8
chloride	RbCl	1	w	2.8	717	1381	91
fluoride	RbF	1	w		833	1410	131
iodide	RbI	1	w	3.6	638	1300	150
nitrate	RbNO$_3$		w	3.1	305	dec.	53
sulphate	Rb$_2$SO$_4$		w	3.6	1060	dec.	48

Scandium

Compound	Formula		col.	d.	m.p.	b.p.	sol.
oxide	Sc$_2$O$_3$	10	w	3.9			sp.s

Compound	Formula		col.	d.	m.p.	b.p.	sol.
Selenium							
acid, selenic	H_2SeO_4		w	3.0	58	dec.	570
hydride	H_2Se		w				sp.s
oxide, di-	SeO_2	9	w	4.0	340	317	256
Silicon							
chloride	$SiCl_4$		w	1.5(1)	-68	57	hyd.
fluoride	SiF_4	0	w		-77	-95	hyd.
hydride	SiH_4		w	0.7(1)	-133	-14	hyd.
oxide	SiO_2	10	w	2.6	1700		sp.s
Silver							
acetate	AgO_2CCH_3		w	3.3	dec.		1.04
bromide	$AgBr$	1	y	6.5	430		sp.s
carbonate	Ag_2CO_3		w	6.1	dec.		.002
chloride	$AgCl$	1	w	5.6	455	1564	sp.s
chromate	Ag_2CrO_4		r	5.6			.0025
cyanide	$AgCN$		w	3.9	350		.00002
fluoride	AgF	1	w	5.9	435		170
iodide	AgI	4	y	5.7	557	1506	sp.s
nitrate	$AgNO_3$		w	4.4	209	dec.	217
nitrite	$AgNO_2$		w	4.5	dec.		0.34
oxalate	$Ag_2C_2O_4$		w	5.0	dec.		.0034
oxide	Ag_2O	10	bn	7.1	dec.		.002
perchlorate	$AgClO_4$		w.	2.8	dec.		525
phosphate	Ag_3PO_4		y	6.4	850		.0006
sulphate	Ag_2SO_4		w	5.5	657		0.8
sulphide	Ag_2S	10	bk	7.3	842		sp.s
thiocyanate	$AgSCN$		w		dec.		.00002
Sodium							
acetate	NaO_2CCH_3		w	1.5	324	dec.	146
arsenate, hydrogen	Na_2HAsO_4		w				39
arsenite	$NaAsO_2$		w	1.9			s
borate	$NaBO_2$		w		966	1450	25
borate, pyro-	$Na_2B_4O_7$		w				2.5
bromate	$NaBrO_3$		w	3.3	381		37

Compound	Formula		col.	d.	m.p.	b.p.	sol.
bromide	NaBr	1	w	3.2	747	1390	91
carbonate	Na$_2$CO$_3$		w	2.5	854	dec.	21
hydrogen	NaHCO$_3$		w	2.2	dec.		9.6
chlorate	NaClO$_3$		w	2.5	255		101
chloride	NaCl	1	w	2.2	800	1465	36
chromate	Na$_2$CrO$_4$		y				85
dichromate	Na$_2$Cr$_2$O$_7$		o				185
cyanide	NaCN		w		562	1496	59
ferricyanide	Na$_3$Fe(CN)$_6$		o				s
ferrocyanide	Na$_4$Fe(CN)$_6$		y				19
fluoride	NaF	1	w	2.8	992	1700	3.9
hydride	NaH	1	w	0.9			hyd.
hydroxide	NaOH		w	2.1	322	1378	109
hypochlorite	NaClO		w		dec.		s
hypophosphite	NaH$_2$PO$_2$		w		dec.		s
iodate	NaIO$_3$		w	4.3	dec.		8.5
iodide	NaI	1	w	3.7	662	1300	179
nitrate	NaNO$_3$		w	2.6	310	dec.	87
nitrite	NaNO$_2$		w	2.2	271	dec.	82
oxalate	Na$_2$C$_2$O$_4$		w	2.3			3.3
oxide	Na$_2$O	6	w	2.3	dec.		hyd.
per-	Na$_2$O$_2$		y		dec.		hyd.
perchlorate	NaClO$_4$		w		482	dec.	202
phosphate	Na$_3$PO$_4$		w		1340		12.1
hydrogen	NaHPO$_4$		w				7.9
dihydrogen	NaH$_2$PO$_4$		w				85
pyro-	Na$_4$P$_2$O$_7$		w	2.5	970		6.2
meta-	NaPO$_3$		w	2.5	988		s
silicate	Na$_2$SiO$_3$		w		1088		s
sulphate	Na$_2$SO$_4$		w	2.7	884		19.4
hydrogen	NaHSO$_4$		w	2.7	320		s
sulphite	Na$_2$S	6	w	1.9	120		19
sulphide	Na$_2$SO$_3$		w	2.6			26.5
thiocyanate	NaSCN		w		323		136
thiosulphate	Na$_2$S$_2$O$_3$		w	1.7	dec.		70

Compound	Formula		col.	d.	m.p.	b.p.	sol.
Strontium							
bromide	$SrBr_2$	10	w	4.2	643		102
carbonate	$SrCO_3$		w	3.7	1497		.001
chloride	$SrCl_2$	6	w	3.1	872		53
sulphate	$SrSO_4$		w	4.0	dec.		.01
Sulphur							
acid, sulphuric	H_2SO_4		w	1.8	10	dec.	misc.
pyro-	$H_2S_2O_7$		w	1.9	35	dec.	hyd.
bromide, thionyl	$SOBr_2$		w	2.7	-50	140	hyd.
chloride, di-	SCl_2		r	1.6	-80	59	hyd.
mono-	S_2Cl_2		o	1.7	-80	138	hyd.
sulphuryl	SO_2Cl_2		w	1.7	-54	69	hyd.
thionyl	$SOCl_2$		w	1.6	-104	75	hyd.
fluoride, hexa	SF_6		w	1.9(l)	-55	-63	
sulphuryl	SO_2F_2		w		-120	-52	hyd.
thionyl	SOF_2		w	2.9(l)	-110	-30	hyd.
hydride	H_2S		w		-83	-62	0.38
oxide, di-	SO_2	M	w	1.4(l)	-73	-10	11.3
tri-	SO_3, α trimer	M	w	1.9(l)	17	45	hyd.
		9	w		30		hyd.
Tellurium							
acid, telluric	H_6TeO_6		w	3.1	dec.		53
chloride, di-	$TeCl_2$		bk	7.1	175	324	hyd.
tetra-	$TeCl_4$		w		214	392	hyd.
oxide(IV)	TeO_2	7	y	5.9	sub.	450	hyd.
oxide(VI)	TeO_3		w	5.1	dec.		hyd.
Thallium							
bromide(I)	$TlBr$	2	y	7.6	460	815	.05
chloride(I)	$TlCl$	2	w	7.0	427	807	.33
fluoride(I)	TlF		w			300	80(15°)
oxide(I)	Tl_2O		y		300	dec.	hyd.

Compound	Formula		col.	d.	m.p.	b.p.	sol.
oxide(III)	Tl_2O_3	10	bk	10.2	759		hyd.
sulphate(I)	Tl_2SO_4		w	6.8	632	dec.	4.9
Thorium							
chloride	$ThCl_4$	10	w	4.6	820		s
nitrate	$Th(NO_3)_4$		w		dec.		190
oxide	ThO_2	6	w	9.7	>2800		10^{-6}
sulphate	$Th(SO_4)_2$		w		dec.		1.4
Tin							
bromide(II)	$SnBr_2$		w	5.1	232	620	s
bromide(IV)	$SnBr_4$		w	3.3(1)	30	202	hyd.
chloride(II)	$SnCl_2$		w		247	623	270
chloride(IV)	$SnCl_4$		w	2.2(1)	-33	113	hyd.
hydroxide(II)	$Sn(OH)_2$		w		dec.		.00016
oxide(II)	SnO	8	bk	6.9			sp.s
oxide(IV)	SnO_2	7	w	7.0	1127		sp.s
Titanium							
chloride(III)	$TiCl_3$	8	v		sub.	430	s
chloride(IV)	$TiCl_4$		w	1.7(1)	-23	136	hyd.
oxide	TiO_2	7	w	4.3	1825		sp.s
Tungsten							
oxide	WO_3	10	y	7.2	>2130		sp.s
Uranium							e,
acetate, uranyl	$UO_2(O_2CCH_3)_2$		y	2.9	dec.		7.7
chloride, uranyl	UO_2Cl_2		y				320
fluoride, hexa-	UF_6		y	4.7	69	56	hyd.
nitrate, uranyl	$UO_2(NO_3)_2$		y		dec.		122
oxide(IV)	UO_2	6	bn	10.9	2180		sp.s

Compound	Formula		col.	d.	m.p.	b.p.	sol.
oxide(VI)	UO_3	10	y	7.3	dec.		sp.s
oxide(IV/VI) (pitchblende)	U_3O_8	10	bk	7.3	dec.		sp.s
sulphate uranyl	UO_2SO_4		y	3.3	dec.		21
Vanadium							
chloride(II)	VCl_2	8	g	3.2	sub.	1000	s
chloride(III)	VCl_3	8	v	3.0	dec.		s
oxide, penta-	V_2O_5	8	o	3.6	800		hyd.
Xenon							
fluoride(IV)	XeF_4	M	w		90		hyd.
oxide(VI)	XeO_3		w				
Zinc							
acetate	$Zn(O_2CCH_3)_2$		w		dec.		40
bromide	$ZnBr_2$	8	w	4.2	394	650	450
carbonate	$ZnCO_3$		w				.07
chloride	$ZnCl_2$	8,10	w	2.9	283	732	368
chromate	$ZnCrO_4$		y				sp.s
fluoride	ZnF_2	7	w	4.8	872		1.6
hydroxide	$Zn(OH)_2$		w	3.1	dec.		.0004
Oxide	ZnO	4	w	5.5	1970		hyd.
sulphate	$ZnSO_4$		w	3.7	dec.		54
sulphide	ZnS	3,4	w	4.1	sub.	1645	.0007
Zirconium							
chloride	$ZrCl_4$		w			331	hyd.
oxide	ZrO_2	10	w	5.5	2720		sp.s

V.4 Glossary in Inorganic Chemistry

* ### Actinides

They include the last fifteen elements in the periodic table, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lw. The fourteen 5f electrons are added formally (though not necessarily actually) from Thorium (Z = 90), onward and the 5f shell is complete at Lawrencium (Z = 103). The energies of the 5f, 6d, 7s and 7p orbitals in the actinide series are comparable and they are prone to complex formation with π-bonding ligands like alkylphosphines and thioethers, as well as with ions like halides and sulphate. They form cationic species, the principal ions being M^{3+}, M^{4+}, MO_2^+, MO_2^{2+} for the oxidation states +3 to +6.

* ### Alloys

Mixtures of two or more metals. They can be simple mixtures, where the component metals are mutually insoluble in each other in the solid state or solid solutions, where the atoms of one component fit themselves into the crystal lattice of the other (substituted solid solutions or interstitial solid solutions).

* ### Back Bonding

The stability of transition metal carbonyls, for example, cannot be explained in terms of a simple metal-carbon σ-bond. It is assumed that in these compounds there is an additional metal-carbon π bond as a result of the overlap of filled $d\pi$ or hybrid $dp\pi$ metal orbital with an empty antibonding $p\pi$ orbital of the carbon monoxide (back bonding). Such back bonding is postulated in several systems such as silicon-nitrogen compounds and complexes of transition metals with trivalent phosphorus, arsenic etc.

* ### Catenation

Carbon and to a lesser extent other elements like sulphur and silicon show a tendency to form chains (or rings) of identical atoms. Only elements with a valence of at least two which forms strong bonds with itself will undergo catenation.

* ### Chelate Compounds

Polydentate ligands permit the attachment of two or more donor sites to the same metal ion simultaneously, thus giving rise to complexes possessing five- or six-membered rings. The name chelate stems from the Greek Chele or "claw".

* ### Clathrate Compounds

Compounds in which a molecule of one component is completely enclosed by one or more molecules of a second component in such a way that its escape is prevented unless the forces which bind its surrounding together are overcome. Their properties are roughly those of the enclosing material. Examples are hydroquinone compounds which have the approximate composition $(C_6H_6O_2)_3X$

(X = HCl, HBr, H_2S, CH_3OH, SO_2, CO_2, HCN etc.), phenol compounds like $(C_6H_6O)_4SO_2$, $(C_6H_6O)_5SO_2$, $(C_6H_6O)_8CO_2$ and certain compounds of the inert gases.

* ## Coordination Compounds (Complex Compounds)

Compounds formed by combinations of apparently saturated materials which are capable of independent existence. They cover a wide range of compounds and may contain either complex anions or cations or both, or they may be neutral molecules. These are indistinguishable in general form ordinary covalent compounds; although the bonding in some cases is more nearly ionic than covalent. They are also referred to as Werner complexes.

* ## Coordination Number

The total number of anions or molecules which may be directly associated with the cation in complex compounds. Common coordination members are 2,3,4,5 and 6. Coordination numbers 7, 8 and 9 are known to occur, but they are relatively rare and, with only few exceptions, confined to compounds of lanthanides and actinides.

* ## Crystal-Field Theory

Electrostatic models, which attempted to account for the properties of complex compounds on the basis of interactions between point charges and/ or dipoles, could not account satisfactorily for the existence of square-planar complexes. The theory was extended to describe the behaviour of metal ions in a crystal lattice, and also the properties of complexes, where the metal ion is under the influence of the charge field created by the ligands.

* ## Electron-Deficient Compounds

Elements with fewer valence electrons than valence shell orbitals (e.g., boron, aluminum, platinum) form covalent compounds in which there are insufficient electrons present to account for electron pair bonds among all the atoms present. Examples are the boron hydrides such as B_2H_6 and B_4H_{10}; the dimeric aluminum alkyls such as $[Al(CH_3)_3]_2$; the tetrameric platinum tetraalkyls such as $[Pt(CH_3)_4]_4$ and certain interstitial compounds.

Oxygen-containing acids in which several simple molecules are condensed

to give materials containing more than a single mole of anhydride. If a single type of anhydride is involved the acid is an isopoly acid, whereas if more than a single type of anhydride is present, the acid is a heteropoly acid. Examples of isopoly acids are polychromic acids, $H_2O.yCrO_3(y>1)$ and of heteropoly acids are polymolybdophosphoric acids, $mH_2O.P_2O_5.yMoO_3$ (y=12 or 24, most commonly).

* ## Isobars

Nuclei having the same mass number but different atomic numbers (e.g., Co^{60} and Cu^{60}) are isobars.

* <u>Isotopes</u>

     Atoms of the same element having different weights; they contain the same number of protons, but different numbers of neutrons.

* <u>Lanthanide Contraction</u>

     It consists of a significant and steady decrease in the size of the atoms and ions with increasing atomic number; lanthanum has the greatest and lutetium the smallest radius. The cause of the lanthanide contraction is due to the imperfect shielding of one electron by another in the same subshell. The nuclear charge and the number of 4f electrons increases by one at each step as we proceed through the lanthanide series. With each increase, the effective nuclear charge experienced by each 4f electron increases, thus causing a reduction in size of the entire 4f shell; the accumulation of these successive contractions is the total lanthanide contraction.

* <u>Nonstoichiometric Compounds</u>

     Compounds which do not possess the exact compositions as predicted from electronic considerations are referred to as nonstoichiometric compounds. Examples are certain metallic hydrides such as $VH_{0.56}$, $CeH_{2.69}$; certain oxides such as $TiO_{1.7}$; $TiO_{1.7-1.8}$; $Fe_{0.95}O$, $WO_{2.88-2.92}$; such sulphides, selenides and tellurides as $Cu_{1.7}S$, $Cu_{1.6}Se$, $Cu_{1.65}Te$, $CuFeS_{1.94}$; the tungsten bronzes, Na_xWO_3; etc. Lack of true stoichiometry of this type is associated with defect crystal lattices (Frenkel and Schottky defects.)

* <u>Octet Rule</u>

     It is an empirical rule which states that atoms tend to be surrounded by eight electrons in their compounds (in the valence shell). Violation of octet rule are common in compounds of elements beyond the first two eight-membered groups in the Periodic Table.

* <u>Oxidation Number</u>

     The charge which an atom appears to have when electrons are counted as per some arbitrary rules. Electrons shared between two unlike atoms are counted with the more electronegative atom and the electrons shared between two like atoms are divided equally between the sharing atoms. In the free elements, each atom, has an oxidation number of zero and in simple ions, the oxidation number is equal to the charge on the ion

* <u>Oxidation Potential</u>

     Inherent tendency toward electron gain or loss in a particular system can be measured as an electrical driving force and expressed as a potential value. They are commonly expressed relative to some arbitrarily selected standard. As bases for absolute comparison, standard oxidation potentials (E°) are employed; they characterize half-reactions at 25°C (298°K) in which all metals are considered as solids, all gases are taken to be at one atmosphere pressure, and all ions are measured at unit activity. As a standard of

reference, the reaction summarized by the equation

$$\tfrac{1}{2} H_2 \ (1 \ \text{atom.}) \rightleftharpoons H^+ \ (a = 1) + e^-$$
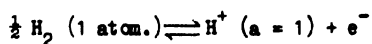
is assumed to have a potential value of zero at 25°C (i.e., $E^o_{298} = 0.000 \text{volt}$) and all other potentials are referred to this value.

* Radioactivity

Elements such as polonium (Z = 84) and radium (z = 88) having high nuclear charges and mass numbers show a tendency to emit radiation and disintegrate to newer elements. The types of emitted radiation are, α-rays (positively charged), β-rays (negatively charged) and γ-rays (noncharged). The decay of an element is commonly expressed in terms of its half-life period which is the time required for just one-half of the atoms of that type in a sample to decay.

* Decay Mechanisms of Some Common Radioactive Nuclides

Nuclide	Daughter Product	Emitted Particle	Associated Radiation	Half-life
$^{239}_{94}Pu \longrightarrow$	$^{235}_{92}U$ +	α +	γ	24,300 yrs
$^{238}_{92}U \longrightarrow$	$^{234}_{90}Th$ +	α +	γ	4.51×10^9 yrs
$^{235}_{92}U \longrightarrow$	$^{231}_{90}Th$ +	α +	γ	7.1×10^8 yrs
$^{232}_{90}Th \longrightarrow$	$^{228}_{88}Ra$ +	α +	γ	1.39×10^{10} yrs
$^{226}_{88}Ra \longrightarrow$	$^{222}_{86}Rn$ +	α +	γ	1620 yrs
$^{131}_{53}I \longrightarrow$	$^{131}_{54}Xe$ +	β^- +	γ	8.05 d.
$^{90}_{38}Sr \longrightarrow$	$^{90}_{39}Y$ +	β^-	(No γ)	28 yrs
$^{60}_{27}Co \longrightarrow$	$^{60}_{28}Ni$ +	β^- +	2 γ	5.2 yrs
$^{40}_{19}K \longrightarrow$ and	$^{40}_{20}Ca$ + $^{40}_{18}A$	β^- +	γ	1.3×10^9 yrs
$^{22}_{11}Na \longrightarrow$	$^{22}_{10}Ne$ +	β^+ +	γ	2.6 yrs
$^{14}_{6}C \longrightarrow$	$^{14}_{7}N$ +	β^-	(no γ)	5700 yrs
$^{3}_{1}H \longrightarrow$	$^{3}_{2}He$ +	β^-	(no γ)	12.26 yrs

* Origin and Properties of Nuclear Radiations

Radiation	Origin		Properties			
	Cause of Nuclear Instability	Mechanism	Type of Radiation	Mass (relative to hydrogen atom)	Charge (relative to proton)	Penetration (precise value depends on energy
α	Too many protons and neutrons (i.e high atomic mass)	Emission of helium nucleus (2protons + 2 neutrons)	particle	4	+2	Few cm of air
β^-	neutron:proton ratio too high	Conversion of neutron into proton $n \to p + \beta^- + \gamma$	particle	$\frac{1}{1840}$	-1	Up to few mm of aluminium
β^+	proton:neutron ratio too high	Conversion of proton into neutron $p \to n + \beta^+ + \gamma$	particle	$\frac{1}{1840}$	+1	Up to few mm of aluminium
γ	Excess energy (usually following particle emission)	De-excitation	electro-magnetic	-	-	Several cm of lead

V. 5 Inorganic Analysis

(i) **Qualitative Analysis:** Inorganic compounds are chiefly ionic in nature. In the separation of both cations and anions, different types of equilibrium are generally involved. The most important ones are, (a) solid-solution equilibrium (solubility product), (b) complex-ion equilibrium, (c) acid-base equilibrium and (d) oxidation-reduction equilibrium.

The solubility product principle has three important applications in qualitative analysis: (a) to predict the conditions under which the precipitate of an electrolyte is formed, (b) to predict the conditions under which a solid electrolyte may be expected to dissolve, and (c) to estimate the concentrations of ions in a saturated solution.

The important applications of complex formation in qualitative analysis are: (a) masking reactions in which an element or a compound is changed to an inactive form without effecting physical separation, (b) in precipitating ions, (c) for dissolving precipitates, and (d) in colour-forming reactions. Ammonia complexes such as $[Ag(NH_3)_2]^{2+}$, $[Cd(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)]^{2+}$ and sulphide complexes such as $(AsS_3)^{3-}$, $(AsS_4)^{3-}$, $(SbS_3)^{3-}$, $(SnS_3)^{2-}$, and $(HgS_2)^{2-}$ are examples.

Acid-base equilibrium is employed in the separation of several cations and the systems of primary interest are:

$$H_2S \rightleftharpoons HS^- + H^+ \quad ; \quad HS^- \rightleftharpoons S^= + H^+$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad ; \quad H_2O \rightleftharpoons H^+ + OH^-$$
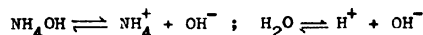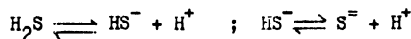
Tests for Cations: Cations commonly present in inorganic compounds can be classified under different groups, depending on their properties.

Group I: Includes Ag^+, Hg^+ and Pb^{2+}. They are characterized by the insolubility of their halides $(AgCl$, Hg_2Cl_2 and $PbCl_2)$ in dilute HCl.

Group II: The cations belonging to this group are Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sn^{2+}, Sn^{4+}, Sb^{3+} and Sb^{5+}. They all form sulphides which are insoluble in dilute HCl.

Group III A: Fe^{3+}, Al^{3+} and Cr^{3+} belong to this group and they all give hydroxides which are insoluble in a mixture of ammonium chloride and ammonium hydroxide.

Group III B: Includes Co^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}. They give sulphides (CoS, NiS, ZnS, MnS) which are insoluble in a mixture of ammonium hydroxide.

Group IV: The cations belonging to this group are Ba^{2+}, Sr^{2+}, Ca^{2+} and they are precipitated as their carbonates in alkaline medium (ammonium carbonate and ammonium hydroxide).

Group V: Cations like Mg^{2+}, NH_4^+, Na^+ and K^+ are identified by their

individual specific tests.

Tests for Anions: Some of the anions which are commonly encountered in simple inorganic compounds are: carbonate (CO_3^{2-}), nitrite (NO_2^-), nitrate (NO_3^-), sulphide (S^{2-}), sulphite (SO_3^{2-}), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), halides (F^-, Cl^-, Br^-, I^-), acetate ($CH_3CO_2^-$), oxalate ($C_2O_4^{2-}$) and tartarate ($C_4H_4O_6^{2-}$). These anions are detected on the basis of their behaviour towards several reagents like dilute hydrochloric acid, concentrated nitric acid, concentrated sulphuric acid and acetic acid.

Reaction of Anions with concentrated Sulphuric Acid:

   (a) Tartarates heated with H_2SO_4 turn brownish black and give an odour of burnt sugar.

   (b) Carbonates give off CO_2, which turns lime water milky.

   (c) Some sulphides give off H_2S (foul odour and it turns lead acetate-paper black).

   (d) Nitrites will give off brown fumes immediately (NO_2).

   (e) Bromides will oxidize slowly with the evolution of bromine vapours (reddish brown colour).

   (f) Iodides will liberate free iodine (purple colour).

   (g) Sulphites give off SO_2 (odour of burning sulphur).

   (h) Oxalates will give a mixture of CO and CO_2; the CO can be ignited.

   (i) Acetates heated with H_2SO_4 liberate acetic acid (odour of vinegar).

(ii) Quantitative Analysis: Quantitative procedures for the analysis of inorganic compounds are classified as gravimetric and volumetric, on the basis of the property which is measured.

* Gravimetric Analysis: It involves the separation of the desired constituent into a form which is of known percentage composition and which can be weighed accurately. Further classification of the methods of gravimetric analysis may be made on the basis of how the desired constituent is separated into a weighable form.

Precipitation Methods: A solution of the sample to be analyzed is treated with a reagent which can form an insoluble precipitate. For example, the chloride content of a sample may be determined by adding excess of silver nitrate to an aqueous solution of the sample, whereby silver chloride is precipitated. From the weight of the silver chloride obtained and the weight of the original sample, the percentage of chloride in the given sample may be calculated.

Electrodeposition Methods: The desired constituent is separated from a solution of the unknown sample by deposition on an electrode. This separation is based on the oxidizability or reducibility of the desired constituent at

the electrode. For example, copper can be determined by applying a voltage of sufficient magnitude to cause electrical current to flow between two platinum electrodes immersed in a moderately acidic solution of the sample. In course of time all the copper ions will be deposited upon the negative electrode as metallic copper, and the difference between the initial and final weights of this electrode indicates directly the copper content of the sample.

Volatilization Methods: The desired constituent is separated from the sample by virtue of its volatility with heat or with certain reagents. Two examples may be mentioned. The water of hydration of barium chloride crystals may be determined by heating the sample around 150° until no more loss of weight occurs. A second example is the determination of the CO_2 content of a carbonate sample. The sample is treated with acid to liberate CO_2 gas which is absorbed in a vessel containing an appropriate absorbant. The gain in weight of the absorbant indicates the amount of CO_2 gas liberated.

Volumetric Analysis: Measurements of volumes are involved in this method of analysis. Volumetric methods may be grouped under different headings depending on the mode of carrying out the determination or on the chemical principle underlying the method. These include titrimetric methods, optical methods and electrical methods. Of these, the most commonly used are the titrimetric methods.

Titrimetric Methods: A solution of the desired constituent is allowed to react with a standard solution of a reagent. Titrimetric methods may further be classified on the basis of the reaction between the desired constituent and the reagent, (a) <u>neutralization methods</u> (e.g., the determination of the carbonate content of soda ash by reaction with hydrochloric acid), (b) <u>precipitation methods</u> (e.g., volumetric determination of chloride ion employing silver nitrate), (c) <u>oxidation-reduction methods</u> (e.g., the determination of ferrous ion with a standard solution of ceric sulphate), (d) <u>complex formation methods</u> (e.g., determination of calcium ion by reaction with the sodium salt of ethylene diamine tetraacetic acid), and (e) <u>gasometric methods</u> (e.g., analysis of gaseous mixtures).

* Gravimetric Factor

It is the ratio of the formula weight of the substance sought to the formula weight of the substance known (weighed as), with the formula weights multiplied by appropriate digits which are relative numbers of each substance as indicated in the chemical equation relating the two substances. Few examples are given below:

Sought	Weighed on	Grav. factor
FeS_2	$BaSO_4$	$FeS_2/2BaSO_4$
P_2O_5	$Mg_2P_2O_7$	$P_2O_5/Mg_2P_2O_7$
Fe_3O_4	Fe_2O_3	$2Fe_3O_4/3Fe_2O_3$

V.6 Instrumental Methods of Analysis

(i) <u>Physical Properties Useful in Analysis</u>: The following are some of the physical properties which are applicable to chemical analysis. This list includes all properties which have been investigated in detail.

(a) <u>Extensive Properties</u>: (1) Mass (or weight), (2) Volume (of a liquid or a gas);

(b) <u>Mechanical Properties</u>: (1) Specific gravity (or density), (2) Surface tension (3) Viscosity (4) Velocity of sound (in a gas);

(c) <u>Properties Involving Interaction with Radiation</u>: (1) Absorption of radiant energy (X-rays, ultraviolet, visible, infrared, microwaves), (2) Turbidity, (3) Emission of radiation (following excitation), (4) Raman effect, (5) Rotation of the plane of polarized light, (6) Refractive index, (7) Dispersion, (8) Fluorescence and phosphorescence (9) Diffraction of X-rays and electrons, (10) Nuclear and electron magnetic resonance;

(d) <u>Electrical Properties</u>: (1) Half-cell potentials, (2) Current-voltage characteristics, (3) Electrical conductivity, (4) Dielectric constant, (5) Magnetic susceptibility;

(e) <u>Thermal Properties</u>: (1) Transition temperatures (melting or boiling points, etc.), (2) Heats of reaction (combustion, neutralisation etc.), (3) Thermal conductivity (of a gas);

(f) <u>Nuclear Properties</u>: Radioactivity.

(ii) <u>Optical Methods</u> Substances absorbing (for emitting) radiation in the ultraviolet, visible or infrared regions (see Section IV.7 for the discussion of Molecular Spectroscopy) can be determined quantitatively by optical methods if Beer's law is applicable. Optical methods are employed by inorganic, organic and biological chemists for single or multi-component quantitative analysis (see, Sec. IV.7A for a discussion of Beer's law).

* <u>Turbidimetry and Nephelometry</u>

The quantity of solid material in a colloidal suspension can be determined by measuring the transmitted (turbidimetry) or scattered (nephelometry) light.

* <u>Photometric Titration</u>

Absorbance at a wave-length when plotted against the volume of the reagent shows a sharp change at the equivalence point in certain acid-base or other titrations.

* <u>Fluorimetry</u> makes use of fluorescence of substances for analytical purposes.

* <u>Emission Spectrography</u> is employed for the determination of elements (particularly metals) in samples employing a spectrograph with prism or grating monochromator, photographic (later densitometer) or photoelectric detection, spark or arc excitation of solid samples and use of internal or external standards.

* **Flame Photometry** employs a gas flame as the light source for those elements in which emission is easily excited (e.g. Na, Ba, Sr, V, Ti).

* **X-Ray Absorption** is a particularly valuable tool for analysis where a sole heavy element is to be determined (e.g., sulfur in gasoline).

* **X-Ray Diffraction** is useful for the analysis of crystalline materials (mixture of different polymorphs of the same substance or of different substances).

* **X-Ray Emission** Analysis makes use of the fluorescence by a sample (target) irradiated by X-rays. This is good for trace analysis.

* **Polarimetry** makes use of the optical rotation of substances as the basis for analysis (e.g., sugar).

(iii) Electrochemical Methods

* **Potentiometry** involves the measurement of a reversible potential of a reversible electrode which in turn permits the calculation of the concentration of a component in solution (Nernst Equation).

* **Potentiometric Titrations** are titrations (acid-base, redox, etc.) in aqueous or non-aqueous media which can be followed by potentiometric measurements. pH titrations also form part of this kind of titrations.

* **Voltametry and Polarography:** If an electrolysis cell consists of one electrode which is polarizable and the other which is not, the system is easily studied by current-voltage curves. This method of determining the composition is generally called voltametry. If the polarizable electrode is dropping mercury, it is often referred to as polarography. The limiting current in the current-voltage curve (called the diffusion current) directly depends on the concentration of the reducible species.

$$i_d = 607n \; CD^{1/2} \; m^{2/3} \; t^{1/6} \quad \text{(Ilkovic equation)}$$

where i_d = diffusion current (a), n = no. of electrons involved in the cathodic reduction, C = concentration of reducible substance (millimoles/liter), D = diffusion coefficient (cm^2/sec), m = mass of mercury flowing through capillary (mg/sec) and t = time between successive drops (sec). Polarography can be employed for both inorganic and organic analysis.

* **Amperometric Titration** involves following the titration by the observation of diffusion current after successive additions of reagent.

* **Coulometry** is based on the application of Faraday's law of electrolysis for quantitative analysis and can be used for an electrochemical reaction with 100% current efficiency. In a coulometric titration, an electrolytically generated soluble species reacts quantitatively with the substance sought.

* **Conductimetry** is a method where analysis is carried out on the basis of the electrical conductance of the species (ions) in solution. The course

of a titration followed by conductance is called a <u>conductometric titration</u>. (e.g., complexation, acid-base or precipitation reactions).

(iv) <u>Radioactivity as a Tool in Analysis</u>: Radioactive isotopes with reasonable (a few hours to a few thousand years) half-lives are useful for analytical purposes. The radiation emitted by an isotope (detected by GM or scintillation or BF_3 counters depending on the radiation or particle emitted) provides the tool for analysis. Analysis of activity in samples bombarded by energetic particles provides the basis for <u>activation analysis</u>.

(v) <u>Mass Spectrometry</u> may be used for analysis of positively charged atomic or molecular ions produced by electron bombardment or photo-ionization. Ions differing in m/e exhibit different peaks in the mass spectrum. Mass spectrometry is used for determining molecular weights and fragmentation patterns of organic substances, besides as an analytical tool (e.g., petroleum fractions or gas-phase kinetics).

(vi) <u>Chromatography</u> is a technique by which separation of similar substances is achieved by differential migration. The sample is taken in the mobile phase (liquid or gas) and is passed through a column of the stationary phase (solid or liquid held by a solid). This technique is also used for quantitative analysis. Paper chromatography has now become a routine technique and can be made quantitative by the use of a spectrophotometer to scan the chromatograms. Gas (or vapor phase chromatography (VPC)) is ideal for the analysis of mixtures of organic liquids or low melting solids.

(vii) <u>Thermal Methods</u>

<u>Thermogravimetric Analysis</u> (TGA) allows to quantitatively study changes in the weight of a solid as a function of temperature. Along with <u>differential thermal analysis</u> (DTA), TGA is a useful tool for the study of solid state reactions. DTA measures heat changes due to transformations in the sample relative to an inert reference.

In <u>thermometric titrations</u>, the course of a reaction is followed by noting the heat liberated (e.g. benzene in cyclohexane, acid-base). These titrations are also known as enthalpy titrations.

V.7 <u>Bibliography</u>

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PERIODIC TABLE

IA																	O
1 H	IIA											IIIA	IVA	VA	VIA	VIIA	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 A
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 †Ac															

* Lanthanoid Series

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

† Actinoid Series

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99	100			

VI ORGANIC CHEMISTRY

VI.1 Nomenclature

The following rules for the naming of organic compounds are largely based on the "Definitive Rules for the Nomenclature in Organic Chemistry", adopted by the International Union of Pure and Applied Chemistry. For a detailed description, see, Journal of the American Chemical Society, 82, 5545 (1960).

* Acyclic Hydrocarbons

Saturated acyclic hydrocarbons (C_nH_{2n+1}) are called alkanes, the first four being methane, ethane, propane and butane. Higher members of this series contain a numerical prefix (e.g., penta) indicating the number of carbon atoms and the ending "ane", e.g., pentane C_5H_{12}, decane $C_{10}H_{22}$, eicosane $C_{20}H_{42}$. Branched chain hydrocarbons are named by prefixing the designations of the side chain to the name of the longest chain present in the formula, the longest chain being numbered from one end to the other by arabic numerals. The direction is so chosen as to give the lowest numbers possible to the side chains: e.g., 3-methylhexane, $CH_3CH_2CH_2\overset{4}{C}H\overset{3}{C}H_2\overset{1}{C}H_3$ where several
$\overset{6}{}\ \overset{5}{}\ \overset{4}{}\ \overset{CH_3}{\underset{2}{}}\ \overset{1}{}$
different side chains are attached, the order of stating them is either according to increasing complexity (e.g., methyl, ethyl, propyl, butyl) or

according to alphabetical order: e.g., $CH_3CH_2CH_2\overset{4}{C}H-\overset{3}{C}HCH_2CH_3$ is 4-ethyl-3-
$\overset{7}{}\ \overset{6}{}\ \overset{5}{}\ \overset{CH_3CH_2CH_3}{}\ \overset{}{}\ \overset{2}{}\ \overset{1}{}$
methylheptane.

Unbranched acyclic hydrocarbons containing one double bond are named by replacing the ending "ane" of the name of the corresponding saturated hydrocarbon with the ending "ene". If there are two or more double bonds, the ending will be "adiene", "atriene", etc. The names ethylene for $CH_2=CH_2$ and allene for $CH_2=C=CH_2$ are retained in the systematic nomenclature. The numbering of the carbon chain containing double bonds is done in such a way as to give the lowest possible numbers to the double bonds: e.g., 1-petene, $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$ and 1,4-hexadiene, $\overset{6}{C}H_3\overset{5}{C}H=\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$.

Unsaturated branched acyclic hydrocarbons are named as derivatives of the unbranched hydrocarbons which contain the maximum number of double bonds

e.g., 5,5-dimethyl-1,3-heptadiene, $\overset{7}{C}H_3\overset{6}{C}H_2-\overset{5}{\underset{CH_3}{\overset{CH_3}{C}}}-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$

Unsaturated hydrocarbons having one triple bond are named by replacing the ending "ane" of the name of the corresponding hydrocarbon with the ending "yne". The first member of the series H-C≡C-H is called acetylene. If there are two or more triple bonds, the ending will be "adiyne", "atriyne" etc., e.g., 1-butyne, $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}≡\overset{1}{C}-H$; and 1,4-heptadiyne, $\overset{7}{C}H_3\overset{6}{C}H_2-\overset{5}{C}≡\overset{4}{C}-\overset{3}{C}H_2-\overset{2}{C}≡\overset{1}{C}-H$

Unsaturated acyclic hydrocarbons having both double and triple bonds are named by replacing the ending "ane" of the name of the corresponding saturated hydrocarbon with the ending "eyne", "adienyne", "atrienyne", "enedienyne" etc. e.g., 1,3-hexadien-5-yne, $H-\overset{6}{C}≡\overset{5}{C}-\overset{4}{C}H=\overset{3}{C}H\overset{2}{C}H=\overset{1}{C}H$; 3-penten-1-yne $\overset{5}{C}H_3\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}≡\overset{1}{C}-H$; and 1-penten-4-yne, $H-\overset{5}{C}≡\overset{4}{C}-\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2$.

* ## Cyclic Hydrocarbons

The names of saturated monocyclic hydrocarbons (C_nH_{2n}) are formed by attaching the prefix "cyclo" to the name of the saturated unbranched Hydrocarbon with the same number of carbon atoms: e.g., cyclopropane, C_3H_6; cyclopentane, C_5H_{10}.

The names of unsaturated monocyclic hydrocarbons are formed by substituting "ene", "adiene", "atriene", "yne" etc. for "ane" in the name of the corresponding hydrocarbon.

Cyclohexene   1,3-Cyclohexadiene   1-Cyclodecen-4-yne
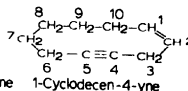
* ## Groups (Radicals)

Univalent groups (radicals) derived by removal of hydrogen from a terminal carbon atom are named by replacing the ending "ane" of the name of the hydrocarbon by "yl": e.g., pentyl, $CH_3(CH_2)_4-$. Univalent, branched groups are named using the largest branch as a parent structure and assigning the number 1 to the carbon atom having a free valence: e.g.,

1-methylpentyl, $CH_3CH_2CH_2CH_2CHCH_3$ $\overset{5\ \ 4\ \ 3\ \ 2\ \ 1}{}$. The common names of a number of groups

are retained in the systematic nomenclature: e.g., isopropyl, $(CH_3)_2CH-$; isobutyl, $(CH_3)_2CHCH_2-$; sec-butyl, $CH_3CHCH_2CH_3$; tert-butyl, $(CH_3)_3C-$;

isopentyl, $(CH_3)_2CHCH_2CH_2-$; neopentyl, $(CH_3)_3CCH_2-$; tert-pentyl $CH_3CH_2C(CH_3)_2$; vinyl, $CH_2=CH-$; allyl, $CH_2=CHCH_2-$; benzyl, $C_6H_5CH_2-$ and phenyl, C_6H_5-.

* ## Functional Groups

Compounds containing functional groups are named by shortening the endings "ane", "ene" and "yne" of the names of the hydrocarbon to "an" "en" and "yn" and then adding an additional ending to indicate the nature of the functional group. Few examples are given below:

HCO_2H

Methanoic acid
(Formic acid)

$HO_2C(CH_2)CO_2H$

Octanedioic acid

$CH_3CH_2CH_2OH$

Propanol

$CH_3CH=CHCCH_3$

3-Penten-2-one

$CH_3CH_2CH_2CHO$

Butanal

$CH_3CHCH_2C-NH_2$ (with OH and O substituents)

3-Hydroxypentanoic amide

$CH_3CH-CH-CN$ (Cl and NH_2 substituents)
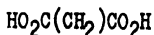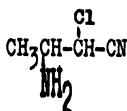
3-Amino-2-chloro-butanonitrile

$CH_3CH_2CHCOCl$ (Br substituent)
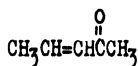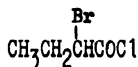
2-Bromobutanoyl chloride

$HC\equiv C-C\equiv CCH_2CO_2H$
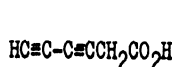
Hexa-3,5-diynoic acid

When two or more different functional groups occur within the same molecule, only one suffix can be used to form a systematic name. The other functional

groups must be considered as substituents: e.g., $HOCH_2CH_2\overset{\text{O}}{\overset{\|}{C}}CH_3$ is 4-hydroxy-2-butanone and not 4-butanol-2-one. The following order of preference is followed in assigning the principal functional group.

(a) First preference is given to acidic groups and to other groups that by their nature should terminate chains: e.g., $-CO_2H$, $-SO_3H$, $-SO_2NH_2$, $-SO_2R$, $-CONH_2$, $-CN$, $-CO_2R$, $-CHO$.

(b) Groups like keto, amino and hydroxyl are given last preference and in the order $CO > N > OH$.

(c) All other groups are listed as substituents.

* Table of Prefixes and Endings generally used

Functional Class	Prefix	Ending
Acid (Carboxylic)	carboxy	oic acid
Alcohol	hydroxy	ol
Aldehyde	oxo, aldo, or formyl	al, carboxaldehyde
Amide	carboxamido	amide, carboxamide
Amine	amine	amine
Double bond	–	ene
Ether	alkoxy, or aryloxy	–
Ethylene oxide	epoxy	–
Halide	halo	–
Ketone	oxo or keto	one
Mercaptan	mercapto	thiol
Nitrile	cyano	nitrile
Nitro	Nitro	–
Nitroso	nitroso	–
Nitrogen (quaternary)	–	onium, inium
Sulphide	alkylthio or arylthio	–
Triple bond	–	yne

* Aromatic Hydrocarbons (Arenes)

The parent member of this series is benzene (C_6H_6). The trivial names of a number of fused polycyclic hydrocarbons are retained in the systematic nomenclature.
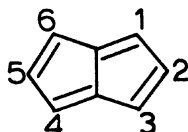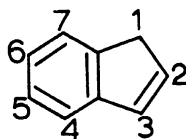
Benzene   Pentalene   Indene   Naphthalene
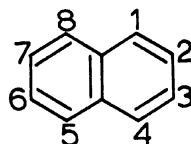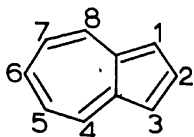
Azulene
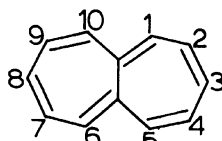
Heptalene
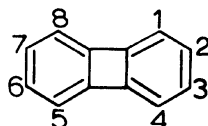
Biphenylene
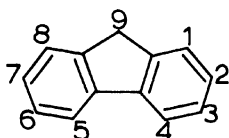
Fluorene
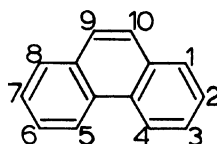
Phenanthrene
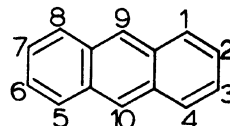
Anthracene
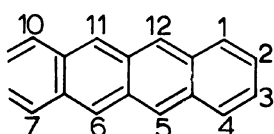
Naphthacene
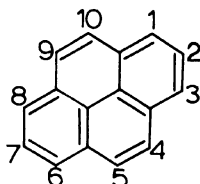
Pyrene
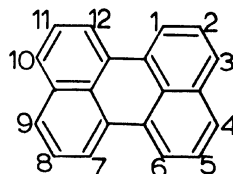
Perylene

The position of substituents in arenes is indicated by numbers. In benzene, when only two substituents are present, their positions 1,2-, 1,3-, and 1,4- may be indicated as o-(ortho), m-(meta) and p-(para), respectively.

1,2-Dichlorobenzene
(O-Dichlorobenzene)

1-Methyl-3-nitrobenzene
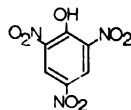
2,4,6-Trinitrophenol

* **Bridged compounds**

        Saturated alicyclic hydrocarbons containing two rings and having two or more atoms in common, take the name of an open chain hydrocarbon having the same total number of carbon atoms, preceded by the prefix "bicyclo". The number of carbon atoms in each of the three bridges connecting the two tertiary carbon atoms is indicated in brackets in descending order. Numbering commences from one of the bridge-head atoms and along the longest possible length to the second bridge-head; numbering is then continued from this atom by the longer unnumbered path back to the first bridge-head and is completed by the shortest path: e.g.,

Bicyclo[1 1 0]butane

Bicyclo [2 2 1] hept-2-ene
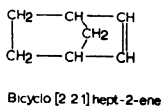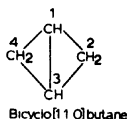
A polycyclic ring is regarded as containing a number of rings equal
to the number of scissions required to convert the system into an open chain
compound. These compounds are named by using the appropriate prefix "tricyclo"
"tetracyclo" etc., before the name of the open chain hydrocarbon containing
the same total number of carbon atoms. The numbering is done the same way
as in the case of bridged bicyclic compounds except that in this case the
numbers within the square bracket indicates the number of carbon atoms in the
two branches of the main ring, the main bridge, and the secondary bridges.
The location of the secondary bridges are shown by superscripts following
the number indicating the number of carbon atoms in the said bridges; e.g.,

Tricyclo [5.3.0.0^{2,6}] decane

Tricyclo [5.4 0 0^{2,9}] undecane
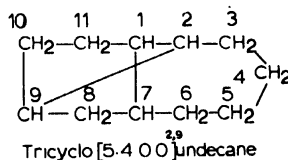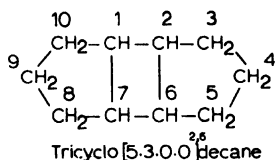
* **Spiro Hydrocarbons**

    Spiro compounds are distinguished as monospiro, dispiro, etc. depend-
ing on the number of "spiro unions" present. Monospiro compounds are named
by placing "spiro" before the name of the normal acyclic hydrocarbon of the
same total number of carbon atoms. The carbon atoms are numbered consecutive-
ly starting with a ring atom next to the spiro atom, first through the smaller
ring (if such be present) and then through the spiro atom and around the
second ring: e.g.,

Spiro[4 5]decane

Spiro[4 5]deca -1,6-diene
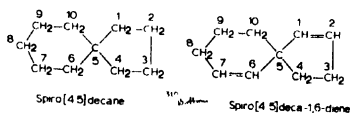
* **Heterocyclic Compounds**

    Rules for naming heterocyclic compounds are extensive and only a
brief summary is given. The trivial names of a large number of ring systems
have been accepted by the IUPAC system. An extension of the Hantzch-Widman
system is also employed. ·In this system, monocyclic compounds containing
one or more hetero atoms in three to ten membered ring are named by combining
the appropriate prefix or prefixes, which indicate the nature of the hetero
atom present, with stems which indicate the size of the ring. The prefixes
characteristic of common hetero atoms are listed in parenthesis: Oxygen (oxa),
sulphur (thia), selenium (selena), tellurium (tellura), nitrogen (aza),
phosphorus (phospha), arsenic (arsa), antimony (stiba), bismuth (bisma),
silicon (sila), germanium (germa),tin (stanna), lead (plumba) and mercury
(mercura).

The following table lists the stems commonly used, to denote the
size of the rings. The stems listed in columns 2 and 4 under "unsaturation"
are used for naming rings that contain the maximum number of conjugated
double bonds. The names listed in the "saturation" columns are used only
for compounds containing no double bonds. Compounds of intermediate degrees
of unsaturations are named by using prefixes dihydro, tetrahydro, etc., with
the unsaturated name.

No. of members in the ring	Rings containing Nitrogen		Rings containing no Nitrogen	
	Unsaturation	Saturation	Unsaturation	Saturation
3	-irine	-iridine	-irene	-irane
4	-ete	-etidine	-ete	-etane
5	-ole	-olidine	-ole	-olane
6	-ine	*	-in	-ane
7	-epine	*	-epin	-epane
8	-ocine	*	-ocin	-ocane
9	-onine	*	-onin	-onane
10	-ecine	*	-ecin	-ecane

* In these cases "perhydro" is prefixed to the name of the
corresponding unsaturated compound.

Some representative examples of names are indicated below:

Oxirane   Azirine   1-Methyl-1,3-oxazetidine

The following list contains the accepted names of some of the
heterocyclic ring systems in organic chemistry. For an extensive listing
of ring compounds and systems, see the annual subject index of Chemical
Abstracts; Patterson, Capell and Walker: "The Ring Index", 2nd edition (1959),
McGregor and Werner, Inc.

Furan   Thiophene   Pyrrole   Pyrazole   Imidazole

Isoxazole   Oxazole   Thiazole   2H-Pyran   1,2-Pyrone

Pyridine   Pyridazine   Pyrimidine   Pyrazine   1,3,5-Triazine
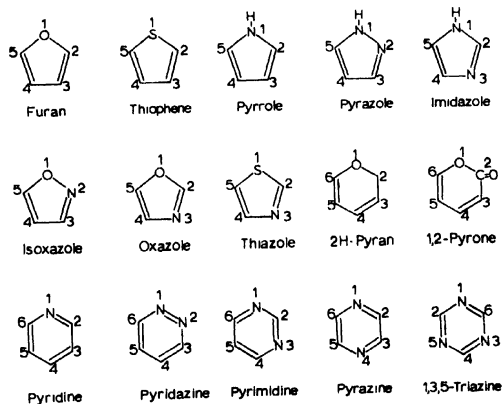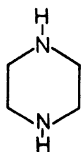
Piperazine
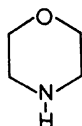
Morpholine
(Tetrahydro 1,4-
isoxazine)
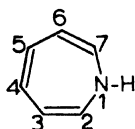
Azepine
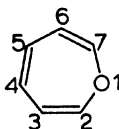
Oxepin
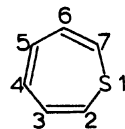
Thiepin
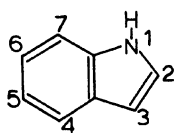
Indole
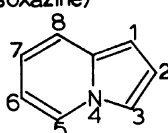
Indolizine
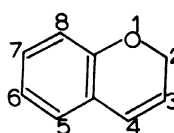
2H-Chromene
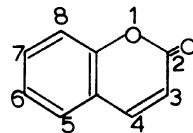
1,2-Benzpyrone
(Coumarin)
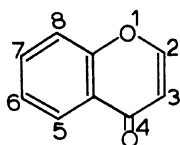
1,4-Benzopyrone
(Chromone)
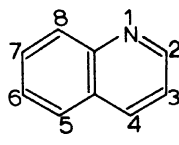
Quinoline
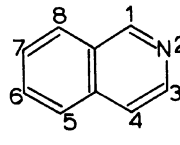
Isoquinoline
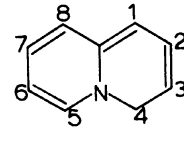
4H-Quinolizine
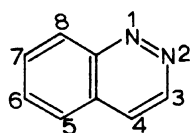
Cinnoline
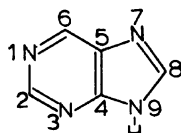
Purine
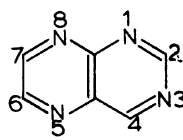
Pteridine
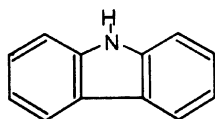
Carabazole
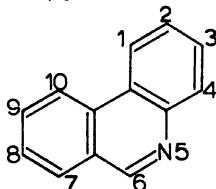
Phenanthridine
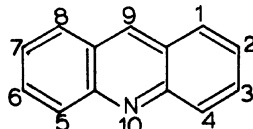
Acridine

VI.2 Organic Reactions

Organic reactions are essentially bond breaking and making processes. Homolytic fission of a bond occurs either thermally or photochemically giving rise to free-radical intermediates. Heterolytic fission leads to ionic intermediates (carbonium ions, carbanions, etc.) and such reactions are often catalyzed by acids or bases and are influenced strongly by variations in the polarity of the solvent.

* Reaction Intermediates

Most organic reactions involve the formation of short-lived ($\sim 10^{-12}$ sec), intermediates. Common reaction intermediates include, carbonium ions, carbanions, free-radicals, carbenes, nitrenes, unstable molecules and excited states of molecules.

Carbonium Ions ($-\overset{|}{C}\oplus$): A carbonium ion can be regarded as a fragment of an organic molecule in which an atom or a group of atoms has been removed with a pair of electrons in a heterolytic cleavage. The carbon atom bearing the positive charge is generally sp^2 hybridized and is planar.

Carbanions ($-\overset{|}{C}\ominus$): Carbon anions formed in a heterolytic bond fission are isoelectronic with amines. They probably have a pyramidal shape.

Free radicals ($-\overset{|}{C}\bullet$): Neutral (unchanged) species formed by the homolysis of a covalent bond and may either be planar or pyramidal in shape.

Carbenes ($\supset C\colon$) and Nitrenes ($-\overline{N}$): Diavalent carbon compounds (carbenes) have only a transient existense and are of two kinds, one in which the spins of the two electrons are paired (singlet state) or unpaired (triplett state).

Nitrenes are electron deficient and neutral species formed in certain reactions (e.g., photochemical decomposition of organic azides).

Unstable Molecules: Many unstable molecules like $\propto$-acetolactone, benzyne etc. are formed as intermediates in organic reactions. They undergo further reaction and only end products are isolated.

$$CH_2 - C = O$$
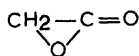
α -Acetolactone   Benzyne

Excited States of Molecules: In photochemical reactions, for example, molecules absorb energy and are converted into their excited states in which electrons occupy high-energy orbitals. These are highly reactive species.

* Classification of Reagents

Reagents are classified as electrophiles (electron-attracting) and

nucleophiles (nucleus-attracting). Examples of electrophilic reagents are, electron deficient species (both positively charged and neutral) and substrates containing polarizable groups.

$$H^+ \, . \, R^+, \quad Br^+, \, NO_2^+, \, BF_3, \quad AlCl_3, \, ZnCl_2, \, SO_3, \, R\overset{O}{\overset{\|}{C}}\!-R', \text{ etc.}$$
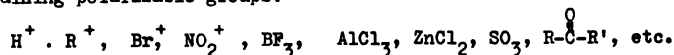
Nucleophilic reagents are attracted towards electron deficient centres and they include negatively charged species or neutral species containing lone pairs of electrons.

$$H^-, \, R^-, \, OH^-, \, Cl^-, \, Br^-, \, I^-, \, CN^-, \, CH_3CO_2^-, \, H_2O, \, NH_3, \, R\text{-}OH, \, RNH_2, \, R_3N, \text{ etc.}$$
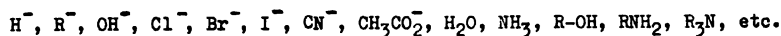
* Types of Organic Reactions

The three fundamental types of organic reactions are substitution, addition and elimination.

* Substitution Reactions

In a substitution reaction one atom or a group is displaced by another atom or group. Depending on the nature of the reactants, substitution reactions are classified as nucleophilic substitution at saturated carbon, nucleophilic substitution at unsaturated carbon, electrophilic substitution and radical substitution.

Nucleophilic Substitution at Saturated Carbon: In reactions of this type, a nucleophile (amines and substances containing lone pairs of electrons) displaces a leaving group attached to a saturated carbon atom. The reaction of methyl chloride with hydroxide ion, for example, gives methanol. Based on kinetic data and stereochemical studies, nucleophilic displacements at saturated carbon can be distinguished as S_N2, S_N1, and $S_N i$ reactions.

$$HO^- \quad + \quad CH_3\text{-}Cl \quad \longrightarrow \quad HO\text{-}CH_3 + Cl^-$$

S_N2 Reaction (Nucleophilic substitution, second-order): The reaction of (-) 2-bromooctane with sodium hydroxide to give (+) 2-octanol is an example.

(-) 2-Bromooctane   Activated complex   (+)2-Octanol
                         (Transition state)
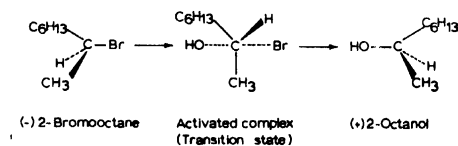
Reactions of this type follow second order kinetics and proceed with inversion in configuration at the asymmetric centre (Walden inversion). The order of reactivity of simple alkyl halides in S_N2 reactions is, primary > secondary > tertiary.

S_N1 **Reaction (Nucleophilic substitution, first-order):** The hydrolysis of tert-butyl bromide to give tert-butanol proceeds through a two-step process, of which the first step is the rate determining one.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \xrightarrow{Slow} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\bullet \xrightarrow{H_2O} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$
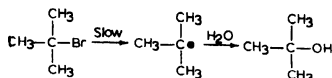
S_N1 reactions, generally proceed with recemization. In S_N1 reactions, the order of reactivity of simple alkyl derivatives is, tertiary > secondary > primary. Good ionic solvents favour these reactions.

$S_N i$ **Reaction (Nucleophilic substitution, internal):** The reaction of optically active α-phenyl ethanol with thionyl chloride proceeds with retention in configuration. It involves an internal attack of the chlorine atom in the chlorosulphite intermediate.
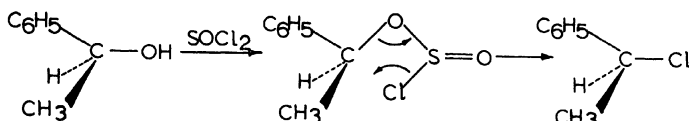
S_N2', S_N1' and S_Ni' reactions are analogous to S_N2, S_N1, and S_Ni type of displacements, but they proceed with rearrangement.

Nucleophilic substitution at unsaturated carbon: Reactions of this type involve substitutions at a carbon atom that is attached by a double bond to oxygen, sulphur, nitrogen or other carbon atoms. They proceed through a multistep process involving the initial addition of a nucleophile, followed by elimination. The reaction of benzoyl chloride with ethanol, for example, gives ethyl benzoate.

Electrophilic substitution: Substitution reactions in which the attacking regents are electrophiles like Br^+, NO_2^+, RCO^+, SO_3, etc. Most substitution reactions of aromatic compounds come under this category. The example of the nitration of benzene is given below:
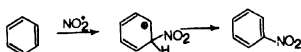
Addition Reactions

Unsaturated compounds (containing double and triple bonds) undergo addition reactions. These reactions can be classified as nucleophilic, electrophilic, cycloadditions, etc., depending upon the reaction conditions and mechanistic details.

Nucleophilic Additions: Addition reactions of carbonyl compounds come under this class. The example of cyanohydrin formation is illustrated. This reaction is base-catalyzed and the role of the
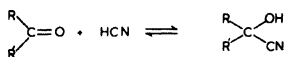
base is to provide free CN⁻ ions

Electrophilic Additions: Acid-catalyzed hydration of olefins, addition
of hydrogen halides and bromine to multiple bonds, etc., are examples
of electrophilic addition. The acid-catalyzed hydration of olefins can
be pictured as follows:
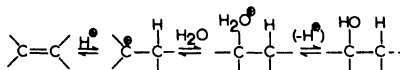
The stereochemistry of such addition is trans. A bromonium ion
intermediate is involved in the bromine-addition to olefins. Addition
of bromine to trans-2-butene gives meso-2,3-dibromobutane, whereas,
the product from cis-2-betene is dl-2,3-dibromobutane.

| trans-2-Butene | Bromonium ion
Intermediate | meso-2,3-Dibromobutane |
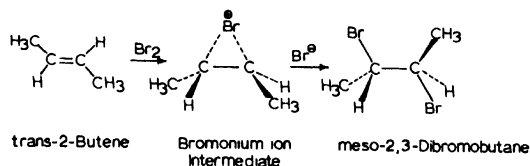
Cycloadditions: Addition reactions in which a reagent adds to a
double bond by simultaneous attack on both the carbon atoms (attached
to the double bond). Addition of carbenes to olefins (1,1-addition),
cyclodimerization of olefins (1,2-addition), the Huisgen reaction
(1,3-addition) and the Diels-Alder reaction (1,4-addition) are all cases
of cycloadditions. Representative examples are listed below:

Cyclohexene Dichlorocarbene Adduct   1,1-Addition

Tetrafluoroethylene   Perfuoro-   1,2-Addition
                       cyclobutane

Phenylazide Acetylenicester Triazole   1,3-Addion
                                           (Huisgen Reaction)

Cyclopentadiene Acrylonitrile Adduct   1,4-Addition
                                           (Diels-Alder Reaction)
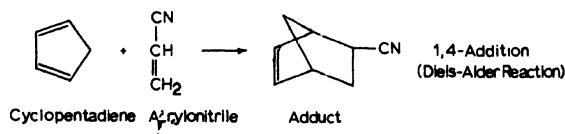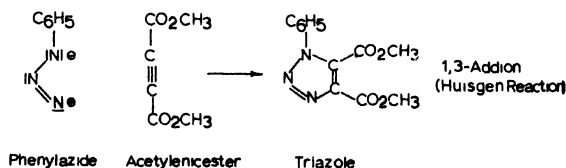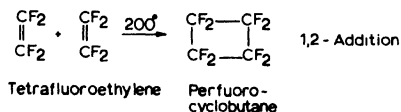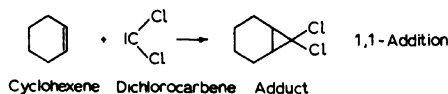
* Elimination Reactions

Elimination reactions are the reverse of addition reactions and are classified as α-eliminations, 1,2-eliminations (or β), 1,3-eliminations etc., depending on the positions of the two leaving groups in the parent molecule.

α-Eliminations: Both groups leave from the same carbon. The reaction of chloroform with alkali gives rise to a dichlorocarbene intermediate.
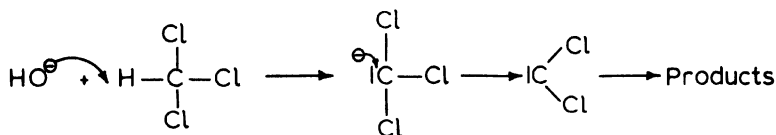
β-Elimination (or 1,2-Elimination): In a β-elimination, two groups are lost from neighbouring atoms, to form a carbon-carbon double bond. Different mechanisms (E_1, E_2 and E_1cB) can be operating in β-eliminations.

The E_1 Mechanism (Elimination Unimolecular): The base-catalyzed elimination of hydrogen chloride from tert-butyl chloride involves the initial ionization of the halide (by a slow step) to give a carbonium ion, which then looses a proton giving rise to isobutylene.
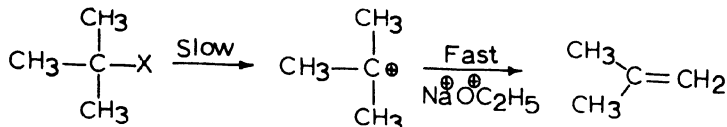
The E_1 elimination and S_N1 reaction often occur simultaneously.

The E_2 Mechanism (Elimination Bimolecular): If ethyl bromide is heated in the presence of a strong base (e.g. sodium ethoxide) elimination of HBr occurs and ethylene is formed. The rate of olefin formation is proportional to both ethyl bromide and ethoxide ion concentrations.
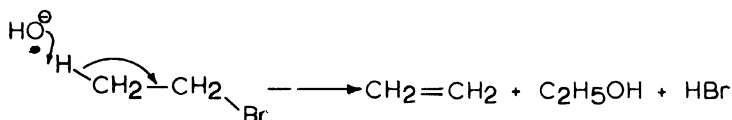
Where there is a possibility for the formation of a mixture of olefins, the product ratio is governed by several factors (see, Hofmann and Saytzeff's rules under section VI.4). The stereochemistry of E_2 eliminations supports the picture of a concerted trans-elimination.

The E_1cB Mechanism (Elimination Unimolecular Conjugate Base): The ionization of a proton occurs before the loss of the other leaving group. Such a process can only occur if the carbanion is strongly stabilized and if the leaving group is sufficiently poor that it will not be lost from the developing anion by an E_2 elimination.

$$-\overset{|}{\underset{|}{C}}-\overset{X}{\underset{|}{C}}- \quad \overset{B^{\ominus}}{\underset{Fast}{\rightleftharpoons}} \quad \overset{X}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad \overset{(-X^{\ominus})}{\underset{Slow}{\longrightarrow}} \quad \rangle C=C\langle$$
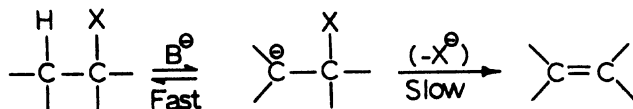
1,3-Eliminations: Example of the formation of cyclopropane from 1,3-di-bromopropane.

$$BrCH_2CH_2CH_2Br \xrightarrow{Zn} \overset{CH_2}{\underset{H_2C-CH_2}{\triangle}} + ZnBr_2$$
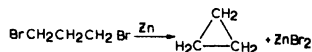
Thermal Eliminations: Elimination occurs by a unimolecular process without the attack of external reagents. The pyrolysis of esters, xanthates and amine oxides are examples. These eliminations are of the cis-type

$$\xrightarrow{500°} \rangle C=C\langle + CH_3CO_2H$$

Acetate pyrolysis

$$\xrightarrow{300°} \rangle C=C\langle + CH_3SH + COS$$

Xanthate pyrolysis

$$\longrightarrow \rangle C=C\langle + (CH_3)_2 N-OH$$

Amine oxide pyrolysis
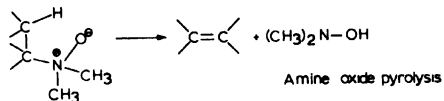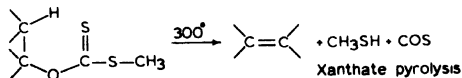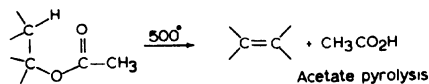
* Free Radical Reactions

Reactions involving free-radical intermediates occur either in the gas phase or in solution (mostly non polar solvents). They are of two types, substitutions and additions.

Radical Substitution: Photochlorination of methane gives rise to a mixture of halogenated products and is an example of a radical substitution. These reactions proceed by a free-radical chain mechanism

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \longrightarrow CH_2Cl_2 \longrightarrow CHCl_3 \longrightarrow CCl_4$$
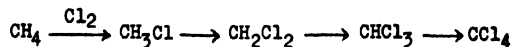
as is illustrated in the formation of CH_3Cl.

$$Cl_2 \xrightarrow{hv} Cl \xrightarrow{CH_4} CH_3 \xrightarrow{Cl_2} CH_3Cl + Cl\cdot$$
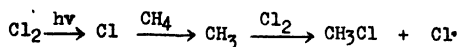
Radical Addition: The "abnormal" ("anti-Markownikoff") addition of HBr to olefins are catalyzed by light or peroxides. The steps involved in the addition of HBr to propylene in the presence of benzoyl peroxide are listed below:

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2\cdot \xrightarrow{HBr} C_6H_5CO_2H + Br\cdot$$

$$Br\cdot + CH_3CH = CH_2 \longrightarrow CH_3\overset{\cdot}{C}HCH_2Br \xrightarrow{HBr} CH_3CH_2CH_2Br + Br\cdot$$
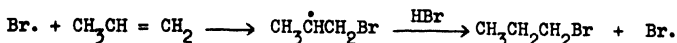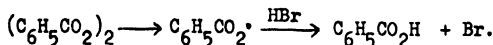
Free-radical induced polymerization of alkenes involve radical additions and are commercially important.

VI.3 Name Reactions in Organic Chemistry

* Acyloin Condensation

Acyloins (α-hydroxy carbonyl compounds) are formed by heating aliphatic carboxylic esters with sodium in inert solvents in the absence of air. This reaction proceeds through the formation of 1,2-diketones and a free radical mechanism has been suggested.

$$\underset{\displaystyle R-\overset{\displaystyle O}{\overset{\|}{C}}-OR'}{} \xrightarrow{Na} \underset{\displaystyle R-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{OH}{CH}-R}{}$$
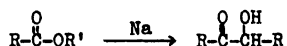
* Aldol Condensation

Aldols (β-hydroxy carbonyl compounds) result from the addition of compounds containing active methylene groups to the carbonyl of an aldehyde or a ketone in the presence of catalytic amounts of acids or bases. Aldol addition is reversible.

$$R-CHO + CH_3-CHO \xrightarrow{OH^-} R-\underset{OH}{CH}-CH_2-CHO$$
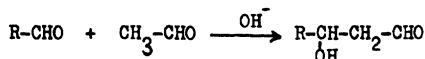
* Arndt-Eistert Synthesis

A method of homologating carboxylic acids. The acid is converted to its chloride and the acid chloride is treated with diazomethane to generate the diazomethyl ketone. Decomposition of the diazoketone with silver oxide in the presence of water gives the next higher homologous acid. The Arndt-Eistert synthesis is applicable to aliphatic, aromatic, acyclic and heterocyclic carboxylic acids.

$$RCO_2H \xrightarrow{RCOCl} RCOCH_2N_2 \xrightarrow{H_2O} RCH_2CO_2H$$

* **Baeyer-Villiger Oxidation**

    Oxidation of aldehydes or ketones with hydrogen peroxide or peracids, gives esters (or derivatives therefrom). Diketones give acid anhydrides, α,β-unsaturated acids give enol esters. An ionic mechanism was proposed by Criegee.

$$R-CO-R' \longrightarrow R-\overset{O}{\underset{}{C}}-OR'$$

* **Barbier-Wieland Degradation**

    Carboxylic acids are converted to their next lower homologues. The ester is treated with phenylmagnesium bromide to a tertiary alcohol. The alcohol, when heated with acetic anhydride looses water to give an olefin which is oxidized with chromic acid to a carboxylic acid containing one carbon atom less than the starting acid.

$$RCH_2CO_2R' \xrightarrow{C_6H_5MgBr} R-CH_2-\overset{OH}{\underset{R}{C}}-(C_6H_5)_2 \longrightarrow R-CH=\overset{R'}{C}(C_6H_5)_2 \xrightarrow{CrO_3} RCO_2H$$
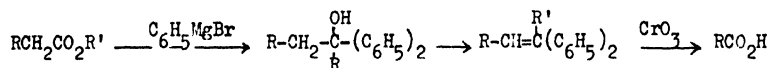
* **Beckmann Rearrangement**

    Ketoximes are converted to amides by reagents like PCl_5, acid chlorides, concentrated acids, etc. The reaction involves an interchange of the hydroxyl group of the oxime with the group situated anti (trans) to it.

$$\overset{R}{\underset{R'}{>}}C = N_{\diagdown OH} \longrightarrow R'-CONHR$$
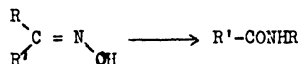
* **Benzil-Benzilic Acid Rearrangement**

    Benzil and other 1,2-diketones, when heated with strong alkali (aqueous alcoholic solution) are converted to α-hydroxy acids. The rearrangement proceeds irreversibly.

$$C_6H_5-\overset{O}{\underset{}{C}}-\overset{O}{\underset{}{C}}-C_6H_5 \xrightarrow{OH^-} (C_6H_5)_2C\overset{OH}{\underset{CO_2H}{\diagup}}$$
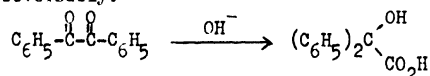
* **Benzoin Condensation**

    Aromatic aldehydes when boiled with an aqueous alcoholic potassium or sodium cyanide solution give α-hydroxy ketones (or benzoins). Many heterocyclic aldehydes also give this reaction.

$$R-CHO \xrightarrow{CN^-} R-CHOH-CO-R$$
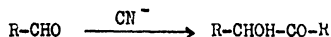
* **Birch Reduction**

    Unsaturated and aromatic compounds are reduced by sodium in ammonia. Alcohol is commonly employed as a proton donor. Isolated double bonds are not attacked. The reaction proceeds through radical anions and dianion

intermediates.

$$\text{naphthalene} \xrightarrow[\text{liquid NH}_3]{\text{Na}} \text{tetralin}$$
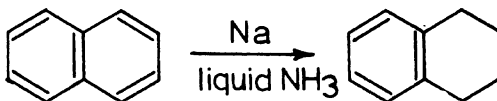
* **Bouveault-Blanc Reduction**

Esters of aliphatic carboxylic acids are readily reduced to primary alcohols by treatment with sodium and ethanol.

$$RCO_2R' \xrightarrow{C_2H_5OH, Na} R-CH_2OH + R'OH$$
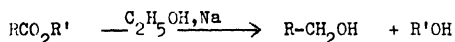
* **Brown Hydroboration**

Addition of diborane to olefinic double bonds gives triorganoboranes. Oxidation of the trioganoborane with H_2O_2 and hydrolysis gives rise to alcohols. The olefin is hydrated by this process (cis addition).

$$\text{C=C} + B_2H_6 \longrightarrow (H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-)_3B \xrightarrow[OH^-]{H_2O_2} H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-OH$$
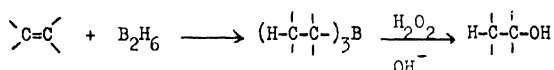
* **Cannizzaro Reaction**

Aromatic aldehydes undergo disproportionation in the presence of sodium or potassium hydroxide to give the corresponding alcohol and acid. Formaldehyde and many heterocyclic aldehydes which do not contain an active hydrogen on the -carbon undergo cannizzaro reaction.

$$R-CHO \xrightarrow{OH^-} R-CO_2H + RCH_2OH$$
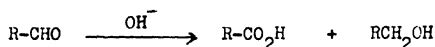
* **Claisen Condensation**

Compounds containing reactive methylene groups condense with esters in the presence of bases giving rise to acylated products. Acetoacetic ester, for example, is formed by the self condensation of two molecules of ethyl acetate in the presence of sodium ethoxide.

$$2 \ CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{NaOC_2H_5} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}OC_2H_5$$
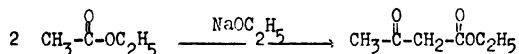
* **Claisen Rearrangement**

Allyl ethers of enols and phenols are thermally rearranged, in the absence of any catalyst, to C-allyl derivatives. The allyl group unusually migrates to the ortho position, but goes to the para position, if both ortho positions are blocked.

$$\text{C}_6\text{H}_5\text{O-CH}_2\text{-CH=CH}_2 \xrightarrow{\text{heat}} \text{o-HO-C}_6\text{H}_4\text{-CH}_2\text{-CH=CH}_2$$
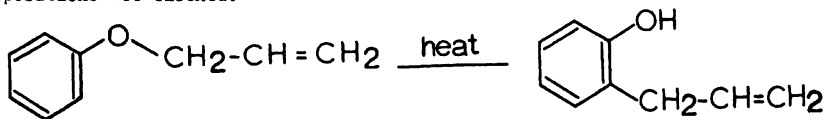
* Clemmensen Reduction

The carbonyl group in ketones and some aldehydes can be reduced to a methylene group by means of amalgamated zinc and hydrochloric acid.

$$R_2CO \xrightarrow[HCl]{Zn(Hg)} R_2CH_2$$
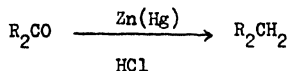
* Curtius Rearrangement

A method of replacing a carboxyl group by an amino group. The acid ester or chloride is first converted to the acid azide which when heated in an inert solvent (benzene or chloroform) gives the amine. Isocyanates are involved as intermediates in this reaction.

$$R \ CON_3 \longrightarrow R-N=C=O \longrightarrow RNH_2$$
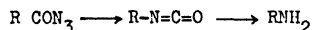
* Dieckmann Cyclization

Esters of dibasic acids undergo intramolecular condensation in the presence of a base to give a cyclic β-keto ester. This is a special case of Claisen condensation.
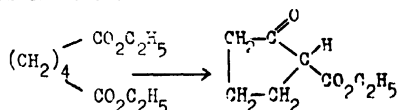
* Diels-Alder Reaction

The 1,4-addition of an activated double or triple bond (dienolphiles) on to a conjugated diene. The reaction is of wide sysnthetic utility. A one-step mechanism will explain most of the experimental results. Suggestions of a two-step and a radical mechanism have also been made.
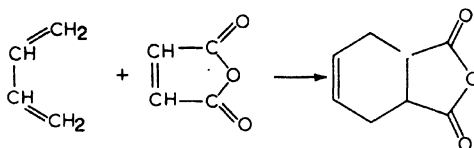
* Favorski Rearrangement

α-Halo ketones give acids or esters in the presence of a basic catalyst. 2-Chlorocyclohexanone, for example, gives cyclopentanecarboxylic acid, when treated with potassium ethoxide. Cyclopropanes are the suggested intermediates.
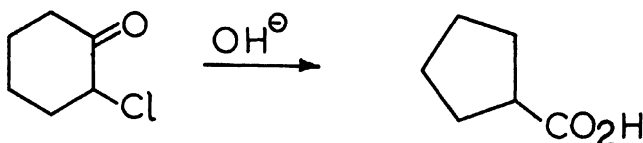
* Frieldel-Crafts Reaction

     Aromatic compounds are alkylated and acylated by treatment with alkyl or acyl halides in the presence of aluminum chloride. Different alkylating agents (alkyl halides, olefins, alcohols, and esters), acylating agents (acids, acid halides halides and acid anhydrides) and catalysts (AlCl$_3$, AlBr$_3$, H$_2$SO$_4$, BF$_3$, HF, H$_3$PO$_4$, P$_2$O$_5$, ZnCl$_2$, SnCl$_4$, etc.) have been used in this reaction.

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3$$

$$C_6H_6 + CH_3-\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} C_6H_5COCH_3$$
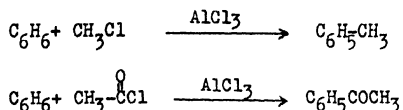
* Gattermann Reaction

     The diazonium group in an aromatic compound can be replaced by halide, cyanide, or other anions using metallic copper (freshly prepared from copper sulphate and zinc dust) as catalyst. Chlorobenzene, for example, is formed by adding powdered copper to a solution of benzenediazonium chloride in hydrochloric acid.

$$C_6H_5N_2Cl \xrightarrow[HCl]{Cu} C_6H_5Cl + N_2$$
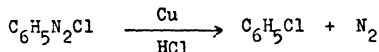
* Gattermann-Koch Reaction

     An aldehyde group can be directly introduced into the benzene ring (or other aromatic hydrocarbons) by means of carbon monoxide and hydrogen chloride, in the presence of catalysts like aluminum chloride or cuprous chloride. A formyl chloride-aluminum chloride complex has been suggested as intermediate.
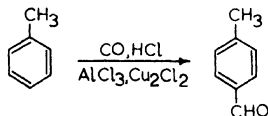
* Grignard Reaction

     Alkyl or aryl halides react with magnesium in anhydrous ether to give a solution of an organomagnesium compound (Grignard reagent). The Grignard reagent reacts with a variety of functional groups. Alcohols, for example, are formed from aldehydes or ketones by this reaction.

$$C_6H_5Br \xrightarrow[Ether]{Mg} C_6H_5MgBr \xrightarrow{R_2CO} R_2C\overset{\displaystyle \diagup OH}{\diagdown C_6H_5}$$
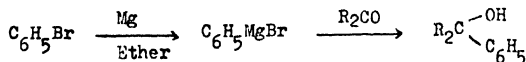
* Hell-Volhard-Zelinsky Reaction

     α-Chloro or α-bromo acids can be prepared by treatment of aliphatic

carboxylic acids with chlorine or bromine in the presence of a small amount
of the corresponding phosphorus trihalide. The reaction proceeds through
the acid halide stage, α-halogenation of the acid halide and finally a
transhalogenation, to give the   -halogenocarboxylic acid.

$$RCH_2-CO_2H \xrightarrow{Br_2, PBr_3} RCHBr-CO_2H \cdot$$
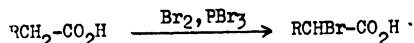
* Hofmann Degradation

     Thermal decomposition of quaternary ammonium hydroxides give olefin
and a tertiary amine.

$$C_2H_5\overset{+}{N}(CH_3)_3\overset{-}{O}H \longrightarrow CH_2=CH_2 + N(CH_3)_3 + H_2O$$
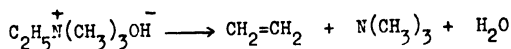
When several different substituents are attached to the nitrogen atom,
decomposition of the quaternary ammonium hydroxide will give the olefin
with the smallest number of alkyl groups attached to it (Hofmann's rule).

* Hofmann Rearrangement

     Carboxamides are converted to amines by treatment with sodium
hypochlorite or hypobromite (free halogen and alkali). The reaction proceeds
through an isocyanate intermediate.

$$R-CONH_2 \xrightarrow{NaOBr} R-N=C=O \xrightarrow{H_2O} R-NH_2$$
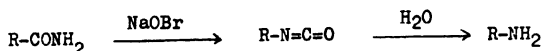
* Huisgen Reaction

     The reaction between a 1,3-dipolar species and dipolarophiles
(activated double and triple bonds) gives rise to five-membered heterocyclic
compounds. A one-step concerted mechanism has been suggested. This react-
ion is of wide synthetic application.

Phenylazide   Acetylenicester   Triazole
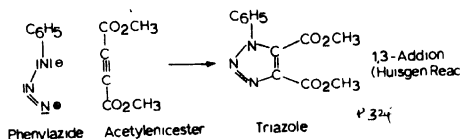
* Hunsdieckar Reaction

     Silver salts of carboxylic acids are decarboxylated, on treatment
with bromine or iodine to give alkyl halides. Most unsaturated acids and
some aromatic acids also undergo this reaction.

$$RCO_2Ag + X_2 \longrightarrow R-X + CO_2 + AgX$$
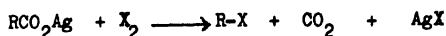
* **Knoevenagel Reaction**

Compounds containing active methylene groups can condense with an aldehyde or ketone in the presence of organic bases (either a primary or secondary amine) to give α,β-unsaturated compounds.

$$R\text{-CHO} + CH_2(CO_2C_2H_5)_2 \longrightarrow R\text{-CH=C}(CO_2C_2H_5)_2$$
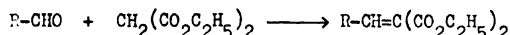
* **Lossen Rearrangement**

Thermal decomposition of hydroxamic acids or their acyl derivatives in inert solvents give isocyanates. Also reagents like thionyl chloride, acetic anhydride or phosphorus pentoxide can be used to bring about this rearrangement.

$$R\text{-}\underset{\displaystyle O}{\overset{\displaystyle O}{C}}\text{-N}\overset{\displaystyle H}{\underset{\displaystyle OH}{\diagdown}} \longrightarrow R\text{-N=C=O} \overset{H_2O}{\longrightarrow} R\text{-NH}_2$$

(OAc)
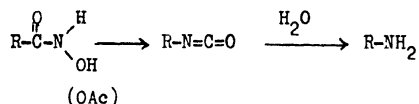
The reaction is similar to Hofmann and Curtius rearrangements.

* **Mannich Reaction**

Compounds containing one or more active hydrogen atoms (of carbonyl compounds and other acidic CH compounds) undergo aminomethylation (replacement of a hydrogen by aminomethyl group), when treated with formaldehyde and ammonia (or a primary or secondary amine)

$$R\text{-CO-CH}_3 + CH_2O + (CH_3)_2NH \longrightarrow R\text{-CO-CH}_2CH_2N(CH_3)_2$$
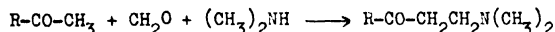
Meerwein-Pondorf-Verley Reduction

Carbonyl compounds (aldehydes and ketones) can be selectively reduced to alcohols in the presence of aluminum alkoxides (isopropoxide or ethoxide).

$$RR'CO + R''_2CHOH \longrightarrow RR'CHOH + R''_2CO$$
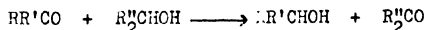
The reaction is reversible (Oppenauer oxidation) and can be used for the dehydrogenation of alcohols to carbonyl compounds.

* **Michael Addition**

Compounds containing reactive methylene groups add onto α,β-unsaturated compounds (carbonyl compounds, esters, nitriles, etc.) in the presence of basic catalysts (piperidine, diethylamine, sodium ethoxide, etc.)

$$CH_3\text{-CO-CH}_2\text{-CO}_2C_2H_5 + CH_2\text{=CH-CN} \longrightarrow \underset{\displaystyle CH_2CH_2CN}{CH_3\text{-CO-CH-CO}_2C_2H_5}$$
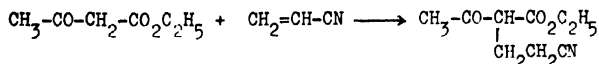
* Oppenauer Oxidation

     Secondary alchols are oxidized to ketones by treatment with aluminium t-butoxide (or isopropoxide) in combination with acetone.

$$RR'CHOH + (CH_3)_2CO \longrightarrow RR'CO + (CH_3)_2CH-OH$$

This reaction is the reverse of Meerwein-Pondorf-Verley reduction.

* Perkin Reaction

     The condensation of an aryl aldehyde with an anhydride in the presence of a base gives rise to β-substituted acrylic acids. The base is usually the sodium or potassium salt of the acid corresponding to the anhydride.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2K} C_6H_5CH=CHCO_2H + CH_3CO_2H$$
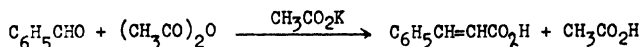
This reaction is a special case of the base-catalyzed aldol condensation.

* Reformatsky Reaction

     α-Hydroxy esters are prepared by the reaction of α-halo esters with aldehydes or ketones in the presence of zinc in an inert solvent like ether, benzene or toluene.

$$\underset{CH_3\overset{\underset{|}{Br}}{C}HCO_2C_2H_5}{} + Zn \longrightarrow CH_3\overset{\underset{|}{ZnBr}}{C}H-CO_2C_2H_5 \xrightarrow{R_2CO} \overset{R_2\overset{|}{C}-OH}{CH_3-CH-CO_2C_2H_5}$$
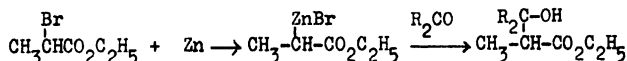
This reaction is quite similar to the Grignard reaction.

* Reimer-Tieman Reaction

     Phenols when heated with chloroform and alkali undergo C-formylation, yielding o- and p-substituted aldehydes.
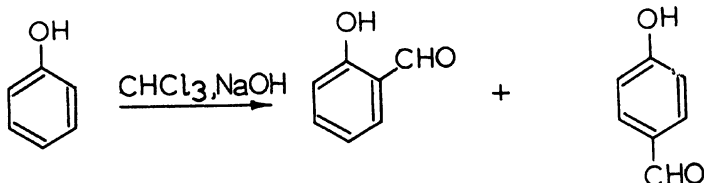
Reaction conditions, solvent etc., markedly affect the ratio of o- and p-isomers. The reaction proceeds through a dichlorocarbene intermediate. Bromoform, iodoform and trichloroacetic acid can be used instead of chloroform. Pyrrole and indole give the corresponding carboxaldehydes under Reimer-Tieman conditions.

* Rosenmund Reduction

     Acid chlorides are reduced to aldehydes with elementary hydrogen in the presence of palladium catalysts.

$$R-COCl + H_2 \xrightarrow{Pd-BaSO_4} R-\overset{\overset{O}{\|}}{C}-H + HCl$$
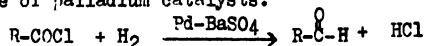
* **Sandmeyer Reaction**

The diazonium group in an aromatic compound can be replaced by nucleophiles like SCN^-, NO_2^-, SH^-, N_3^- and halides, by treatment of the aromatic diazonium salt with the corresponding cuprous salt

$$C_6H_5N_2Cl \xrightarrow{Cu_2(CN)_2} C_6H_5CN$$
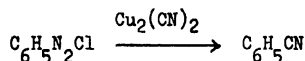
* **Schiemann Reaction**

Aromatic diazonium fluoroborates on thermal decomposition give fluorohydrocarbons.

$$C_6H_5N_2Cl \xrightarrow{HBF_4} C_6H_5N_2BF_4 \longrightarrow C_6H_5F + N_2 + BF_3$$
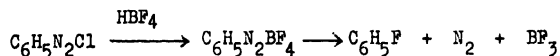
Mono and polynuclear hydrocarbons, as well as pyridines and quinolines can be fluorinated by this procedure.

* **Schmidt Rearrangement**

Carbonyl compounds (acids, aldehydes and ketones) react with hydrazoic acid in concentrated sulphuric acid. Carboxylic acids give amines, aldehydes give nitriles and ketones give amides.

$$RCO_2H + HN_3 \longrightarrow RNH_2; \quad RCHO + HN_3 \longrightarrow RCN; \quad R_2CO + HN_3 \longrightarrow RCONHR$$
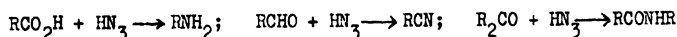
* **Schotten-Bauman Reaction**

Alcohols and phenols are acylated with acid chlorides in the presence of dilute alkali

$$ROH + R'COCl + NaOH \longrightarrow ROCOR' + NaCl + H_2O$$
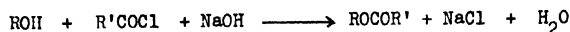
* **Stobbe Condensation**

The condensation of aldehydes and ketones with succinic esters in the presence of a basic catalyst to give alkylidenesuccinic acids.

$$R_2CO + (CH_2CO_2C_2H_5)_2 \xrightarrow[\text{2)H , H}_2\text{O}]{\text{1)NaOC}_2\text{H}_5} R_2C=C\begin{smallmatrix} CO_2H \\ CH_2CO_2H \end{smallmatrix}$$
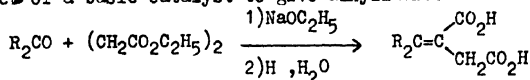
The mechanism involves a cyclic paraconic ester as intermediate.

* **Ullmann Reaction**

Biaryls are formed when halogenated aromatic compounds are heated with copper powder

$$2 C_6H_5I \xrightarrow{Cu} C_6H_5-C_6H_5 + CuI_2$$
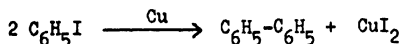
Evidence for free-radical mechanism has been reported.

* Witting Reaction

The oxygen atom in a carbonyl compound (aldehydes or ketones) can be replaced by a methylene group by treatment with alkyldenephosphoranes

$$(C_6H_5)_3P{=}CH_2 \; + \; R_2CO \longrightarrow R_2C{=}CH_2 \; + \; (C_6H_5)_3P{=}O$$
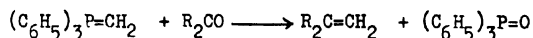
The reaction proceeds through a four-membered cyclic transition state.

* Wolff-Kishner Reduction

By heating the hydrazone of a carbonyl compound with sodium ethoxide or hydroxide to high temperatures ($\sim 200°$), the corresponding methylene compound is formed, with the loss of nitrogen.

$$R_2CO \xrightarrow{N_2H_4} R_2C{=}NNH_2 \xrightarrow{NaOH} R_2CH_2 + N_2$$
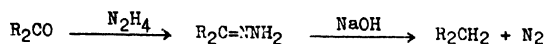
VI.4 Glossary in Organic Chemistry

* Absolute Configuration

The actual position in space of the four different groups surrounding an asymmetric carbon atom.

* Ambident Ion

Anions which are capable of reacting at two different sites forming different products. Nucleophilic attack by silver nitrite, for example, gives a mixture of nitro alkane (N-alkylated product) and alkyl nitrite (O-alkylated product).

* Anchimeric Assistance (Neighbouring group participation)

The rate and stereochemical course of a chemical reaction may be influenced by the presence of functional groups (carboxyl, amino, hydroxyl etc.) adjacent to the reaction site.

* Anionotropy

A tautomeric rearrangement in which a negatively charged group (halogen, hydroxy, acetoxy, etc.) migrates from one site to another with simultaneous reorganization of the bonds in the molecule.

$$R{-}\overset{X}{C}H{-}CH{=}CH_2 \rightleftharpoons RCH{=}CH{-}CH_2{-}X$$
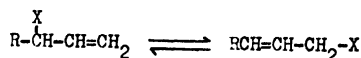
* Aromatic Character

Compounds like benzene and other arenes are characterized by high resonance stabilization, ease of both ionic and free-radical substitution etc. Also other conjugated cyclic systems (homocyclic and heterocyclic) which obey Huckel's rule ($4n+2$ = no of electrons in the π-system) are regarded as aromatic.

* Asymmetric Compounds

     Compounds which have neither a centre of symmetry nor a plane of
symmetry show, optical activity. Compounds which contain asymmetric carbon
atoms (bonded to four different groups) are asymmetric, as well as those
which have restricted rotation.

* Asymmetric Synthesis (Asymmetric induction)

     Syntheses leading to the preferential formation of one of the optical
isomers over the other one. They occur frequently in biological systems and
can be achieved in the laboratory under suitable conditions.

* Autoxidation

     Oxidations which take place at ordinary temperatures by molecular
oxygen. These are mostly free-radical processes. Autoxidation of hydrocar-
bons are commercially important.

* Axial and Equatorial Bonds (a,e)

     Of the twelve carbon-hydrogen bonds in the chair form of cyclohexane,
six are directed outwards and parallel to the plane of the ring (equatorial
bonds). The remaining six are directed up and down (three each) in a plane
perpendicular to the ring (axial bonds).

* Boat Conformation

     One of the conformations of cyclohexane, which has a boat shape and
in which four carbon atoms are in one lane and two out of this plane, on the
same side.

* Bredt's Rule

     No double bond can exist in a bicyclic compound between the bridge-
head atoms and adjacent carbon atoms, except in cases where the rings are
very large.

* B-Strain (Back-strain)

     Strain imposed on a molecule by overcrowding of groups attached
to the same carbon atoms; may acceterate reactions leading to less crowded
products.

* Cage Effect

     Each solute particle in a solution is surrounded by a "cage" of solvent
molecules and the solvent cage prevents the diffusion of the solute (and of
the products from the solute). The cage effect will enhance the probability
of recombination of products formed by ionic or free-radical dissociation.

* Chair Conformation

     One of the conformations of cyclohexane (chair shape) in which four

carbon atoms are in one plane and the two remaining carbon atoms out of this
plane and on opposite sides of it.

* Charge-transfer Complex

    A molecular complex formed between an electron-rich and electron
deficient compounds.

* cis-Elimination

    A 1,2-elimination reaction in which both leaving groups were originally
attached to the same side of the molecule.

* Configuration

    The arrangement of atoms that characterizes a particular stereoisomer.

* Conformation

    Different arrangements of atoms that can be converted into one another
by rotation about a carbon-carbon single bond.

* Copolymerization

    Polymerization of a mixture of two or more monomers to give long-
chain molecules consisting of each monomer units.

* Cross-linked Polymers

    Polymers in which the chains are linked together in several places
forming a three-dimensional net work.

* Diastereoisomers

    Stereoisomers (of compounds containing more than one asymmetric
carbon atom) which are not mirror images of each other. They differ in
chemical and physical properties.

* Eclipsed and Staggered Conformations

    An eclipsed conformation of a molecule is one in which the groups
attached to one carbon atom are in eclipsing positions (one over the other,
when viewed from one end of the C-C axis) with respect to the attachments
on the adjacent carbon.

    In the staggered conformation all the groups attached to both carbon
atoms occupy positions, as far apart as possible. The eclipsed and staggered
conformations of ethane (as per Newman Projection) are shown.

Eclipsed   P 330   Staggered
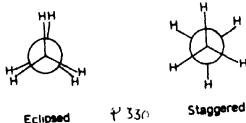
* Enantiomers (Optical isomers, Optical antipodes, Antimers)

     Isomeric compounds (containing asymmetric carbon atoms) which are
mirror images of each other. They are identical in almost all physical and
chemical properties, but differ in their optical properties. Enantiomers
show optical rotation of plane-polarized light, equal in magnitude for both,
but with opposite sign. They are designated as d (dextro rotatory) and
l (laevo rotatory) isomers.

* Epimers

     A pair of diastereoisomers which differ in configuration at one of
the asymmetric centres. Glucose and mannose are epimers. The interconversion
of these isomers is referred to as epimerization.

* F-Strain (Front-strain)

     Hindrance caused by bulky groups which will slow down a reaction.
The addition compounds between triethyl amine and other electron acceptors,
for example are less stable than those of trimethyl amine.

* Gauche Conformation (Skew conformation)

     One of the staggered conformations, in which the two bulky groups
are not trans to each other. The gauche and trans conformation of butane
are illustrated.

Gauche(Skew)   Trans
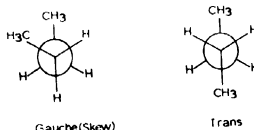
* Geometrical Isomerism (cis-trans Isomerism)

     Isomers arising due to restricted rotation about a double bond or a
rigid part of the molecule. The isomers are referred to as cis (same side)
and trans (opposite side) from, depending on the spatial arrangement of the
groups. Cis and trans isomers differ both in physical and chemical proper-
ties and can be interconverted under suitable conditions. Maleic and Fumaric
acids are cis-trans isomers.

$$HC-CO_2H \qquad\qquad HC-CO_2H$$
$$\|\qquad\qquad\qquad\qquad \|$$
$$HC-CO_2H \qquad\qquad HO_2C-CH$$

     Maleic acid   Fumaric acid
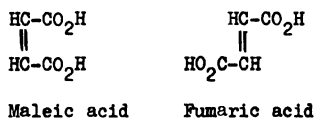
* Hammett Equation

     Based on the assumption that changes in rates and equilibria are
proportional to changes in the free energy of a reaction (linear free-energy
relationship), the relation between equilibrium constants (or rates), in the
reaction of a substituted and an unsubstituted aromatic compound can be

expressed as: $\log(k/ko) = \rho\sigma^-$, where, k refers to the substituted compound, ko, to the unsubstituted one, ρ is the reaction constant and σ^-, the substituent constant. Prediction of rates of equilibria of reactions with different substituents is possible, if the appropriate σ-values are known.

* Hofmann's Rule

   In olefin forming eliminations involving quarternary ions, the least substituted olefin will be formed in major amounts.

$$CH_3-CH_2-\underset{\underset{+N(CH_3)_3}{|}}{CH}-CH_3 \xrightarrow{OH^-} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 5\% \qquad\qquad 95\%$$
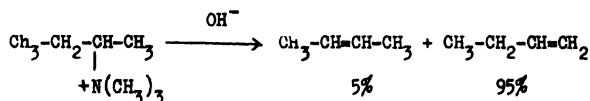
* Hyperconjugation

   Enhanced electron release from an alkyl group due to non-bonded interaction between carbon and hydrogen

* Inductive Effect

   Permanent polarization of a molecule can be caused by substituent groups which are electron-donating (+I effect) or electron-withdrawing (-I effect).

* Inhibitors

   Compounds which slow down or stop completely free-radical reactions. Iodine and quinones are frequently used to inhibit polymerization, and phenols and aromatic amines for the inhibition of autoxidation.

* Initiators

   Organic peroxides, hydroperoxides, azo compounds etc., are capable of initiating free-radical chain reactions.

* Internal Return

   The collapse of an intinate ion pair to give its parent unionised molecule or a rearranged product.

* Isomers

   Compounds having the same molecular formula, but differ in chemical and physical properties.

* I-strain (Internal strain)

   Some of the reactions of small ring compounds are explained in terms of a postulated internal strain.

* Kinetic Control

   If the products formed in a chemical reaction are not in equilibrium

with each other (or the rate of their interconversion is negligible), then the relative amounts of these products (formed in that reaction) will depend only on the rate of formation (kinetic control).

* Lewis Acids and Bases

Electron acceptors (compounds possessing atoms with incomplete electron shells) like $AlCl_3$, BF_3, $SnCl_4$, $FeCl_3$, etc. are Lewis acids. Compounds which contain unshared electron pairs (ammonia, amines, ethers, hydroxy compounds, carbonyl compounds, etc.) are Lewis bases.

* Markownikoff Rule

In the ionic addition of a hydrogen halide to an unsymmetrical olefin, the hydrogen atom adds on to that carbon which has the larger number of hydrogens and the halogen to the carbon containing the smaller number of hydrogens.

$$CH_3-CH=CH_2 + HCl \longrightarrow CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$$
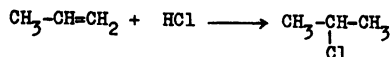
In the presence of peroxides, the direction of addition is reversed and the reaction proceeds by a free-radical mechanism.

* Meso Form

One of the isomeric forms of a substance containing two asymmetric carbon atoms, but does not show any optical activity. The optical activity due to the two asymmetric centres are internally compensated in this form.

* Microscopic Reversibility

Every reversible reaction proceeds through exactly identical intermediate stages in both direction.

* Mutarotation

The change in the optical rotation associated with the conversion of either one of a pair of diastereoisomers (anomers like α-and β-glucose) into an equilibrium mixture of the two. The interconversion of α and β-glucose (having cyclic structures) proceeds through an open-chain intermediate (free aldehydic form).

* Octane Number

The rating efficiency of a liquid fuel in an internal combustion engine. Two arbitrary standards, with values zero for n-hetane and 100 for iso-octane have been adopted and other fuels are rated accordingly.

* Optical Activity

Asymmetric compounds, in general, are able to rotate the plane of polarised light either to the right or left. Quartz shows optical activity

in the solid state, but optical activity is usually a property of the individual molecules. The magnitude and sign of rotation of a compound under specified conditions is a constant (specific rotation).

* Optical Rotatory Dispersion (ORD)

Measurement of optical rotation as a function of wave length. Optical rotatory dispersion curves are often quite sensitive to small changes in structure and have been successfully employed in structure and conformation problems.

* Polymerization

The formation of high molecular weight compounds (polymer) by the combination of several units of the starting material (monomer). Polymerizations take place by either ionic or free-radical chain processes.

* Prototropy

Migration of a proton from one site of an organic molecule to another with a simultaneous reorganization of the bond system.

$$\text{>CH-C=C<} \rightleftharpoons \text{>C=C-CH<}$$
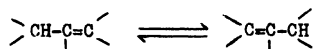
* Racemization

The conversion of an optically pure isomer (enantiomer) to a mixture of equal amounts of both dextro and levo forms (racemic mixture).

* Resonance

A concept to explain the properties of substances like benzene, which cannot be satisfactorily accounted for in terms of conventional valence-Bond structures.

* R_f Value

An expression of the mobility of a component (of a mixture separated by chromatography) to that of the solvent and is used for the characterization and identification of compounds.

* Saytzeff Rule

In a 1,2-elimination involving neutral substrates, the predominant product is the most highly substituted olefin

$$CH_3\text{-}CH_2\text{-}\underset{\underset{Br}{|}}{CH}\text{-}CH_3 \xrightarrow{C_2H_5ONa} CH_3\text{-}CH=CH\text{-}CH_3 + CH_3\text{-}CH_2\text{-}CH=CH_3$$
$$\text{2 parts} \qquad \text{1 part}$$
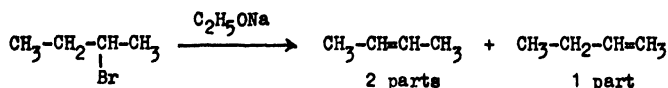
* Solvolysis

The reaction between an organic compound and solvent; hydrolysis

(with water), alcoholysis (with alcohol), ammonomysis (with ammonia) etc.
are examples.

* Stereoisomerism

     Isomerism of compounds with the same structural formulae, but having
different spatial arrangements of the various groups. Geometrical and
optical isomerism are examples.

* Steric Effects

     The influence of the size and shape of various groups attached to an
organic molecule. It can be one of assistance or hindrance depending upon
the type of reaction.

* Tautomerism

     The interconversion of two forms of a compound which differ in the
location of a mobile group such as a hydrogen atom (prototropy) or a halogen
atom (anionotropy). The two forms exist in equilibrium and the change from
one to the other is rapid. Keto-enol tautomerism, lactam-lactim tautomerism,
nitro-aci-nitro tautomerism are examples.

* Thermochromism

     Some organic compounds like bianthrone change their colour with
temperature and the colour change is reversible.

* Thermodynamic Control

     The distribution of products formed in a chemical reaction will be
determined by their thermodynamic stability, if their rates of formation
are comparable to the rate of interconversion (equilibrium between the
products).

* Thermoplastic Polymers

     Polymers (which are solids at ordinary temperatures) soften or melt
without decomposition on heating. They regain their original properties on
cooling. Linear polymers like polyethylene, polystyrene, acrylic polymers
etc. come under this category.

* Thermosetting Polymers

     Polymers which undergo irreversible structural changes during their
preparation and are infusible and insoluble. Bakelite and glyptal resins
with cross-linked structures are examples.

* Trans-Elimination

     An olefin forming elimination in which the leaving groups or atoms
are trans (opposite side) to each other.

* Transition State

     In a chemical reaction, as the reactants are transformed to the

products, the system passes through an activated complex (transition state) composed of one or more molecules and having the maximum potential energy. The activation energy is a measure of the energy required for the reactants to reach the activation state.

* Walden Inversion

       The inversion in configuration of an asymmetric centre during an S_N2 displacement reaction.

* Zwitterions (Dipolar ion)

       An internal salt formed between an acidic and a basic group present in the same molecule.

$$H_2NCH_2CO_2H \rightleftharpoons \overset{+}{H_3}NCH_2\overset{-}{CO_2}$$

      Glycine   Zwitterion
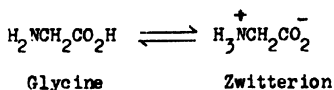
* Table of Hammet Substituent Constants Based on the Ionization of Benzoic Acids.

Group	σ meta	σ para		Group	σ meta	σ para
$-CH_3$	-0.069	-0.170		$-\overset{+}{N}(CH_3)_3$	0.88	0.82
$-C_2H_5$	-0.07	-0.151		$-NO_2$	0.71	0.778
$-CH(CH_3)_2$		-0.151		$-OCH_3$	0.115	-0.268
$-C(CH_3)_3$	-0.10	-0.197		$-OC_2H_5$	0.1	-0.24
$-C_6H_5$	-0.06	-0.01		$-OC_6H_5$	0.252	-0.320
$-CF_3$	0.43	0.54		$-OH$	0.121	-0.37
$-CN$	0.56	0.660		$-CO_2CH_3$	0.39	0.31
$-COCH_3$	0.376	0.502		$-SCH_3$	0.15	0.00
$-CO_2C_2H_5$	0.37	0.45		$-SH$	0.25	0.15
$-CO_2H$	0.35	0.46		$-SO_3^-$	0.05	0.09
$-CO_2^-$	-0.1	0.00		$-F$	0.337	0.062
$-Si(CH_3)_3$	-0.04	-0.07		$-Cl$	0.373	0.227
$-NH_2$	-0.16	-0.66		$-Br$	0.391	0.232
$-N(CH_3)_2$	-0.211	-0.83		$-I$	0.352	0.18

VI.5 Organic Analysis

The elements commonly occuring in organic compounds, in addition to carbon and hydrogen, are oxygen, the halogens, sulphur, nitrogen and phosphorus. The analysis of an organic compound includes the detection and estimation of the elements and the functional groups present in it.

*. Qualitative Elemental Analysis

The elements present in an organic compound are held together by covalent bonds and hence they are to be converted to water soluble ionic compounds before applying simple qualitative tests. Fusion with sodium converts the elements to ions (indicated within parentheses) which are tested as shown below:

Nitrogen (Cyanide, CN^-); Prussian blue test: Add a few drops of ferrous sulphate to the cyanide solution; heat to boiling and acidify with dilute HCl. A blue colour (or precipitate) indicates nitrogen.

Sulphur (Sulphide, S^{2-}): Nitroprusside test: Addition of a few drops of sodium nitroprusside solution to the sulphide solution results in the formation of a purple colour.

Halogens (Halide, F^-, Cl^-, Br^-, I^-): Silver nitrate test: If CN^- or S^{2-} are present, then boil the halide solution with dil. HNO_3 to remove H_2S and HCN; add $AgNO_3$. The formation of a precipitate indicates halide ions : white (Cl^-), pale yellow (Br^-), and yellow (I^-) . Fluoride ions can be tested as cerium fluoride (CeF_3) by adding cerium nitrate solution.

Phosphorus (Phosphide P^{3-}): Ammonium molybdate test: Heat the solution with conc. HNO_3 to convert the phosphide to phosphate; add ammonium phosphomolybodate. A yellow precipitate indicates phosphate.

* Quantitative Elemental Analysis

Carbon and Hydrogen: The determination of carbon and hydrogen is done in one procedure. Burning the compound in a stream of oxygen in the presence of cupric oxide (CuO) converts carbon to carbon dioxide and hydrogen to water. These are absorbed over suitable absorbing agents and weighed.

Nitrogen: The amount of nitrogen can be determined in two ways. In the Dumas method, the nitrogen is liberated as the free element and the volume measured. The Kjeldahl method involves the conversion of the organically bound nitrogen to ammonia, which is then analyzed for by standard volumetric procedures.

Sulphur: Oxidation with sodium peroxide converts the sulphur to sulphate, which is then precipitated as the barium salt and analyzed gravimetrically.

Halogens: Halogens are converted to the corresponding halide ions, which may then be quantitatively determined, either volumetrically or gravimetrically.

* **Functional Group Tests**

Organic compounds contain different functional groups and exhibit properties characteristic of these groups. Some of the common functional groups and their characteristic tests are listed below:

Functional Group		Test
Alcohol	R-OH	Esterification, followed by test for ester. To distinguish between primary, secondary and tertiary, the Lucas test (conc.HCl and $ZnCl_2$) : the order of reactivity is tertiary > secondary > primary.
Aldehyde	$-\overset{\text{O}}{\overset{\|}{C}}-H$	2,4-Dinitrophenylhydrazine or hydroxylamine, to test the presence of a carbonyl group. Then Tollen's test to distinguish between an aldehyde and a ketone [ammonical silver nitrate is reduced to silver by aldehydes, whereas ketones do not react] .
Alkanes	$-\overset{\|}{\underset{\|}{C}}-\overset{\|}{\underset{\|}{C}}-$	Generally inert; no specific test.
Alkenes	$\underset{/}{\overset{\backslash}{C}}=\overset{/}{\underset{\backslash}{C}}$	Alkaline $KMnO_4$ solution is decolourised (Baeyer test); bromine water is decolorised; dissolves readily in conc. H_2SO_4
Alkynes	$-C\equiv C-$	Alkaline $KMnO_4$ and bromine water are decolorised; dissolves in conc. H_2SO_4. Terminal alkynes ($-C\equiv C-H$) form insoluble silver salts (caution!)
Amide	$R-\overset{\text{O}}{\overset{\|}{C}}-N$	Hydrolysis, followed by test for the acid and amine.
Amine	RNH_2, R_2NH, R_3N	Acetylation with acetic anahydride converts primary and secondary amines to the corresponding amides; tertiary amine is unaffected. Reaction with nitrous acid [primary aliphatic amines give alcohols, with evolution of nitrogen; aromatic primary amines give diazonium salts; secondary amines (aliphatic and aromatic) give nitrosamines; tertiary aliphatic amines do not react with nitrous acid, whereas tertiary aromatic amines give substitution products (in the ring)] .
Arenes	$(\underset{/}{\overset{\backslash}{C}}=\overset{/}{\underset{\backslash}{C}})$	Electrophilic substituiin reaction (nitration, sulphonation etc.).
Carboxylic acid	$R-\overset{\text{O}}{\overset{\|}{C}}-OH$	Esterification, followed by test for ester.

Functional Group		Test
Ester	O R-C-OR	Saponification, followed by tests for the acid and alcohol. Hydroxamic acid test treatment with hydroxylamine gives a hydroxamic derivative, which gives a violet coloured complex salt with few drops of ferric chloride .
Ether	R-O-R	Cleavage with conc. H_2SO_4 in presence of acetic acid gives an ester, which is then tested.
Halide	R-X	Silver nitrate test [tertiary, allyl or benzyl halide reacts rapidly with alcoholic $AgNO_3$ soln. giving a precipitate of the silver halide; secondary aliphatic halides react slowly (precipitate appears within 5-10 mins.); primary halides react very slowly (to be heated); aryl and vinyl halides do not react].
Ketone	$\diagdown$C=O	2,4-Dinitrophenylhydrazine test, followed by a negative test for aldehyde.
Mercaptan	R-SH	Nitroprusside test [a purple colour with sodium nitroprusside solution]. Forms insoluble mercuric and lead salts.
Nitrile	-C≡N	Acid-hydrolysis to carboxylic acid and ammonia.
Nitro	-NO$_2$	Reduction of aromatic nitro compounds to arylhydroxylamines (ArNHOH) by zinc and acetic acid and test with Tollen's reagent [Tollen's reagent is reduced to silver by hydroxylamines].
Phenols	Ar-OH	Esterification, followed by hydroxamic test. Coupling test with aromatic diazonium salts (deeply coloured precipitates are formed).

* Quantitative Organic Analysis (via Functional Groups)

Hydroxy Compounds: Alcohols: Acetylated by treatment with a known excess of acetic anhydride (and pyridine) and the amount of unreacted anhydride is determined (titration with NaOH). Aldehydes, at times, interfere and in such cases the use of phthalic anhydride is preferred.

Phenols: Treatment with a known excess of a brominating agent (a mixture of potassium bromide and bromate in presence of acid) and determining the amount of unreacted reagent by iodimetric titration (treatment of the mixture with KI liberates iodine which can be titrated against sodium thiosulphate).

Alkoxy Groups: The alkoxyl group present in an organic ompound is cleaved by hydriodic acid to an alkyl iodide, which can be determined acidimetrically or iodometrically. In the acidimetric method, the reaction mixture containing alkyl iodide and hydriodic acid is treated with pyridine which converts the alkyl iodide to the pyridinium iodide. The mixture is then subjected to a differentiating potentiometric titration using tetrabutyla-mmonium hydroxide. The iodimetric method is based on the following

reaction sequence.

$$RI + Br_2 \rightarrow RBr + IBr; \quad IBr + 3H_2O + 2Br_2 \rightarrow HIO_3 + 5HBr ; \quad HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$
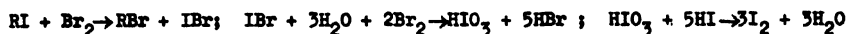
Carbonyl Compounds: Both aldehydes and ketones can be determined employ-
ing reactions like oxime formation, bisulphite addition, schiff base
formation and hydrazone formation. In the oxime formation, for example,
the carbonyl compound is treated with hydroxylamine hydrochloride and the
amount of hydrochloric acid formed is titrated (potentiometrically using
NaOH).

$$R_2C=O + NH_2OH.HCl \rightleftharpoons R_2C=NOH + H_2O + HCl$$
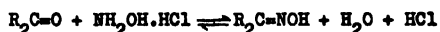
Aldehydes react at room temperature, but in the case of ketones, heating
is necessary. Pyridine has been added in some cases to speed up the
reaction and eliminate equilibrium problems.

Carboxylic Acids and Derivatives: Carboxylic Acids: Majority of carboxylic
acids are readily titrable with sodium hydroxide. An aqueous system is
usually adequate if the sample dissolves in water. If the sample is
insoluble in water, it may dissolve in excess aqueous alkali, and the
excess alkali is titrated. Potentiometric titration may be employed.

Esters: May be determined by employing the saponification reaction. A
known excess amount of sodium hydroxide is added to the sample and the
excess is determined by titration with acid.

Anhydrides: Morpholine reacts with carboxylic acid anhydrides to produce
equimolecular quantities of amide and acid. In a methanolic medium using
mixed methyl yellow-methylene blue indicator, all the components of the
reaction are neutral except morpholine. If a measured excess of morpholine
reacts with a sample containing anhydride, the anhydride reacts preferen-
tially with morpholine, and the excess can be titrated with standard
methanolic hydrochloric acid. The morpholine consumed is a measure
of the anhydride; if free acid is present in the sample, it can be
determined by ascertaining the total acidity using NaOH and then sub-
tracting the anhydride value.

Amino Groups: Aliphatic Amines: They are usually basic enough to be
titrated directly in aqueous solutions using standard acids. In the case
of weakly basic amines, solvents like acetic acid and nitromethane can
be used. Primary and secondary amines can also be determined on the
basis of their reaction with acetic anhydride.

Aromatic Amines: Aromatic amines have reactions specific to them which
can be employed for their determination. Aromatic amines can be bromi-
nated like phenols using potassium bromate-bromide and acid. Primary
aromatic amines can be diazotised with nitrous acid which can be measured.
Titration method is also applicable, but solvents like acetic acid, dioxane
or nitromethane have to be used as the amines are weakly basic.

Active Hydrogen: A hydrogen atom attached to atoms like oxygen (alcohols,
acids), nitrogen (amines, amides) and sulphur (mecraptans) can be easily

replaced by reaction with a Grignard reagent (RMgX). Methyl Grignards
are commonly used and the amount of methane liberated can be measured
gasometrically.

$$R-OH + R'MgX \longrightarrow R-OMgX + R'H$$

Unsaturation: The common reactions available for determining carbon to
carbon unsaturation are, bromination, catalytic hydrogenation, addition
of iodine monohalides (iodine number) and addition of mercuric salts.

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VI.7 Physical Constants of Organic Compounds

Abbreviations: M.W., molecular weight; m.p., melting point, °C; b.p., boiling point, °C; d, density, g ml^{-1} at 20°C; n, refractive index at 20°C for the D line of sodium; sol., solubility at 20°C in water [∞ (v.s.), refers to solubilities in excess of 50% by weight; s, between 10% and 50%; δ (sl.s.), between 1% and 10%; and i, less than 1%; d, decomposes].

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
Acenaphthene	$C_{12}H_{10}$	154.2	96	278	1.0242^{99}_{4}	1.6066^{99}	i
Acenaphthenequi-none	$C_{12}H_6O_2$	182.2	261	...	...	...	i
Acetaldehyde	C_2H_4O	44.1	−124.6	20.8	0.7834	1.3316	∞
Acetic acid	$C_2H_4O_2$, Ethanoic acid	60.1	16.6	118.5	1.0491^{85}_{A}	1.3721	∞
−, amide	C_2H_5ON, Acetamide	59.1	82.3	221.2	0.9986_A	...	s
−,−,N−phenyl	C_8H_9NO, Acetanil-ide	135.2	113.4	307	1.2105^{4}_{4}	...	δ
−, anhydride	$C_4H_6O_3$	102.1	−73.1	136.4	1.0820	1.3906	▼
−, chloride	C_2H_3OCl	78.5	−112	51.2	1.1039	1.3898	d
−, ethyl ester	$C_4H_8O_2$, ethyl acetate	88.1	−83.6	77.1	0.9005	1.3701	s
−, methyl ester	$C_3H_6O_2$, methyl acetate	74.1	−98.1	57	0.9723	1.3617	▼
−, nitrile	C_2H_3N, acetoni-trile	41.1	−45.7	80.1	0.7856	1.3441	∞
−, chloro	$C_2H_3O_2Cl$	94.5	63	189	1.4043^{40}	$1.4297^{6'}$	▼
−, dichchloro	$C_2H_2O_2Cl_2$	128.9	10.8	192−3	1.5634	1.4658	∞
−, trichloro	$C_2HO_2Cl_3$	163.4	56.3	197.6	1.62	1.4603	▼
−,−,ethyl ester	$C_4H_5O_2Cl_3$	197.4	..	167.5	1.3826	1.4507	i
Acetophenone	C_8H_8O	120.1	19.6	202	1.0281	1.5363	i
Adamantane	$C_{10}H_{16}$	136.2	268	...	1.07	1.568	
Amine −, diphenyl	$(C_6H_5)_2NH$	169.2	52.8	302	1.160	...	i
−, triethyl	$(C_2H_5)_3N$	101.2	−115	89−90	0.7255^{25}	1.4003	s

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
-,trimethyl	$(CH_3)_3N$	59.1	-117	3.5	0.6079^0_4		v
Aniline	$C_6H_5NH_2$	91.1	-6.2	184.3	1.6216	1.5863	s
-,2-bromo	C_6H_6NBr	172.0	32	229	1.578	1.6113	i
-,3-bromo	C_6H_6NBr	172.0	18.5	251	1.5793	1.6260	δ
-,4-bromo	C_6H_6NBr	172.0	66.4	d	1.4970^{100}	...	i
-,2-chloro	C_6H_6NCl	127.6	-14	208.8	1.2126	1.5884	i
-,3-chloro	C_6H_6NCl	127.6	-10.4	229.9	1.2161	1.5941	
-,4-chloro	C_6H_6NCl	127.6	72.5	232	1.429	1.5346	s
-,N,N-dimethyl	$C_6H_5N(CH_3)_2$	121.2	2.5	194.2	0.9563	1.5587	δ
-,2-nitro	$C_6H_6N_2O_2$	138.1	71.5	284	1.442	...	δ
-,3-nitro	$C_6H_6N_2O_2$	138.1	112.5	305.7	1.1747^{160}	...	δ
-,4-nitro	$C_6H_6N_2O_2$	138.1	147.8	331.7	1.437	...	i
-,2,4,6-tribromo	$C_6H_4Br_3N$	329.9	122	300	2.35	...	i
Anthracene	$C_{14}H_{10}$	178.2	216	340	1.25^{27}	...	i
9,10-Anthraqui-none	$C_{14}H_8O_2$	208.2	286 (sub)	379.8	1.438	...	i
Arsine,-triphenyl	$(C_6H_5)_3As$	306.0	59-60	360	1.2634^{48}	1.6888^{21}	i
Azobenzene (trans)	$C_{12}H_{10}N_2$	182.2	68.5	295-7	1.203	1.6266^{78}	δ
Azoxybensene (trans)	$C_{12}H_{10}N_2O$	198.2	36	d	1.159^{20}	1.652^{20}	i
Azulene	$C_{10}H_8$	128.2	98.5-9	270(d)	...	...	i
Benzaldehyde	C_6H_5CHO	106.1	-55.6	178.1	1.0415^{25}	1.5463	δ
-,phenythydrazone	$C_6H_5CH=NNHC_6H_5$	196.2	156	...	...	...	δ
-,4-bromo	C_7H_5BrO	185.0	57	...	...	...	i
-,4-chloro	C_7H_5ClO	140.6	47	213-4	1.196^{61}	1.5552^{61}	s
-,2-hydroxy	$C_7H_6O_2$	122.1	-11	197	1.1467^{25}	1.5702	δ
-,3-hydroxy	$C_7H_6O_2$	122.1	106	240^{160}	...	...	δ
-,4-hydroxy	$C_7H_6O_2$	122.1	116	...	1.129^{130}	...	δ
-,2-methyl	C_8H_8O, o-Tolualdehyde	120.2	...	197	1.0386^{19}	1.549^{19}	δ
-,3-methyl	C_8H_8O, m-Tolualdehyde	120.2	...	199	1.0189^{21}	1.5411^{21}	δ
-,4-methyl	C_8H_8O p-Tolualdehyde	120.2	...	204.5	1.0194^{17}	1.547^{17}	δ
-,4-nitro	$C_7H_5NO_3$	151.1	106	...	1.496	...	δ
Benzene,	C_6H_6	78.1	5.5	80.1	0.8737^{15}	1.5011	δ

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d.	n_D	sol
-,1-amino-2,3-dimethyl	$C_8H_{11}N$ — 2,3-Xylidine	121.2	←-15	224	0.9931	1.5684	δ
-,1-amino-3,5-dimethyl	$C_8H_{11}N$ — 3,5-Xylidine	121.2	..	220-1	0.972	1.5581	δ
-,bromo	C_6H_5Br	157.0	-31	155-6	1.5219^0	1.6598	i
-,chloro	C_6H_5Cl	112.6	-45	132	1.1064	1.5248	i
-,1-chloro-2,4-dinitro	$C_6H_3ClN_2O_4$	202.6	53	315	1.4982	1.5857^{60}	i
-,1,2-diamino	$C_6H_8N_2$ — O-Phenylene diamine	108.1	102-3	256-8	...	...	δ
-1,3-diamino	$C_6H_8N_2$ — m-phenylene diamine	108.1	63-4	282-4	1.0696^{58}	1.6339^{58}	v
-1,4-diamino	$C_6H_8N_2$ — p-phenylene-diamine	108.1	140	267	...	...	s
-,1,2-dibromo	$C_6H_4Br_2$	235.9	6.7	221	1.9557	1.6081	i
-,1,3-dibromo	$C_6H_4Br_2$	235.9	-7	220	1.9523	1.6083^{17}	i
-1,4-dibromo	$C_6H_4Br_2$	235.9	87	218-9	1.8322^{100}	1.5742	i
-,1,2-dichloro	$C_6H_4Cl_2$	147.0	-17	179	1.3048	1.5485	i
-,1,3-dichloro	$C_6H_4Cl_2$	147.0	-25	172	1.2881	1.5457	i
-,1,4-dichloro	$C_6H_4Cl_2$	147.0	53	174	1.533^0	1.521^{80}	i
-,1,2-dihydroxy	$C_6H_6O_2$ Catechol	110.1	105	240	1.371	1.604	s
-,1,3-dihydroxy	$C_6H_6O_2$ — Resorcinol	110.1	111	281	1.2717	...	s
-,1,4-dihydroxy	$C_6H_6O_2$ — Hydroquinone	110.1	170	285	1.328^{15}	...	s
-,1,2-dimethyl	C_8H_{10} o-Xylene	106.2	-25	144	0.8968	1.5058	i
-,1,3-dimethyl	C_8H_{10} m-Xylene	106.2	-47.4	139	0.8684^{15}	1.4973	i
-,1,4-dimethyl	C_8H_{18} p-Xylene	106.2	13-4	138	...	...	i
-,1,2-dinitro	$C_6H_4N_2O_4$	168.1	118	319	1.3119^{120}	...	δ
-,1,3-dinitro	$C_6H_4N_2O_4$	168.1	90	291	1.575^{18}	...	i
-,1,4-dinitro	$C_6H_4N_2O_4$	168.1	172	299	1.625^{18}	...	i
-,fluoro	C_6H_5F	96.1	-39.2	85	1.0244	1.4677	i
-,iodo	C_6H_5I	204.0	-31.4	189	1.8230^{25}	1.6197	i
-,isopropyl	C_9H_{12}, Cumene	120.2	-96	152-3	0.864	1.4911	i
-,mercapto	C_6H_6S, Thiophe-nol	110.2	70-1	169.5	1.0728^{26}	1.5879^{24}	i
-,methoxy	C_7H_8O, Anisole	108.1	...	153.8	0.9954	1.5179	i

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
-,nitro	$C_6H_5NO_2$	123.1	5.7	210.8	1.2037	1.5562	δ
1,2,3-trihydroxy	$C_6H_6O_3$, Pyrogallol	126.1	132.8	309	1.453^4	...	v
Benzenesulfonic acid	$C_6H_5SO_3H$	158.2	525	...	...	...	s
-,amide	$C_6H_5SO_2NH_2$	157.2	150-1	...	...	...	i
-,chloride	$C_6H_5SO_2Cl$	176.6	14.5	251-2d	1.3766^{25}	...	i
Benzil	$C_6H_5COCOC_6H_5$	210.2	95	346-8	1.084^{102}	...	i
Benzoic acid	$C_6H_5CO_2H$	122.1	122.4	249(d)	1.2659^{15}	1.504^{132}	δ
-,amide	$C_6H_5CONH_2$	121.1	132.5 -3.5	290	1.0792^{130}	...	δ
-,chloride	C_6H_5COCl	140.6	-1	197.2	1.2105	1.5537	d
-,ethylester	$C_6H_5CO_2C_2H_5$	150.2	-34.6	213	1.0458^{25}	1.5057	i
-,nitrile	C_6H_5CN	103.1	-13	190.7	1.0102^{15}	1.5289	δ
-,2-amino	$C_7H_7NO_2$ Anthranilic acid	137.1	146	...	1.412	...	i
-,2-bromo	$C_7H_5BrO_2$	201.0	150	sub.	1.929^{25}	...	δ
-,4-bromo	$C_7H_5BrO_2$	201.0	254.5	1.894	...	...	δ
-2-chloro	$C_7H_5ClO_2$	156.6	142	sub.	...	...	s
-,4-chloro	$C_7H_5ClO_2$	156.6	241.5	...	...	...	i
-,3,5-dinitro	$C_7H_4N_2O_6$	212.1	205	...	...	...	δ
-,2-hydroxy	$C_7H_6O_3$	138..	159	211	1.443	1.565	δ
-,3-hydroxy	$C_7H_6O_3$	138.1	201.5	...	...	...	δ
-,4-hydroxy	$C_7H_6O_3$	138.1	214.5-215.5	...	...	...	δ
-,2-methyl	$C_8H_8O_2$ o-Toluic acid	136.2	107-8	258-9	1.062^{115}	1.512^{115}	i
-,3-methyl	$C_8H_8O_2$ m-Toluic acid	136.2	111-3	263	1.054^{112}	1.509	δ
-,4-methyl	$C_8H_8O_2$ p-Toluic acid	136.2	179-80	274-5	...	...	i
Benzoin (dl)	$C_6H_5CH(OH)COC_6H_5$	212.3	137	344	1.310	...	δ
Benzophenone	$C_6H_5COC_6H_5$	182.2	48.1	305.9	1.146	1.6077^9	i
-,phenylhydrazone	$(C_6H_5)_2C=NNHC_6H_5$	272.3	137	...	...	...	
1,4-benzoquinone	$C_6H_4O_2$	108.1	115-7	sub	...	...	δ
Biphenyl	$C_{12}H_{10}$	154.2	70	256	1.9896	1.588	i
-,4,4'-diamino	$C_{12}H_{12}N$ Benzidine	184.2	128	400		...	δ
Borneol(dl)	$C_{10}H_{18}O$	154.3	210.5	sub	1.001	...	i

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
1,3-Butadiene	$CH_2=CH-CH=CH_2$	54.1	-108.9	-4.4	...	1.4292^{25}	i
Butanal	$CH_3CH_2CH_2CHO$	72.1	-99	75.7	0.8170^{20}	1.3843	s
-,phenylhydrosone	$C_{10}H_{14}N_2$	162.2	...	152^{14}	...	...	
Butane,	C_4H_{10}	58.1	-138.3	-0.5	0.6012^0	1.3543^{-15}	v
-,1-amino	$C_4H_9NH_2$ n-butylamine	73.1	-50.5	77.8	0.764^{25}	1.401	∞
-,2-amino(dl)	$C_4H_9NH_2$ sec-Butylamine	73.1	<-72	66.8	0.7271	1.395^{17}	
-,1-bromo	C_4H_9Br n-Butyl bromide	137.0	-112.3	101.3	1.2764	1.4398	i
-,2-bromo(dl)	C_4H_9Br sec-Butyl bromide	137.0	-112.1	91.2	1.2556	1.4336	
-,1-chloro	C_4H_9Cl n-Butyl chloride	92.6	-123	78.4	0.8865	1.4021	i
-,1-iodo	C_4H_9I n-Butyl iodide	184.0	-103	130	1.6123	1.5001	i
2,3-Butanedione	$CH_3COCOCH_3$ Biacetyl	86.1	...	89.90	0.9808^{18}	1.3933^{18}	v
-,dioxime	$C_4H_8N_2O_2$ Dimethylgly- oxime	116.1	245.6	...	...	...	δ
Butanoic acid	$C_4H_8O_2$ Butyric acid	88.1	-6.5	163.5	0.964	1.3991	∞
-, ethyl ester	$C_3H_7CO_2C_2H_5$	116.2	-97.8	120	0.8785	1.4000	δ
1-Butanol	C_4H_9OH	74.1	-89.8	117.5	0.8098	1.3992	s
2-Butanol(dl)	$CH_3CH_2CHOHCH_3$ sec-Butyl alcohol	74.1	<-100	99.5	0.8063	1.3978	v
2-Butanone	$CH_3COC_2H_5$ Ethyl methyl ketone	72.1	-87	79.6	0.8054	1.3814	v
1-Butene	$CH_3CH_2CH=CH_2$	56.1	-185.4	-6.3	0.5946	1.3962	i
2-Butene(cis)	$CH_3CH=CHCH_3$	56.1	-138.9	3.7	0.6213	1.3931	i
2-Butene(trans)	C_4H_8	56.1	-105.6	0.9	0.6041	1.3848^{-25}	
2-Butynedioic- acid	$HO_2CC\equiv CCO_2H$ Acetylene dicar- boxylic acid	114.1	175.6	...	...	...	v
-,dimethyl ester	$CH_3O_2CC\equiv CCO_2CH_3$	142.1	...	195.8	1.5638	1.4466	
Caffeine	$C_8H_{10}N_4O_2$	194.2	237	sub 178	1.23	...	δ
Camphor(dl)	$C_{10}H_{16}O$	152.2	174	sub 179	...	...	

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
Camphoric acid (dl)	$C_{10}H_{16}O_4$	200.2	202	...	1.228	...	▼
Camphor sulphonic acid (dl)	$C_{10}H_{16}O_4S$	232.3	202d	...	...	...	▼
Carbodiimide diphenyl	$C_6H_5N=C=NC_6H_5$	194.2	168–170	331	...	...	δ
Carbondioxide	CO_2	44.0	–56(at 5.2 atm)	–78.5 sub	0.0019	...	
Carbon disulphide	CS_2	76.1	–112	45	1.2628	1.6255	▼
Carbon monoxide	CO	28.0	–205	–191	0.8142	...	
Cellulose	$(C_6H_{10}O_5)_x$	$(162.1)_x$	260–70d	...	1.27–1.61	...	i
Cholesterol	$C_{27}H_{46}O$	386.7	148.5	360d	1.067	...	δ
–,acetate	$C_{29}H_{48}O_2$	428.7	115	...	...	...	δ
Chloic acid	$C_{24}H_{40}O_5$	408.6	198	...	...	...	i
Cinnamaldehyde	$C_6H_5CH=CHCHO$	132.2	–7.5	253	1.0497	1.6195	
Cinnamic acid, (trans)	$C_9H_8O_2$	148.2	135.6	300	1.2475	...	i
–,ethyl ester (trans)	$C_6H_5CH=CHCO_2C_2H_5$	176.2	7.5	271.5	1.0491	1.5598	i
Citric acid	$C_3H_8O_7$	192.1	153	d	1.542^{18}	...	▼
Coumarin	$C_9H_6O_2$	146.1	71	301.7	0.935	...	s
Cyanogen bromide	$NCBr$	105.9	52	61.4	2.015^{20}	...	s
Cycloheptane	C_7H_{14}	98.2	–12	118.5	0.8109	1.4449	i
Cycloheptanone	$C_7H_{12}O$	112.2		178.5	0.9508	1.4608	
1,3,5-Cyclohepta-triene	$C_7H_{12}O$	92.1	–79.5	116–8	...	1.5208^{25}	i
2,4,6-Cyclohepta-trienone	C_7H_6O Tropone	106.1	–7	113^{15}	1.095^{22}	1.607^{25}	∞
1,3-Cyclohexadiene	C_6H_8	80.1	–98	80.5	0.8405	1.4153	i
Cyclohexane	C_6H_{12}	84.2	6.5	81	0.7791	1.4266	i
Cyclooctane	C_8H_{16}	112.2	13.5	148.5	0.8337	1.1568	
Cyclooctatetraene	C_8H_8	104.2	–27	142–3	0.925	1.5394	
1,3-Cyclopentadiene	C_5H_6	66.1	–97.2	40.8	0.8021	1.4429	i
Cyclopentane	C_5H_{10}	70.1	–93.9	49.3	0.7510	1.4064	i
–,bromo	C_5H_9Br	149.0	..	136.7	1.3900	1.4882	
Cyclopentanol	$C_6H_{10}O$	86.1	–19	140.9	0.9488	1.4530	δ
Cyclopentanone	C_5H_8O	84.1	–51.3	130.7	0.9509	1.4366	i
Cyclopentene	C_5H_8	68.1	–135	44.2	0.7743^{18}	1.4225	i

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol.
Decalin(cis)	$C_{10}H_{18}$	138.3	-45.4	195	0.8967	1.4811	i
-(trans)	$C_{10}H_{18}$	138.3	-32.5	185.5	0.8700	1.4696	i
Decanedioic acid	$HO_2C(CH_2)_8CO_2H$ Sebacic acid	202.3	134.5	295^{100}	...	1.422^{133}	δ
Decanoic acid	$CH_3(CH_2)_8CO_2H$ Capric acid	172.3	31.5	270	0.8858^{40}	1.4285^{40}	i
Diethyleneglycol -,diethyl ether	$C_8H_{18}O$	162.23	..	189	0.9063	1.4115	v
1,4-Dioxane	$C_4H_8O_2$	88.1	11.8	101	1.0334	1.4224	∞
Ethane	C_2H_6	30.1	-183.3	-88.6	0.572^{-108}	1.0769^0	i
-,amino	$C_2H_5NH_2$ Ethylamine	45.1	-84	16.6	0.6892^{15}		∞
-,bromo	C_2H_5Br Ethyl bromide	109	-118.9	38.4	1.4604	1.4239	δ
-,chloro	C_2H_5Cl Ethyl chloride	64.5	-138.7	13.1	0.9028^{15}	1.3742^{10}	δ
-,1,2-diamino	$NH_2CH_2CH_2NH_2$	60.1	8.5	116.5	0.8995	1.4499	v
-1,2-dibromo	$BrCH_2CH_2Br$	187.9	10.1	131	2.180	1.5389	δ
-,1,2-dichloro	$ClCH_2CH_2Cl$	99.0	-35	84	1.256	1.448	δ
-,1,2-epoxy	C_2H_4O Ethylene oxide	44.1	-111	13.4^{11}	0.882^{10}	1.3597	s
-,iodo	C_2H_5I	156.0	-108	72	1.950	1.5168^{15}	δ
-,dimethyl ether	$CH_3OCH_2CH_2OCH_3$	90.1	-58	83.4	0.8664	1.3813	s
Ethanol	C_2H_5OH	46.1	-117.3	78.5	0.7893	1.3611	∞
-,2-amino	$NH_2CH_2CH_2OH$ Ethanolamine	61.1	10.3	170	1.0180	1.4541	∞
Ethene	C_2H_4 Ethylene	28.1	-169.2	-104	0.0013^0	1.363^{100}	i
-,chloro	$CH_2{=}CHCl$ Vinyl chloride	62.5	-160	-13.9	...	...	δ
-,diethyl	$(C_2H_5)_2O$	74.1	-116.2	34.6	0.714	1.3526	s
Ethyne	C_2H_2	26.0	-81.8	-83.6	0.6181^{-82}	1.0005^0	δ
-,diphenyl	$C_6H_5C{\equiv}CC_6H_5$ (Tolan)	178.2	63.5	170^{19}	0.9657^{100}	...	i
Fluorene	$C_{13}H_{10}$	166.2	116-7	293-5	1.203^0		i
9-Fluorenone	$C_{13}H_8O$	180.2	83	341.5	1.1300^{99}	1.6369^{99}	i
Formaldehyde	HCHO Methanal	30.0	-92	-21	0.815^{-20}		s

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	Sol
Formic acid	HCO_2H	46.0	8.4	100.7	1.220	1.3714	∞
	Methanoic acid						
−,amide	$HCONH_2$	45.0	2.6	$105-6^{11}$	1.134	1.4453	∞
−,−,N,N−dimethyl	$HCON(CH_3)_2$	73.1	−61	153	0.9445^{25}	1.4269^{25}	∞
−,ethyl ester	$HCO_2C_2H_5$	74.1	−80.5	54.3	0.9117	1.3598	s
−,chloro,ethyl ester	$ClCO_2C_2H_5$	108.5	−80-6	95	1.3577	1.3955	d
	Ethyl chloroformate						
Fumaric acid	$HO_2CCH=CHCO_2H$	116.1	286.7	$165^{1.7}_{sub}$	1.635	...	δ
Furan	C_4H_4O	68.1	...	32	0.9366	1.4216	i
Furfural	$C_5H_4O_2$	96.1	−38.7	161.7	1.1598	1.5261	s
Glucose (D)	$C_6H_{12}O_6$	180.2	146	...	...	...	s
−,pentaacetate (D)	$C_{16}H_{22}O_{11}$	390.4	112−3	sub	...	...	δ
Glyceraldehyde(dl)	$HOCH_2CHOHCHO$	90.1	145	...	1.453^{118}	...	s
Glycerol	$HOCH_2CHOHCH_2OH$	92.1	18.6	290d	1.2613	1.4746	∞
Glycine	$NH_2CH_2CO_2H$	75.1	232.6	286−92d	$.828^{17}$	...	v
	Aminoacetic acid						
−,N−phenyl	$C_6H_5NHCH_2CO_2H$	151.2	127	...	...	...	s
Glyoxal	$CHOCHO$	58.0	15	50.4	1.14	1.3626	v
	Ethanedial						
Guanidine	$HN=C(NH_2)_2$	59.1	...	...	...	...	v
Heptane	$CH_3(CH_2)_5CH_3$	100.2	−91	98.4	0.6837	1.3876	i
Heptanedioic acid	$HO_2C(CH_2)_5CO_2H$	160.2	106	272^{100}	1.329^{15}	...	δ
	Pimelic acid						
Heptanoic acid	$CH_3(CH_2)_5CO_2H$	130.2	−10	223	0.9185	1.4216	δ
Hexamethylene-tetramine	$C_6H_{12}N_6$	140.2	280sub	...	1.331^{-5}		v
	Urotropine						
Hexane	C_6H_{14}	86.2	−95	68	0.6594	1.3749	i
−,1−bromo	$CH_3(CH_2)_5Br$	165.1	−85	156	1.1763	1.4478	i
−,1−chloro	$CH_3(CH_2)_5Cl$	120.6	−83	132.3	0.8784	1.4199	i
1,6−Hexanedial	$OHC(CH_2)_4CHO$	114.2	...	92.4^9	1.003^{19}	1.4307^{19}	δ
	Adipaldehyde						
Hexanedioic acid	$HO_2C(CH_2)_4CO_2H$	146.1	153	267	1.360^{25}	...	δ
	Adipic acid						
−,diethyl ester	$C_2H_5O_2C(CH_2)_4CO_2C_2H_5$	202.3	−21	239−41	1.0076	1.4272	i
2,5−Hexanedione	$CH_3CO(CH_2)_2COCH_3$	114.1	−8	194	0.7370	1.4232	v
Hexanoic acid	$CH_3(CH_2)_4CO_2H$	116.2	...	205	0.9274	1.4163	δ
	n−Caproic acid						

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
1-Hexanol	$CH_3(CH_2)_5OH$	102.2	-47	158	0.8136	1.4178	δ
-,1,2-dimethyl-	$CH_3NHNHCH_3$	60.1	...	81	0.8274	1.4209	∞
-,(2,4-dinitrophenyl)	$C_6H_6N_4O_4$	198.1	194	...	...	...	i
-,1,2-diphenyl-	$C_6H_5NH\ NHC_6H_5$ Hydrazobenzene	184.2	131	...	1.158^{16}	...	
-,phenyl	$C_6H_5NHNH_2$	108.1	20	243	1.099	1.6083^{18}	s
Indene	C_9H_8	116.2	-2	182.2	0.9915	1.5642	i
Indole	C_8H_7N	117.2	52.5	254	...	...	s
Isatin	$C_8H_5O_2N$	147.1	203-5	sub	...	...	s
Isoquinoline	C_9H_7N	129.2	24.8	243.3	1.0986	1.6148	i
Ketene	$CH_2=CO$	42.0	-151	-56	...	...	d
-,diphenyl	$(C_6H_5)_2C=CO$	193.2	...	265-70d	1.1107^{14}	1.615^{14}	
Maleic acid	$HO_2CCH=CHCO_2H$ cis-Butenedioic acid	116.1	130.5	...	1.590	...	$\triangledown$
-,anhydride	$C_4H_2O_3$	98.1	56	197-9	...	...	s
-,diethyl ester	$C_8H_{12}O_4$	172.2	...	225	1.064^{25}	...	i
Malonic acid	$CH_2(CO_2H)_2$	104.1	135.6	d	...	...	$\triangledown$
-,diethyl ester	$CH_2(CO_2C_2H_5)_2$	160.2	-50	199	1.055	1.4143	δ
Mannose (D)	$C_6H_{12}O_6$	180.2	132	...	1.539	...	$\triangledown$
Menthol (dl)	$C_{10}H_{20}O$	156.3	35-6	216	0.904^{15}	1.4615	i
Methane	CH_4	16.0	-182.5	-161.5	0.415^{-164}	...	δ
-,amino	CH_3NH_2	31.1	-93.5	-6.3	0.699^{-11}	...	$\triangledown$
-,bromo	CH_3Br	95.0	-95	3.6	1.732^0	1.4254^{10}	δ
-,chloro	CH_3Cl	50.5	-97	-23.8	0.92	1.3661^{-10}	S
-,chlorotriphenyl	$ClC(C_6H_5)_3$ Trityl chloride	278.8	112.3	310	...	...	i
-,dibromo	CH_2Br_2 Methylene bromide	173.9	-52	97	2.4921	1.5419	δ
-,dichloro	CH_2Cl_2 Methylene dichloride	84.9	-97	40-1	1.335^{15}	1.3348^{15}	δ
-,diiodo	CH_2I_2 Methylene diiodide	267.9	6	181	3.3254	1.7559^{10}	δ
-,diphenyl	$(C_6H_5)_2CH_2$	168.2	26-7	265.6	1.006	1.5768	i
-,fluoro	CH_3F	34.0	-141.8	-78.4	0.8428^{-60}	...	$\triangledown$
-,iodo	CH_3I	141.9	-66.5	42.5	2.28	1.5293	δ

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
-,nitro	CH_3NO_2	61.0	-28.5	100.8	1.1354^{22}	1.3935	s
-,tetrachloro	CCl_4	153.8	-22.9	76.8	1.5942	1.4664	i
-,tetranitro .	$C(NO_2)_4$	196.0	13	126	1.6372^{21}	1.4398^{17}	i
-,triphenyl	$(C_6H_5)_3CH$	244.3	94	358-9	1.014^{99}	1.5839^{99}	
Methanesulphonic acid	CH_3SO_3H	96.1	20	176^{10}	1.4812^{18}	1.4317^{16}	v
-,chloride	CH_3SO_2Cl Methanesulphonyl chloride	114.6	...	161	1.480^{18}	...	i
Methanol	CH_3OH	32.0	-97.8	65.0	0.7914	1.3288	∞
-,diphenyl	$(C_6H_5)_2CHOH$ Benzhydrol	184.2	69	297-8	...	...	δ
Morpholine	C_4H_9ON	87.1	-4.9	128	0.9994	1.4545	∞
Naphthalene	$C_{10}H_8$	128.2	80.2	210.8	1.145_4^{24}	1.4003^{24}	i
-,1-amino	$C_{10}H_9N$ α-Naphthylamine	143.2	50	300.8	1.123_{25}^{25}	1.6703	
-,2-amino	$C_{10}H_9N$ β-Napthylamine	143.2	113	306.1	1.0614^{98}	1.6498^{98}	s
-,1-bromo	$C_{10}H_7Br$	207.1	-6.2	281	1.4887^{17}	1.6588^{19}	s
-,2-bromo	$C_{10}H_7Br$	207.1	59	281.2	1.605^0	...	i
1-Naphtoic acid	$C_{11}H_8O_2$	172.2	160-1	<300	1.398	...	i
2-Naphthoic acid	$C_{11}H_8O_2$	172.2	185	<300	1.077^{100}	...	i
Nonanedioic acid	$HO_2C(CH_2)_7CO_2H$ Azelaic acid	188.2	106.5	360d	1.225^{25}	1.4303^{111}	s
Nonanoic acid	$CH_3(CH_2)_7CO_2H$ Pelargonic acid	158.2	15	253-5	0.9057	1.4343	i
Octane	$CH_3(CH_2)_6CH_3$	114.2	-56.5	125-6	0.7025	1.3975	i
Octanoic acid	$CH_3(CH_2)_6CO_2H$	144.2	16.3	$110-1^4$	0.8615^{80}	1.4278	δ
Oxalic acid	HO_2CCO_2H	90.0	101-2	157	1.90^{17}	...	v
-,dimethyl ester	$CH_3O_2CCO_2CH_3$	118.1	54	163-4	1.148^{15}	1.379^{82}	δ
Paraldehyde	$(CH_3CHO)_3$	132.2	12.5	128	0.9923	1.4049	v
Pentanal	$CH_3(CH_2)_3CHO$ Valeraldehyde	86.1	-91.5	102-3	0.8095	1.3944	δ
Pentane	$CH_3(CH_2)_3CH$	72.2	-129.7	36	0.6262	1.3579	v
-,1-bromo	$CH_3(CH_2)_4Br$ n-Amyl bromide	151.1	-95	129.6	1.2177	1.1444	i

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	Sol
Pentanedioic acid	$HO_2C(CH_2)_3CO_2H$ Glutaric acid	132.1	97.5	302.4	1.424^{25}	1.4188^{106}	▼
2,4-Pentanedione	$CH_3COCH_2COCH_3$ Acetyl acetone	100.1	-23	139	0.9721^{25}	1.4541^{17}	▼
Pentanoic acid	$CH_3(CH_2)_3CO_2H$	102.1	-34.5	186.7	0.939	1.4086	s
Peroxide, -,dibenzoyl	$C_6H_5COOOCOC_6H_5$ Benzoyl peroxide	242.2	106.8	exp	...	1.545	δ
Phenanthrene	$C_{14}H_{10}$	178.2	101	340	1.182	1.5973	i
9,10-Phenanthrene quinone	$C_{14}H_8O_2$	208.2	207	360	1.405	...	δ
Phenol	C_6H_5OH	94.1	182	43	1.0722	1.5509	s
-,4-bromo	C_6H_5BrO	173.0	66.4	238	1.840^{15}	...	s
-,4-chloro	C_6H_5ClO	128.6	43	219.8	1.2651^{40}	1.5579^{40}	s
-,4-methoxy	$C_7H_8O_2$	124.1	53	243	...	...	s
-,2-nitro	$C_6H_5NO_3$	139.1	44.9	216	1.485^{14}	...	δ
-,3-nitro	$C_6H_5NO_3$	139.1	97	194^{70}	1.2797^{100}	...	δ
-,4-nitro	$C_6H_5NO_3$	139.1	114	279d	1.479	...	δ
-,2,4,6-tribromo	$C_6H_3Br_3O_3$	330.8	95-6	282-90	2.55	...	δ
-,2,4,6-trinitro	$C_6H_3N_3O_7$	229.1	122-3	exp300	1.763	...	s
Phenolphthalein	$C_{20}H_{14}O_4$	318.3	261.2	...	1.277^{32}	...	δ
Phosgene	$COCl_2$	98.9	-118	8.0	1.392^{19}	...	d
Phosphine, -,triphenyl	$(C_6H_5)_3P$	262.3	80	>360	1.194	1.5248^{65}	i
Phthalic acid	$C_8H_6O_4$	166.1	206-8	d>191	1.593	...	δ
-,anhydride	$C_8H_4O_3$	148.1	130.8	284.5	1.527^4	...	δ
-,dimethyl ester	$C_{10}H_{10}O_4$	194.2	...	282-5	1.1905	1.515	i
-,imide	$C_8H_5O_2N$	147.1	238	...	...	...	δ
Piperazine	$C_4H_{10}N_2$	86.1	104	145-6	...	1.446^{113}	▼
Piperidine	$C_5H_{11}N$	85.2	-9	106.0	0.8606	1.4534	∞
Propanal	CH_3CH_2CHO	58.1	-81	48.8	0.807	1.3636	s
Propane	$CH_3CH_2CH_3$	44.1	-189.9	-44.5	0.5853^{45}	1.2898	s
-,1-amino	$C_3H_7NH_2$ Propylamine	59.1	-83	49	0.719	1.389	s
-,1-bromo	$CH_3CH_2CH_2Br$	123.0	-109.9	70.8	1.3539	1.4341	δ
-,2-bromo	$(CH_3)_2CHBr$ Isopropylbromide	123.0	-90.8	59.4	1.3097	1.4251	δ

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	sol
-,1-chloro	C_3H_7Cl n-Propylchloride	78.5	-122.8	46.6	0.8923	1.3886	δ
-,2-chloro	$(CH_3)_2CHCl$ Isopropylchloride	78.5	-117	34.8	0.8590	1.3781	δ
-,1-iodo	$CH_3CH_2CH_2I$	170	-101.3	102.5	1.7454	1.5055	δ
Propanoic acid	$CH_3CH_2CO_2H$	74.1	-20.8	141.1	0.992	1.3874	∞
-,ethyl ester	$CH_3CH_2CO_2C_2H_5$	102.1	-73.9	99.1	0.8889	1.3839	δ
-,2-methyl	$(CH_3)_2CHCO_2H$ Isobutyric acid	88.1	-47	154.3	0.9504	1.3930	▼
1-Propanol	$CH_3CH_2CH_2OH$ n-Propyl alcohol	60.1	-127	97.1	0.7796	1.3850	▼
2-Propanol	$(CH_3)_2CHOH$ Isopropyl alcohol	60.1	-89.5	82.4	0.7851	1.3776	∞
-,2-methyl	$(CH_3)_3COH$ tert-Butyl alcohol	74.1	25.5	82.2	0.7856	1.3838	∞
2-Propanone	CH_3COCH_3 Acetone	58.1	-95.4	56.2	0.7908	1.3588	∞
-,2,4-dinitro-phenylhydrazone	$C_9H_{10}N_4O_4$	238.2	128	...	...	...	i
Propenal	$CH_2=CHCHO$ Acrolein	56.1	-87.7	52.5	0.8625	1.3998	▼
Propene	$CH_3CH=CH_2$ Propylene	42.1	-185.2	-47.8	...	...	▼
-,3-bromo	$BrCH_2CH=CH_2$ Allyl bromide	121	-119.4	70	1.398	1.4697	i
-,3-chloro	$ClCH_2CH=CH_2$ Allyl chloride	76.5	-134.5	45	0.9397	1.4154	i
-,2-methyl •	$(CH_3)_2C=CH_2$ Isobutylene	56.1	...	-6.6	...	...	i
Propenoic acid	$CH_2=CHCO_2H$ Acrylic acid	72.1	12-3	141.6	1.0511	1.4224	∞
-,ethyl ester	$CH_2=CHCO_2C_2H_5$ Ethyl acrylate	100.1	...	99.8	0.924	1.405	s
-,nitrile	$CH_2=CHCN$ Acrylointrile	53.1	-82	77.5-9	0.8060	1.393	s
Pyridine	C_5H_5N	79.1	-42	115.5	0.9819	1.5095	∞
-2,4-dimethyl	C_7H_9N 2,4-Lutidine	107.2	...	159	0.9271^{25}	1.4984^{25}	▼
-,2,6-dimethyl	C_7H_9N 2,6-Lutidine	107.2	...	143	0.9200^{25}	1.4953^{25}	∞
-,2-methyl	C_6H_7N α-Picoline	93.1	...	128.8	0.9497^{15}	1.5029^{17}	▼
-2,4,6-trimethyl	$C_8H_{11}N$ γ-Collidine	121.2	...	170-5	0.9166^{22}	1.4959^{25}	s

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	Sol
3-Pyridinecarboxylic acid	$C_6H_5NO_2$ Nicotinic acid	123.1	236–7	sub	1.473	...	δ
4-Pyridinecarboxylic acid	$C_6H_5NO_2$ Isonicotinic acid	123.1	315–6	sub	...	...	s
Pyrrole	C_4H_5N	67.1	...	130–1	0.9669^{21}	...	v
Quinoline	C_9H_7N	129.2	–15.9	237.1	1.0937	1.6268	s
Quinuclidine	$C_6H_{12}N_2$	111.2	158	...	...	...	v
Silane, –,tetramethyl	$(CH_3)_4Si$	88.2	–91.1	26.5	0.648^{19}	...	i
Starch	$(C_6H_{10}O_5)_4$	...	d	...	...	...	i
Stilbene	$C_6H_5CH=CHC_6H_5$ trans-1,2-Diphenyl ethylene	180.3	124	306–7	0.9707	1.6264^{17}	i
Styrene	$C_6H_5CH=CH_2$ Phenylethylene	104.1	–33	145–6	0.909	1.5463	i
Succinic acid	$HO_2CCH_2CH_2CO_2H$	118.1	182	235d	1.572^{25}	1.450	δ
–,anhydride	$C_4H_4O_3$	100.1	119.6	261	...	...	i
–,diethyl ester	$C_2H_5O_2CCH_2CH_2CO_2C_2H_5$	174.2	–22	217.7	1.0406	1.4201	i
–imide	$C_4H_5NO_2$	99.1	126–7	287–8	1.418	...	δ
Sucrose	$C_{12}H_{22}O_{11}$	342.3	185–6	...	1.588^{15}	1.5376	δ
Sulfoxide, dimethyl	CH_3SOCH_3	78.1	6	100d	1.1014	...	s
Sulphuric acid –,dimethyl ester	$(CH_3O)_2SO_2$	126.1	–31.7	188.5d	1.3322	1.3874	s
Tartaric acid (dl)	$C_4H_6O_4$ 2,3-Dihydroxy-succinic acid	150.1	203–4	...	1.788	...	s
Tetralin	$C_{10}H_{12}$	132.2	–31	207.3	0.9729	1.5461	i
Thiophene	C_4H_4S	84.1	–38.4	84.1	1.0583^{25}	1.5256^{25}	
Toluene	C_7H_8	92.1	–95	110.6	0.8669	1.4961	i
–,2-amino	C_7H_9N O-Toluidine	107.2	–27.7	199.7	0.9989	1.5688	δ
–,3-amino	C_7H_9N m-Toluidine	107.2	–43.6	203.2	0.9916^{18}	1.5686	δ
–,4-amino	C_7H_9N p-Toluidine	107.2	43.5	200.4	0.9659^{45}	1.5534^{45}	δ
–,α-bromo	$C_6H_5CH_2Br$ Benzyl bromide	171.0	–3.9	201	1.4380^{22}	...	i

Name	Formula and Synonyms	M.W.	m.p.	b.p.	d	n_D	Sol
-,2-bromo	C_7H_7Br	171.0	-26	181	1.4222^{28}	...	i
	O-Tolyl bromide						
-,3-bromo	C_7H_7Br	171.0	-39.8	183.7	1.4019	1.551	i
	m-Tolyl bromide						
-,4-bromo	C_7H_7Br	171	28.5	184-5	1.3898	1.5490	i
	þ-Tolyl bromide						
-,α-chloro	C_7H_7Cl	126.6	-39	179.3	1.100	1.5391	i
	Benzyl chloride						
-,α,α-dichloro	$C_7H_6Cl_2$	161.0	-16.4	205.2	1.2557^{14}	1.5502^{20}	i
	Benzal chloride						
-, -hydroxy	C_7H_8O	108.1	-15.3	205.4	1.0419	1.5396	s
	Benzyl alcohol						
-,2-hydroxy	C_7H_8O	108.1	30	191-2	1.0465	1.4453	s
	o-Cresol						
-,3-hydroxy	C_7H_8O	108.1	11.1	202.8	1.0336	1.5398	δ
	m-Cresol						
-,4-hydroxy	C_7H_8O	108.1	34.8	201.9	1.0347	1.5395	δ
	þ-Cresol						
-,2-nitro	$C_7H_7NO_2$	137.1	-2.9	220.4	1.1629	1.544^{25}	i
	o-Nitrotoluene						
-,3-nitro	$C_7H_7NO_2$	137.1	15	232.6	1.1571	1.5466	i
	m-Nitrotoluene						
-,4-nitro	$C_7H_7NO_2$	137.	51.7	238.3	1.299^0	1.5382^{15}	i
	þ-Nitrotoluene						
Urea	$C_2H_4N_2O$	60.1	132.7	d	1.32^{18}	1.484	v
	Carbamide						
-,nitrate	$C_2H_4N_2O,HNO_3$	123.1	152d	...	1.63	...	δ
-,oxalate	$C_2H_4N_2O,C_2H_2O_4$	210.2	173d	...	1.585	...	s

VII. MISCELLANEOUS TOPICS

VII.1 Electronic Circuits

A few electronic circuits that are of general interest are given in the accompanying diagram.

*   Standard Resistor Color Coding

1-Brown	6-Blue
2-Red	7-Violet
3-Orange	8-Gray
4-Yellow	9-White
5-Green	10-Black

A - first significant figure; B - second significant figure; C - number of zeros following first two figures (If C is gold the multiplying factor is 0.1, in other words, the resistance is between 1 and 10 Ω; If C is silvered the multiplying factor is 0.01); D - per cent tolerance ($\pm$): Gold 5%, silver 10%, none 20%. Example: A - Brown; B Black; C Red; resistance value 1,000 Ω

*   Standard Capacitor Color Coding

Color coding is similar to that of resistors (cap. values in micro-micro farads $\mu\mu$ Pd= pF.) In addition to the A, B, C, D bands (dots) four other color bands (dots) may be used. The significance of these are as follows: E - third significant figure (old usage); F - D.C. working voltage (in hundreds of volts for molded paper and molded mica capacitors); G - operating characteristics; H - Temperature coefficient.

STANDARD COLOR CODING FOR RESISTORS

A B C D

Axial-lead resistor   Radial-lead resistor

D C A B

356 a
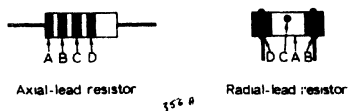
STANDARD COLOR CODING FOR CAPACITORS

H A B C D   H A B C D   H A B C D   F

(a) Axial lead   (b) 5-dot radial   (c) 6-dot radial

H A B C D   A B C

(d) 5-dot disc   356 b   (e) 3-dot disc
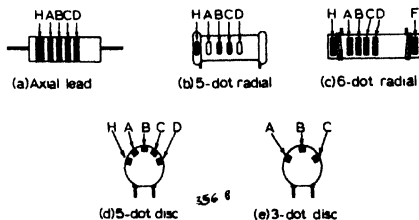
REGULATED POWER SUPPLY(OUTPUT 300 V AT 150 ma)

L1 = 8 henry 40ma choke

S1 = SPST Switch

T1 = Power transformer
375 - 0 - 375V 160ma
6 3 V 3Amp & 5V 3Amp
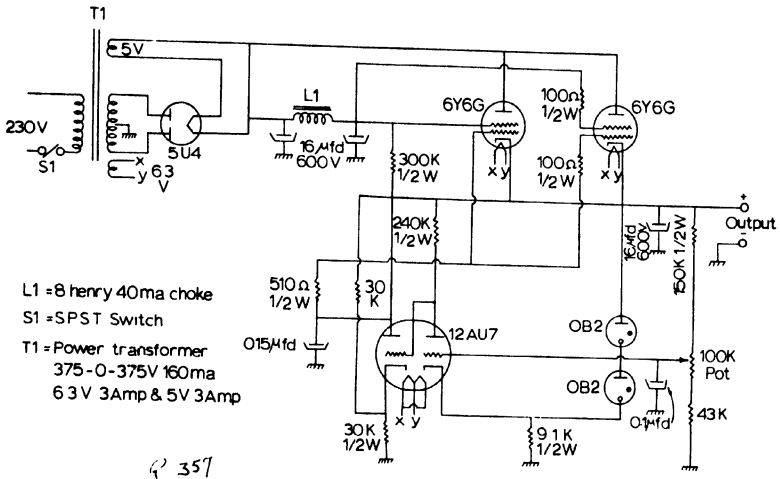
HIGH VOLTAGE REGULATED POWER SUPPLY
(1200V D C)
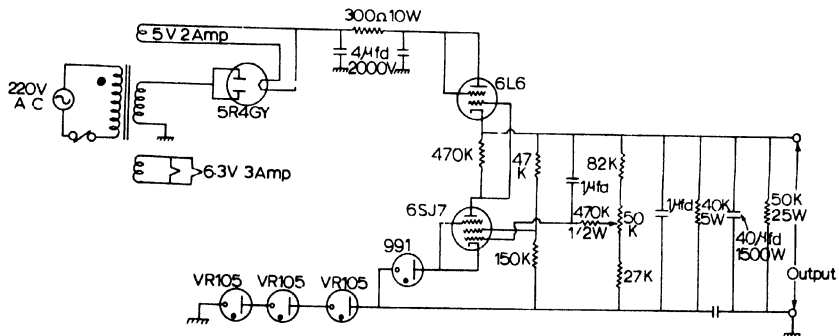
9 VOLT BATTERY ELIMINATOR

P 358
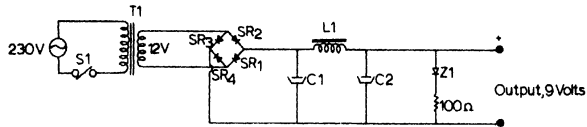
T1 = Power transformer Primary 220V - 230V
                              Sec   12 V

C1, C2 = 1000 Mfd 25 V D C

L1 = AF Choke 500 mh

Z1 = Zener diode type IZ 3 3A manufactured by
       Trombay Atomic Energy Establishment, Bombay

SR1, SR2, SR3, SR4, = SR 100 - Manfd by Semiconductors
                                          Poona - India

TRANSISTORIZED AUDIO AMPLIFIER
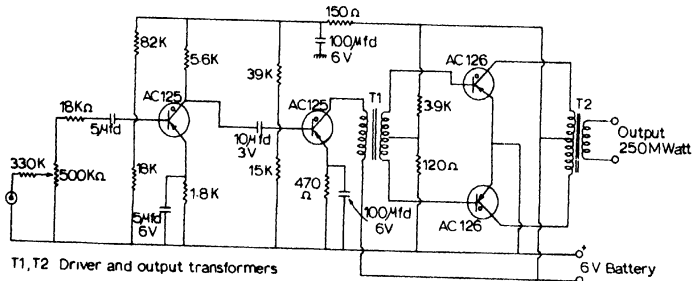
T1, T2 Driver and output transformers

Transistor Equivalents

Bharat Electronics Ltd	Semiconductors Ltd	Philips
AC 125	2N363	OC71
AC 126	2N632	OC72

PRE - AMPLIFIER
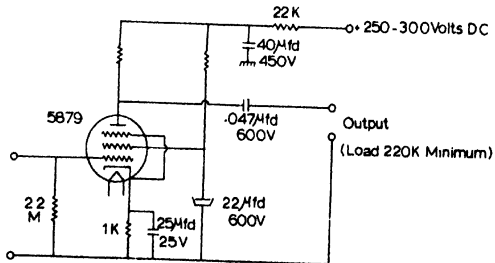
AUDIO AMPLIFIER CIRCUIT

P 357

T1 = Output transformer matching
8 KΩ Impedence for 6V6 Valve
and Variable output Tapping
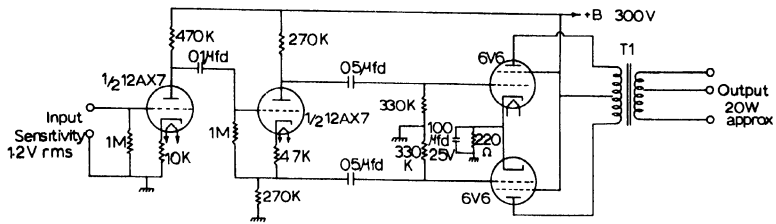
D.C. AMPLIFIER
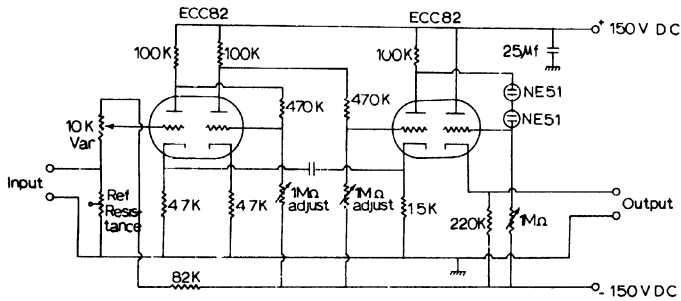
THERMOSTAT RELAY
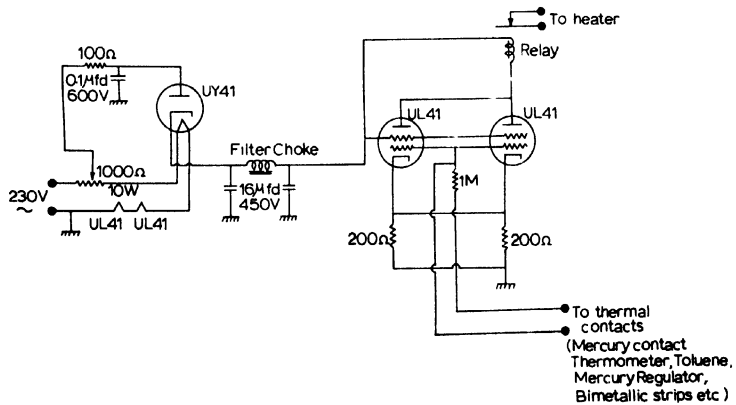
DRAWING SYMBOLS IN ELECTRONICS

ANTENNA	LOOP ANTENNA	DIPOLE ANTENNA	FERRITE ROD ANTENNA
GROUND	CHASSIS	JOINED CONDUCTORS	CONDUCTORS NOT JOINED
TERMINAL	FUSE	THERMOCOUPLE	TWO-TERMINAL JACK
SINGLE-POLE SINGLE-THROW SWITCH (SPST)	SINGLE-POLE DOUBLE-THROW SWITCH (SPDT)	DOUBLE-POLE SINGLE-THROW SWITCH (DPST)	DOUBLE-POLE DOUBLE-THROW SWITCH (DPDT)
SINGLE WAFER SELECTOR SWITCH	MULTIPLE WAFER SELECTOR SWITCH	FIXED RESISTOR	ADJUSTABLE RESISTOR
TAPPED RESISTOR	THERMISTOR	RHEOSTAT	POTENTIOMETER
AIR CORE INDUCTOR	IRON-CORE INDUCTOR	ADJUSTABLE INDUCTOR	TAPPED INDUCTOR
AIR CORE TRANSFORMER	VARIABLE CORE TRANSFORMER	IRON CORE TRANSFORMER	PUSH PULL TRANSFORMER
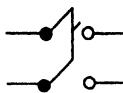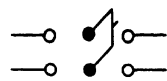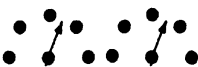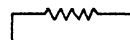
POWER
TRANSFORMER

RELAY

FIXED CAPACITOR

ADJUSTABLE CAPACITOR
(P=PADDER T=TRIMMER)

ELECTROLYTIC
CAPACITOR

VARIABLE CAPACITOR

GANGED VARIABLE
CAPACITOR

COAXIAL CABLE
(SINGLE)

TWIN COAXIAL CABLE

SHIELDED COIL

CRYSTAL DIODE

OSCILLATOR CRYSTAL

CONTACT RECTIFIER

A.C. VOLTAGE SOURCE

BATTERY

PHOTOTUBE

DIODE
(DIRECTLY HEATED
FILAMENT)

DIODE
(INDIRECTLY HEATED
CATHODE)

TRIODE

TETRODE

PENTODE

BEAM POWER
TETRODE

ELECTRON RAY
INDICATOR TUBE
(MAGIC EYE)

COLD CATHODE DIODE
(GAS FILLED)

p-n-p TRANSISTOR

n-p-n TRANSISTOR

TETRODE TRANSISTOR

PENTODE TRANSISTOR

e=EMITTER; b-BASE;
c-COLLECTOR

VII.2 Common Logarithms

* Interpolation in this section of the table is inaccurate

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	*4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	*3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	5	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	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	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

N	0	1	2	3	4	5	6	7	8	9	Proportional Parts								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

GENERAL PHYSICAL CONSTANTS RECOMMENDED BY NAS-NRC (Adopted by NBS[1])

Constant	Symbol	Value	Est.* error limit	Unit Systeme Intern. (MKSA)	Centimeter-gram-second (CGS)
Speed of light in vacuum	c	2.997925	3	$\times 10^8$ m s^{-1}	$\times 10^{10}$ cm s^{-1}
Elementary charge	e	1.60210	7	10^{-19} C	10^{-20} cm$^{1/2}$ g$^{1/2}$ †
		4.80298	20	....	10^{-10} cm$^{3/2}$ g$^{1/2}$ s^{-1} ‡
Avogadro constant	N$_A$	6.02252	28	10^{23} mol^{-1}	10^{23} mol^{-1}
Electron rest mass	m$_e$	9.1091	4	10^{-31} kg	10^{-28} g
Proton rest mass	m$_p$	1.67252	8	10^{-27} kg	10^{-24} g
Faraday constant	F	9.64870	16	10^4 C mol^{-1}	10^3 cm$^{1/2}$ g$^{1/2}$ mol^{-1} †
Planck constant	h	6.6256	5	10^{-34} J s	10^{-27} erg s
Fine Structure Constant	α	7.29720	10	10^{-3}	10^{-3}
Charge to mass ratio for electron	e/m$_e$	1.758796	19	10^{11} C kg^{-1}	10^7 cm$^{1/2}$ g$^{-1/2}$ †
		5.27274	6	....	10^{17} cm$^{3/2}$ g$^{-1/2}$ s^{-1} ‡
Rydberg constant	R$_\infty$	1.0973731	3	10^7 m^{-1}	10^5 cm^{-1}
Gyromagnetic ration of proton	γ	2.67519	2	10^8 rad s^{-1} T^{-1}	10^4 rad s^{-1} G^{-1} †
(Uncorrected for diamagnetism, H$_2$O)	γ'	2.267512	2	10^8 rad s^{-1} T^{-1}	10^4 rad s^{-1} G^{-1} †
Bohr magneton	μ$_B$	9.2732	6	10^{-24} J T^{-1}	10^{-21} erg G^{-1} †
Gas constant	R	8.3143	12	10^0 J °K^{-1} mol^{-1}	10^7 erg °K^{-1} mol^{-1}
Boltzmann constant	k	1.38054	18	10^{-23} J °K^{-1}	10^{-16} erg °K^{-1}
First radiation constant (2πhc^2)	c$_1$	3.7415	3	10^{-16} W m^2	10^{-5} erg cm^2 s^{-1}
Second radiation constant	c$_2$	1.43879	19	10^{-2} m°K	10^0 cm°K
Stefan-Boltzmann constant	σ	5.6697	29	10^{-8} W m^{-2} K^{-4}	10^{-5} erg cm^{-2} s^{-1} K^{-4}
Gravitational constant	G	6.670	15	10^{-11} N m^2 kg^{-2}	10^{-8} dyn cm^2 g^{-2}

*Based on 3 std.dev., applies to last digits in preceding col. † Electromagnetic syst.
‡ Electrostatic syst.   [1] Reprinted from NBS Technical News Bulletin Oct. 1963.

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