Physical Metallurgy of Metals and Alloys

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To my Late Mother

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PREFACE

The significance of Physical Metallurgy in comprehending the functions of metals and alloys within the expanding domain of materials engineering is widely acknowledged towards determining the contemporary technological advancement. Furthermore, students pursuing studies in metallurgical and mechanical engineering express a pressing need for a concise and readily available resource on Physical Metallurgy, encompassing both ferrous and nonferrous alloys. This initiative inspires the creation of a book aimed at delving into current theories and methodologies in Physical Metallurgy, commencing from fundamental concepts.

The book primarily focuses on instructing readers on the Physical Metallurgy of metals and alloys, with a predominant emphasis on the ferrous group. Nonetheless, it also incorporates a substantial discussion towards the end, targeting key nonferrous metals and alloys. Metal and alloy characterization is conducted through the analysis of microstructures and properties, complemented by the inclusion of laboratory test data derived from the author's research endeavours carried out during their tenure. The research findings presented across various chapters are anticipated to offer additional insights and value to potential readers.

The book introduces novel subjects like cyclic heat treatment of steel and semi-solid heat treatment of cast aluminium alloy, which are either absent or not covered extensively in existing textbooks on Physical Metallurgy. These supplementary topics, along with discussions on accelerated spheroidization of high carbon steels and the kinetics of recrystallization of deformed metal, aim to enrich both the depth and breadth of the content, attracting interest from academics and industry professionals alike.

The author expresses gratitude for the invaluable support received from family members, particularly his wife Kalpana, elder son, Abir and daughter-in-law Sukanya throughout the writing process of this book. Special thanks are extended to the faculty and staff of the Department of Metallurgical and Materials Engineering at NIT Durgapur, India, for their assistance and provision of laboratory facilities for conducting tests and experiments. The author also acknowledges the collaboration and assistance of Dr J Maiti and Dr KS Ghosh in sourcing experimental data referenced in the book. Additionally, the author gratefully acknowledges the huge support from his younger son Abhro for his significant contribution in creating all the diagrams and figures featured in this book.

CHAPTER 1

ATOMS, ELEMENTS AND COMPOUNDS

1.1 Introduction

Materials in solid state occur through bonding between atoms, where the nature of bonds between the atoms or their electronic configuration determines the arrangement of atoms appearing in solids. To understand the consolidation pattern of atoms in solids, it is required to know about the internal structure of each atom and also regarding the basic concepts of chemical bonding between them.

Considering the Dalton's atomic theory, atom is the smallest unit of matter and it possesses varying number of protons (positively charged particles) and neutrons (carrying no charge) at the nucleus and electrons (negative charged particles) at the periphery. Chemical nature of a substance depends up on the number of electrons in the outer orbit and protons present in the nucleus, thus giving rise to 92 different types of elements along with some additional varieties composed of atoms, which can cause release of enormous energy following disintegration.

Chemical combination of two or more atoms of either similar or different nature produces somewhat larger configuration, called the molecule. Like-molecules made of atoms of identical nature are responsible for production of chemical elements. Most of the elements are chemically reactive, i.e., they combine to form compounds; while a few, namely, copper, gold and silver may occur uncombined. To form a compound, unalike atoms are held together through the sharing of each's orbital electrons. In contrast, mixtures occur between substances through mechanical entanglement. For example, sulphur powder and iron filings can be mixed at any proportions and separated again with the help of a magnet. Whereas, a compound called iron sulfide occurs through chemical reaction, when the said mixture is heated to a requisite temperature. Decomposition of a compound into the parent elements happens to be quite difficult and so a compound occurs with different identity in comparison to a mixture. A compound reacts with another in simple proportion to produce a series of new compounds keeping the total number of atoms in reactants same as that of products. For example, 56 parts (by weight) of CaO react with 73 parts (by weight) of HCl to produce 111 parts (by weight) of $CaCl_2$ and 18 parts (by weight) of H_2O.

$$\begin{array}{lccccccc} & \mathrm{CaO} & + & \mathrm{2HCl} & = & \mathrm{CaCl_2} & + & \mathrm{H_2O} \\ \textit{atomic mass:} & 40+16 & & 2(1+35.5) & & 40+2(35.5) & & 2(1)+16 \end{array}$$

Chemical reaction occurring during metallurgical practices are usually of oxidation and reduction type. As the term implies, oxidation refers to combination of oxygen with any other element, say, carbon to form carbon dioxide (CO_2) during burning of coal or petroleum releasing heat energy. Incidentally, the strong electropositive base metals, namely, aluminum, magnesium, zinc, iron and lead have greater oxidation potential than has carbon. Alternatively, the term oxidation represents a reaction by which the electronegative or non-metallic constituent of a molecule is increased, as depicted by conversion of ferrous chloride ($FeCl_2$) to ferric chloride ($FeCl_3$). Conversely, separation of oxygen atom from a compound makes reduction reaction possible. Besides, reduction refers to a reaction involving loss of electronegative constituent from a molecule.

1.2 Structure of An Atom

An atom consists of a nucleus made-up of protons and neutrons, around which electrons rotate in fixed orbits. The atomic number Z indicating the number of protons and the neutron number N indicating the number of neutrons appearing at the nucleus are added to obtain the atomic mass number $A\ (= Z + N)$, which is roughly equal to the atomic weight. The electron refers to a particle with a mass of 9.1 x $10^{-31}kg$ and a negative charge of 1.602 x $10^{-19}C$. Whereas, a proton is nearly 1840 times heavier than an electron and carries a positive charge of 1.602 x $10^{-19}C$. A stable (electrically neutral) atom contains equal number(s) of proton and electron. At the nucleus, a neutron of nearly similar size and mass to the proton, but carrying no electrical charge, also occurs, thus causing no disruption to the net charge balance in the atom. The masses of the proton, neutron and electron are $1.00758amu$, $1.00897amu$ and $0.00055amu$, respectively.

The simplest of all atoms is an atom of hydrogen, consisting of one proton and no neutron ($A=Z=1$) and an electron in the orbital around it. Its isotopes (having nuclei with same Z but different N) are deuterium ($N = 1, Z = 1$) and tritium ($N = 2, Z = 1$). Next to hydrogen, helium consists of two protons and two neutrons ($Z = 2, N = 2$) at the nucleus and two electrons in the same shell around the nucleus. Elements are arranged following this sequence up to heavy elements (uranium, neptunium, plutonium, etc.), each having one proton and one or two neutrons more than its predecessor. Thus, the main isotope of uranium has $A = 238$ with $Z = 92$ and $N = 146$, although uranium has two more isotopes, with $A = 234$ and 235, that exist naturally. Niels Bohr proposed the following postulations with regard to the atomic structure:

[1] An atom consists of a nucleus containing a proton and a neutron, with electrons revolving around the nucleus, with tangential velocity u in circular orbit of radius r (Fig. 1-1) without emitting energy. The force of attraction F_e between a revolving electron (of mass m and charge e^-) and the nucleus (of charge Ze^+) is equal to the centrifugal force (F_c) of the revolving electron, i.e.,

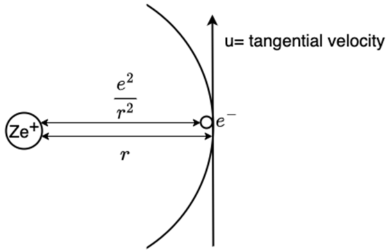


Fig. 1-1 Schematic view of an electron revolving around the nucleus.

$$F_e \left(= \frac{kZe^2}{r^2}\right) = F_c \left(= \frac{mu^2}{r}\right), \quad (1.1)$$

where k = constant = $\frac{1}{4\pi\epsilon} = 9 \times 10^9 \frac{Nm^2}{C^2}$, ϵ = permittivity of free space = $8.854 \times 10^{-12}\ kg^{-1}m^{-3}s^4A^2$. Using the above equalities, $u^2 = (kZe^2)/m\,r$.

[2] Out of the infinite number of possible circular orbitals (electron probability density cloud) around the nucleus, an electron can revolve only in those orbits whose angular momentum (mur) is an integral multiple of $h/2\pi$, i.e. $mur = n(h/2\pi)$, h being the Plank's constant. This issues, $u^2 = (n^2h^2)/4\pi^2m^2r^2$.

Equating the above two expressions of u^2,

$$r = (n^2h^2) / 4\pi^2kZe^2m \quad (1.2)$$

Hence, r for smallest orbit of the hydrogen atom ($Z = 1,\ n = 1$) works out to be $(6.625 \text{ x}10^{-34})^2$ / $[4(3.14)^2$ x $9\text{x}10^9$ x $(1.6 \text{ x } 10^{-19})^2$ x $9 \text{ x } 10^{-31}]$ = 5.368 x $10^{-11}m$.

[3] Each permitted orbit is associated with a definite amount of energy and so corresponds to an energy level. The different energy levels arising out of levels 1, 2, 3, 4, …from the nucleus onward are designated as K, L, M, N, etc. An electron continues to move in a particular orbit without losing energy, thereby leading to a situation called ground state.

[4] If energy is supplied to an electron, it may jump or excite from lower to a higher energy level (say, from 1 to 2, 3 or some higher level) by absorbing one or more quanta of energy. Similarly, an excited electron may fall from higher to a lower energy level by emitting or releasing one or more quanta of energy. The energy difference ΔE between the two levels is related to the frequency ν of the radiation emitted or absorbed following the equation $\Delta E = h\,\upsilon$, where ν = c/λ, λ being the wave length and c the velocity of light.

Based on above postulations, Bohr calculated the radius of various orbits occupied by electrons of the hydrogen-like species (He^+, Li^{++}, etc.) and also the energy of electron in different orbits around nucleus. Now, considering an electron associated with a definite energy level, the Heisenberg uncertainty principle states that it is impossible to specify, at any moment, the momentum as well as the location of an electron. Mathematical representation of the Heisenberg principle is

$$\Delta p.\Delta x = h/2\pi = constant. \tag{1.3}$$

In equation 1.3, Δp is the uncertainty in momentum and Δx is the uncertainty in location. The said equation also suggests that the certainty in determining one of the conjugate properties (by assuming its small value) introduces uncertainty in determining the other (by assigning it a greater value). Further, to predict the probability of locating an electron of particular energy in a given region of space and moment, each electron orbital (also known as quantum state) is assigned a set of quantum numbers, namely, the principal quantum number (n), the angular quantum number or Azimuthal quantum number (l), the magnetic quantum number (m) and the spin quantum number.

Principal quantum number (n) refers to number(s) appearing between 1 and 7 with corresponding designation(s) K, L, M, N, O, P and Q (for atoms of known elements) indicating average distance of the electron from the nucleus. The higher the principal quantum number, greater is the distance of an electron from the nucleus as well as higher its energy. The maximum number of electrons in n-principal quantum number is given by $2n^2$. Angular momentum (Azimuthal) quantum number (l) denotes the sublevel to which the electron belongs and also determines the shape of the orbital and the energy associated. l assumes values from 0 to $(n-1)$ for a given value of n and the corresponding sublevels are assigned with letters s, p, d and f with an order of increasing energies.

For $n = 1$, $n-1 = 0$ $l = 0$ s (sharp) sublevel
For $n = 2$, $n-1 = 1$ $l = 0$ s sublevel, 1 p(principal) sublevel
For $n = 3$, $n-1 = 2$ $l = 0$ s, 1 p, 2 d (diffuse) sublevel
For $n = 4$, $n-1 = 3$ $l = 0$ s, 1 p, 2 d, 3 f (fundamental) sublevel

At higher energy level, the sublevels start overlapping, e.g., $3d$ sublevel overlaps the $4s$ sublevel indicating that the energy of $3d$ sublevel is higher than that of $4s$ sublevel. Magnetic quantum number (m) refers to the preferred orientations of orbitals in space and also the number of orbitals in sub-orbit. For each value of l, there are $2l + 1$ values of m.

For $l = 0$, $m = 1$, i.e., 0, so s sublevel has one orientation.
For $l = 1$, $m = 3$, i.e., -1, 0, +1, so p sublevel has three orientations, p_x, p_y *and* p_z.
For $l = 2$, $m = 5$, i.e., -2, -1, 0 +1, +2, so d sublevel has five orientations, namely, dz^2, $d_{x^2-y^2}$, d_{xy}, d_{yz} *and* d_{zx}.

Boundary surfaces of s-, p- and d- states of an atom are shown in Fig. 1-2. Spin quantum number arises due to spinning of electron about its own axis either clockwise (+½) or anti-clockwise (-½). The two electrons possessing the same sign of spin are said to have parallel spin (↑↑); while the two electrons having opposite sign of spin are said to have opposite or paired spin (↑↓).

Following are the rules based on which electrons are distributed around the nucleus: (*i*) Electrons are added progressively to various orbitals having increasing order of energy starting from the orbital of lowest energy, i.e., $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $4f$, $5d$, $6p$, $7s$, $5f$, $6d$ and $7p$. A new electron enters an empty orbital for which $(n + l)$ is minimum. (*ii*) An orbital cannot have more than two electrons and in an orbital two electrons must have opposite sign of spin. (*iii*) Electron pairing in an orbital (s, p, d or f) cannot take place until each orbital of the same sublevel contains

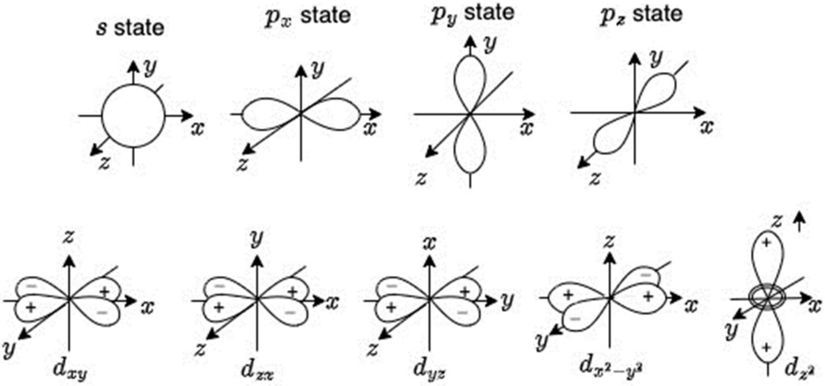
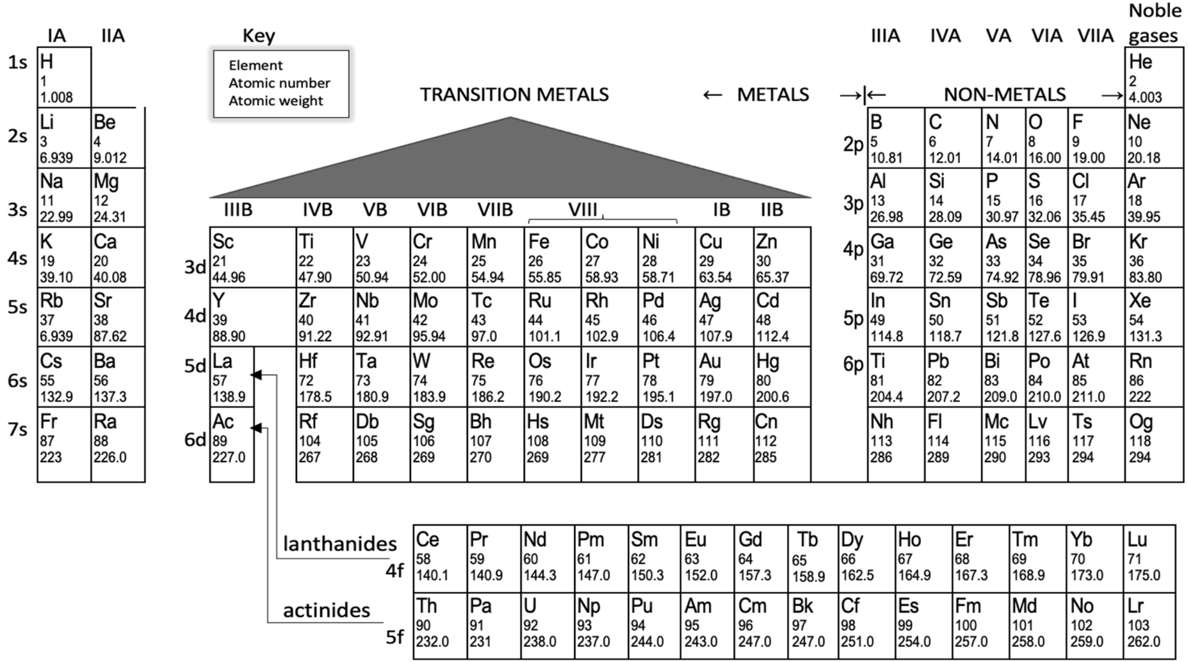


Fig. 1-2 Boundary surfaces of s-, p- and d- states of an atom.

one electron. (*iv*) Orbitals in the same sublevel are completely filled or exactly half-filled of electrons, because such arrangement is considered to be stable with lesser energy. This has been typically illustrated for $_{24}$Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ and $_{29}$Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$.

1.3 The Periodic Table

Arrangement of known elements was made by Demitri Mendeleef in the form of a periodic table (Fig. 1-3) to denote their physical and chemical properties as periodic functions of the atomic number (number of protons in the nucleus). In this table, as the atomic number increases along the successive horizontal rows or periods, the chemical properties recur after the first row of two elements ($_1$H and $_2$He), then after the second and third row, each consisting of eight elements ($_3$Li - $_{10}$Ne and $_{11}$Na - $_{18}$Ar) and again after fourth and fifth row individually consisting of eighteen elements ($_{19}$K - $_{36}$Kr and $_{37}$Rb - $_{54}$Xe). Subsequently, the sixth row consists of thirty-two elements ($_{55}$Cs - $_{86}$Rn), while the last or seventh row is considered to be incomplete accommodating the elements starting with $_{87}$Fr and ending with $_{103}$Lw. Later, some more elements with $Z > 103$ are discovered and accommodated in the seventh row of the periodic table. Elements listed in the periodic table are also presented alphabetically in Table 1-1 along with their symbolic designations. The periodic table has sixteen groups or sub-groups with designations I A to VII A, I B to VII B, VIII and 0. As indicated in Fig. 1-3, elements under sub-groups IA, II A and III A to VII A have complete inner shells or energy levels and incomplete outermost shell, typically



	IA	IIA		IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB		IIIA	IVA	VA	VIA	VIIA	Noble gases
1s	H 1 1.008																			He 2 4.003
2s	Li 3 6.939	Be 4 9.012												2p	B 5 10.81	C 6 12.01	N 7 14.01	O 8 16.00	F 9 19.00	Ne 10 20.18
3s	Na 11 22.99	Mg 12 24.31												3p	Al 13 26.98	Si 14 28.09	P 15 30.97	S 16 32.06	Cl 17 35.45	Ar 18 39.95
4s	K 19 39.10	Ca 20 40.08	3d	Sc 21 44.96	Ti 22 47.90	V 23 50.94	Cr 24 52.00	Mn 25 54.94	Fe 26 55.85	Co 27 58.93	Ni 28 58.71	Cu 29 63.54	Zn 30 65.37	4p	Ga 31 69.72	Ge 32 72.59	As 33 74.92	Se 34 78.96	Br 35 79.91	Kr 36 83.80
5s	Rb 37 6.939	Sr 38 87.62	4d	Y 39 88.90	Zr 40 91.22	Nb 41 92.91	Mo 42 95.94	Tc 43 97.0	Ru 44 101.1	Rh 45 102.9	Pd 46 106.4	Ag 47 107.9	Cd 48 112.4	5p	In 49 114.8	Sn 50 118.7	Sb 51 121.8	Te 52 127.6	I 53 126.9	Xe 54 131.3
6s	Cs 55 132.9	Ba 56 137.3	5d	La 57 138.9	Hf 72 178.5	Ta 73 180.9	W 74 183.9	Re 75 186.2	Os 76 190.2	Ir 77 192.2	Pt 78 195.1	Au 79 197.0	Hg 80 200.6	6p	Ti 81 204.4	Pb 82 207.2	Bi 83 209.0	Po 84 210.0	At 85 211.0	Rn 86 222
7s	Fr 87 223	Ra 88 226.0	6d	Ac 89 227.0	Rf 104 267	Db 105 268	Sg 106 269	Bh 107 270	Hs 108 269	Mt 109 277	Ds 110 281	Rg 111 282	Cn 112 285		Nh 113 286	Fl 114 289	Mc 115 290	Lv 116 293	Ts 117 294	Og 118 294

lanthanides 4f	Ce 58 140.1	Pr 59 140.9	Nd 60 144.3	Pm 61 147.0	Sm 62 150.3	Eu 63 152.0	Gd 64 157.3	Tb 65 158.9	Dy 66 162.5	Ho 67 164.9	Er 68 167.3	Tm 69 168.9	Yb 70 173.0	Lu 71 175.0
actinides 5f	Th 90 232.0	Pa 91 231	U 92 238.0	Np 93 237.0	Pu 94 244.0	Am 95 243.0	Cm 96 247.0	Bk 97 247.0	Cf 98 251.0	Es 99 254.0	Fm 100 257.0	Md 101 258.0	No 102 259.0	Lr 103 262.0

Figure 1-3 Periodic classification of known elements.

Actinium	Ac	Erbium	Er	Mercury	Hg	Rutherfordium	Rf
Aluminum	Al	Europium	Eu	Molybdenum	Mo	Samarium	Sm
Americium	Am	Fermium	Fm	Moscovium	Mc	Scandium	Sc
Antimony	Sb	Flerovium	Fl	Neodymium	Nd	Seaborgium	Sg
Argon	Ar	Fluorine	F	Neon	Ne	Selenium	Se
Arsenic	As	Francium	Fr	Neptunium	Np	Silicon	Si
Astatine	At	Gadolinium	Gd	Nickel	Ni	Silver	Ag
Barium	Ba	Gallium	Ga	Nihonium	Nh	Sodium	Na
Berkelium	Bk	Germanium	Ge	Nitrogen	N	Strontium	Sr
Beryllium	Be	Gold	Au	Niobium	Nb	Sulfur	S
Bismuth	Bi	Hafnium	Hf	Nobelium	No	Tantalum	Ta
Bohrium	Bh	Hassium	Hs	Oganesson	Og	Technetium	Tc
Boron	B	Helium	He	Osmium	Os	Tellurium	Te
Bromine	Br	Holmium	Ho	Oxygen	O	Tennessine	Ts
Cadmium	Cd	Hydrogen	H	Palladium	Pd	Terbium	Tb
Calcium	Ca	Indium	In	Phosphorus	P	Thallium	Tl
Californium	Cf	Iodine	I	Platinum	Pt	Thorium	Th
Carbon	C	Iridium	Ir	Plutonium	Pu	Thulium	Tm
Cerium	Ce	Iron	Fe	Polonium	Po	Tin	Sn
Cesium	Cs	Krypton	Kr	Potassium	K	Titanium	Ti
Chlorine	Cl	Lanthanum	La	Praseodymium	Pr	Tungsten	W
Chromium	Cr	Lawrencium	Lr	Promethium	Pm	Uranium	U
Cobalt	Co	Lead	Pb	Protoactinium	Pa	Vanadium	V
Copernicium	Cn	Lithium	Li	Radium	Ra	Xenon	Xe
Copper	Cu	Livermorium	Lv	Radon	Rn	Ytterbium	Yb
Curium	Cm	Lutecium	Lu	Rhenium	Re	Yttrium	Y
Darmstadtium	Ds	Magnesium	Mg	Rhodium	Rh	Zinc	Zn
Dubnium	Db	Manganese	Mn	Roentgenium	Rg	Zirconium	Zr
Dysprosium	Dy	Meitnerium	Mt	Rubidium	Rb		
Einsteinium	Es	Mendelevium	Md	Ruthenium	Ru		

Table 1-1: List of elements and their symbolic designations as mentioned in the periodic table (refer Fig. 1-3)

called normal elements. Elements under sub-groups I B, II B, III B to VII B and VIII are transition metals having the outermost and penultimate shells incomplete; e.g., $_{24}$Cr:$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ and $_{27}$Co: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$. Elements of 0 group have no incomplete shell and are known as noble or inert gasses. Fourteen elements ($_{58}$Ce – $_{71}$Lu) after $_{57}$La are called the Lanthanides and fourteen more ($_{90}$Th – $_{103}$Lw) beyond $_{89}$Ac are called the Actinides; both are accommodated in two separate rows at the bottom of the periodic table.

In a period, a trend in physical and chemical property is observed when moved from one element to other. For example, size of the atom decreases from left to right, i.e., alkali metals have largest atoms as compared to halogen. Besides, the electronegativity increases from left to right and this corresponds to a transition from metallic to covalent character. Similarly, in a group, elements have similar chemical property and, on descending a group, size of the atom increases, ionization potential decreases, electronegativity decreases and transition from covalent to metallic character becomes prevalent.

Elements in the periodic table may further be classified in to s-, p-, d- and f-blocks according to the type of orbital (s, p, d, f) being filled by the last electron of the respective atom. Group IA (alkali metals) accommodating last electron in the outermost s-orbital and group IIA (alkali earth metals) accommodating last two electrons in the outermost s-orbital are called the s-block elements. Typical examples for s-block elements are $_{11}$Na: $1s^2 2s^2 2p^6 3s^1$ and $_{12}$Mg: $1s^2 2s^2 2p^6 3s^2$]. Group III A – VII A and 0 group elements having the outermost shell configuration ns^2p^1, ns^2p^2, $\ldots ns^2p^6$, thus accommodating the last electron(s) in the p-orbital, are called the p-block elements, e.g., $_5$B: $1s^2 2s^2 2p^1$ and $_8$O: $1s^2 2s^2 2p^4$. Similarly, d-block elements exist in III B – VII B, VIII, I B and II B groups and have outermost shell configurations varying from $(n-1)\ s^2p^6d^1$, ns^2 in group III B to $(n-1)\ s^2p^6d^{10}$, ns^2 in II B, thereby filling the d-orbital by the last electron, as displayed for $_{21}$Sc: $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^1 4s^2$ and $_{30}$Zn: $1s^2 2s^2 2p^6 3s^2 3p^6\ 3d^{10} 4s^2$. Since the properties of these elements occur between those of s-block and p-block elements, they are designated as transition elements with metallic characteristics. They may further be classified into first transition series, i.e., the fourth period elements $_{21}$Sc – $_{30}$Zn accommodating the last electron in the $3d$ orbital, second transition series, i.e., the fifth period elements $_{39}$Y – $_{48}$Cd accommodating the last electron in the $4d$ orbital and third transition series, i.e., the sixth period elements $_{57}$La and $_{72}$Hf – $_{80}$Hg accommodating the last electron in the $5d$ orbital. In f-block elements, the last electron enters in the f-orbital, thus giving rise to the outermost incomplete d-orbital ($5d$ or $6d$) along with incomplete f- orbital ($4f$ or $5f$) and a corresponding outermost shell configuration of $(n-2)\ f^{1\text{-}14}$, $(n-1)\ d^{0\text{-}1}$, ns^2. On the basis of the number of f-orbital ($4f$ or $5f$) being filled, there are $4f$-series, also called Lanthanides, including the elements from $_{58}$Ce to $_{71}$Lu, where the last electron is progressively added in $4f$-orbital and $5f$-series, also called Actinides, including the elements from $_{90}$Th to $_{103}$Lw, where the last electron is progressively added in $5f$-orbital. Example are: $_{71}$Lu: $1s^2 2s^2 2p^6 3s^2 3p^6\ 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^1$ and $_{103}$Lw:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^1$.

1.4 Chemical Bonding

There are mainly three ways of acquiring a stable electronic configuration for an atom, i.e., by gaining electron from another atom or by losing electron to another atom or by sharing electron with another atom. The first two will lead to electrovalent linkage; while the last one is responsible for covalent linkage. Accordingly, the chemical bonds are classified as the electrovalent or ionic type and the covalent type. Electrovalent bonds usually occur between an electropositive metallic element and an electronegative non-metallic element; while covalent bonds appear between two electronegative elements.

1.4.1 Electrovalent or Ionic Bond

The electropositive elements, namely, Na, K, Ca, Ba, Sr, Mg, Al, etc. loss electron(s) and convert into cations and the electronegative elements, namely, O, S and halogens accept electron(s) and convert into anions. Let us consider table salt (NaCl) as a model ionic solid; while other examples are ceramic materials, e.g., Al_2O_3, MgO, etc. The sodium atom has stable filled shells of $1s^2 2s^2 2p^6$ and a single $3s$ electron has a tendency to leave the orbital, to produce sodium cation (Na^+), with a unit positive charge of $1.60 \times 10^{-19} C$. The chlorine atom, on the other hand, has one electron short to the outermost p orbital ($1s^2 2s^2 2p^6 3s^2 3p^5$) and then to achieve a stable filled shell it needs to accept an electron to produce a chloride anion (Cl^-) with unit negative charge of $1.60 \times 10^{-19} C$. Donation of an electron by sodium atom and acceptance of this electron by a chlorine atom result in the generation of equal number sodium cations and chloride anions, which assemble together ultimately to produce a three-dimensional pattern of sodium chloride crystal. Considering the energy due to electrical interaction of all the ions in the crystal and also the strong repulsive energy between the inner cores of adjacent ions at small separations, the total potential energy as a function of separation, r can be derived, as illustrated in Fig. 1-4. At large bonding energy, the total potential energy assumes a minimum at equilibrium separation r_0, where the attractive and repulsive forces between ions just balance each other. If the separation between ions is either increased or decreased from r_0, the total energy of the crystal rises, thus developing a restoring force acting to return the ions to their equilibrium separation r_0.

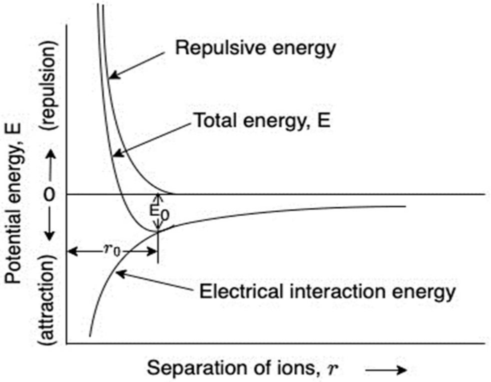
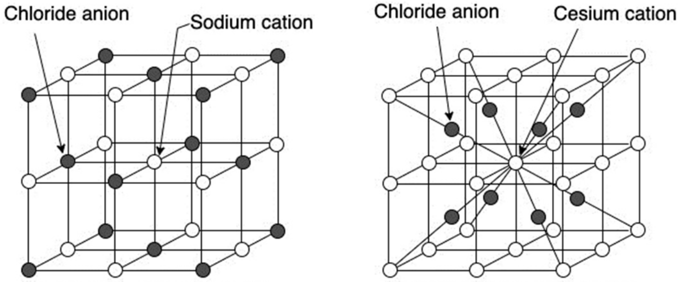


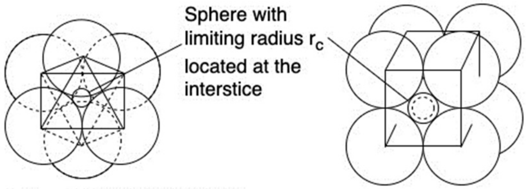
Figure 1-4 Total potential of an ion pair as a function of spacing between ions.

Ionic bond is non-directional, i.e., in a crystal each ion tends to surround itself with as many ions of opposite charge as possible simultaneously. The actual number of ions which can be accommodated is determined, at first, by the geometrical factors and, secondly, by the necessity of acquiring electrical neutrality in a mass of solid. Although, NaCl is quite similar chemically to CsCl, their crystal structures differ significantly following the geometrical restriction, which arises due to the relative size of the ions. In NaCl, six chloride anion neighbors of a sodium cation are placed at the corners of an octahedron with Na^+ ion in the central interstice (Fig. 1-5*a*). If chloride anions were in contact, the radius of the octahedral void or interstice would be $0.414r_a$(also called the limiting radius in Fig. 1-5*c*), where $r_a$is the radius of anion. Considering the electrical repulsion between adjacent anions, ionic bonding is supposed to improve when the cation radius r_c is larger than the limiting radius, $0.414r_a$ and the anions are then located somewhat apart by the central cation. To fulfil this criterion in NaCl, r_c assumes a value of $0.525r_a$. In cesium chloride crystal structure, there is cubic packing of eight anions around a cesium cation, Cs^+ (Fig. 1-5*b*) and the limiting radius for cubic interstice is $0.732r_a$ (Fig. 1-5*d*). A list of possible arrangement of anions, the corresponding co-ordination number of the cation and the limiting radius ratio is given in Table 1-2.



(a) Sodium chloride (NaCl)

(b) Cesium chloride (CsCl)



(c) $r_c/r_a = 0.414$ for octahedral interstice

(d) $r_c/r_a = 0.732$ for cubic interstice

Figure 1-5 Crystal structures of *a*) sodium chloride and *b*) cesium chloride, and limiting radius ratios of *c*) octahedral interstice and *d*) cubic interstice.

Table 1-2 Possible arrangement of the anions around the cation along with the co-ordination number of the cation and the limiting radius ratios

Arrangement of the anions	Co-ordination number	Limiting radius ratio, r_c/r_a
Closed packed	12	1
Cubic	08	0.732
Octahedral	06	0.414
Tetragonal	04	0.225
Triangular	03	0.155

Further, to estimate the ionic character of a bond, Table 1-3, showing electronegativities of elements, may be referred. The ionic character of a bond is noticed to increase with the difference in electronegativities of the participating atoms. Approximating a difference of nearly 1, as appearing in case of HCl, its ionic character to the extent of 15 percent shows up. Thereafter, the ionic character reaches up to 50 percent and then to 85 percent with increased differences of 2 and 3, respectively. Based on this, LiF with a difference in electronegativities of 2.9 appears to be completely ionic; while MgO with 2.3 shows a tendency to form ionic bonds and SiO_2 with 1.7 shows partly ionic and partly covalent character.

Table 1-3 Electronegativities of elements

F	3.9	As, B	2.0	Sc, Y	1.3
O	3.5	Hg, Sb	1.9	Mg	1.2
N, Cl	3.0	Bi, Ge, Pb, Si, Sn	1.8	Ca, Li, Sr	1.0
Br	2.8	Ag, Cu	1.7	Ba, Na	0.9
C, S, I	2.5	Ga, Ti	1.6	K, Rb	0.8
Se	2.4	Al, In, Zn, Zr	1.5	Cs	0.7
Au, H, P, Te	2.1	Be, Cd, Tl	1.4		

1.4.2 Covalent Bond

In this type, there is no loss of electron from an atom to another. Instead, sharing of electrons occurs between the neighboring atoms. For such sharing, overlap of the outermost orbitals having vacant electron state is necessary. When overlapping orbitals are directionally oriented and not spherically symmetric, good overlapping with a net decrease in the potential energy can occur, thereby issuing directionality to the covalent bond. To produce a hydrogen molecule, two hydrogen atoms each having lone electron at $1s$ ground state come closer causing overlap of the respective electron probability clouds. Following the Pauli's principle of accommodating two electrons of opposite spin in the $1s$ orbital, sharing of electrons takes place to produce covalent bond with bond energy 436 $kJmol^{-1}$ and bond length 0.74 Å in a hydrogen molecule. Similarly, to produce a fluorine molecule, two fluorine atoms, each (Z=9, $1s^2 2s^2 2p^5$) having half-filled p_z orbital, come together, so that the directionality of p_z orbitals permit efficient overlapping to form a covalent bond, of bond energy 154 $kJmol^{-1}$ and bond length 1.42 Å. Again, to produce a water molecule, the two unpaired electrons of p_y and p_z orbitals in an oxygen atom (Z=8, $1s^2 2s^2 2p^4$) readily pair-up with the unpaired $1s$ electrons of two hydrogen atoms forming covalent bonds. To form the said covalent bonds, there is sp^3 hybridization (four in number and oriented along the lines joining the center and the four corners of a regular tetrahedron) due to interaction between the $2s$ and $2p$ orbitals of the oxygen atom. Two of the hybridized orbitals of oxygen being filled with paired-up electrons do not take part in bonding; rather, the other two orbitals, bearing one electron in each, are shared with the unpaired 1s electrons of two hydrogen atoms. Following the same mechanism, remaining elements of the sixth (VI A) column form covalent bonds, producing S – S – S bond with bond angle 107°. In case of sulphur, Se – Se – Se bond in selenium and Te – Te – Te bond in tellurium with bond angle of 104° in the latter two. This type of end-to-end overlap of *p* orbitals give rise to what is known as sigma-bond. On the other hand, lateral overlap of *p* orbitals develop pi-bond forming one double bond to hold two oxygen atoms together in a diatomic oxygen molecule. Figure 1-6 illustrates the formation of sigma bond (due to head-to-head overlap of *p* orbitals) and pi bonds (due to lateral overlap of two *p* orbitals) as types of covalent bond. Similarly, the fifth (V A) column element nitrogen has all three 2*p* electrons unpaired and, consequently, forms a diatomic molecule with covalent type triple bonds between two nitrogen atoms. The diamond form of carbon (Z=6, $1s^2 2s^2 2p^2$) and other fourth (IV A) column elements share all the four hybridized orbitals (involving 2*s* and 2*p* electrons) with four neighbors to form four bonds of equal strength developing ideal tetrahedral angle of 109.5° in between.

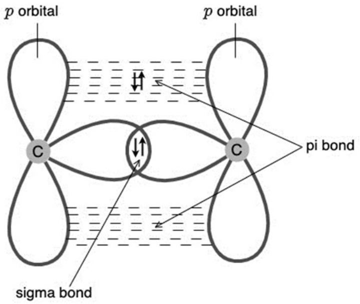


Fig. 1-6 Sigma and Pi bonds.

1.4.3 Metallic Bond

Elements to the left of the fourth (IV A) column exhibit metallic character. For want of sufficient electrons to produce octet or doublet configuration around each atom, sharing of electrons between neighboring atoms becomes delocalized, thereby providing a common pool of free electrons resonating between different atoms. The metallic state thus can be described as an array of positive ions in a cloud of free electrons to which all the metal atoms have contributed their valence electrons. These electrons have freedom to move anywhere within a crystal, simultaneously, holding all the ion cores together. Such an electron mobility characteristic to metal atoms makes the metallic bond non-directional and becomes responsible for good thermal and electrical conductivity, as occurring in case of elements like sodium, potassium, copper, silver and gold. As the number of valence electrons and their closeness to the nucleus increase, they tend to become localized revealing partial covalent nature of the bond. The transition metals (iron, nickel, tungsten and titanium) with incomplete d-shells exhibit a significant part of covalent bonding through hybridization of inner shell electron orbitals, thus, giving rise to their high melting points. This covalent-metallic combination continues up to fourth (IV A) column, where debarring diamond-carbon, other elements are either more metallic like silicon and germanium or most metallic like grey-tin and lead.

1.4.4 Secondary Bonding Forces

Apart from occurrence of the primary force of attraction between atoms or ions in the covalent or ionic bonded molecules, there are forces of attraction of secondary nature, which can hold these molecules either in liquid or solid state. Moreover, the atoms in noble gases, although bearing no valence electron, are observed to attract each other in some way, leading to the occurrence of liquid or solid at low temperatures. For instance, two atoms of argon appearing in close proximity may show momentarily a situation (Fig. 1-7) depicting concentration of electrons and this may arise mutual attraction between the unshielded positively charged nucleus of one atom and the negatively charged electron-pile up of another atom. In a similar way, electrical charges are developed giving rise to regions of positive and negative charges in molecules, thereby generating dipole moments in each of them. For example, in a water molecule, the two electrons contributed by the two hydrogen atoms tend to concentrate in the vicinity of oxygen atom, thus generating negative charge towards the oxygen end, leaving the hydrogen end as positive. As a result, each water molecule possesses a strong dipole moment and the bond occurring between the water molecules due to attraction between the positively charged hydrogen end of one molecule and the negatively charged oxygen end of another molecule is referred to as hydrogen bond having directional nature. Relatively open network of hydrogen bond in ice, as shown in Fig. 1-8, collapses leading to more closely packed molecules in liquid and this accounts for anomalous increase in density on melting.

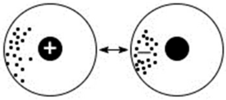


Fig.1-7 Electron concentrations in two atoms appearing in close proximity.

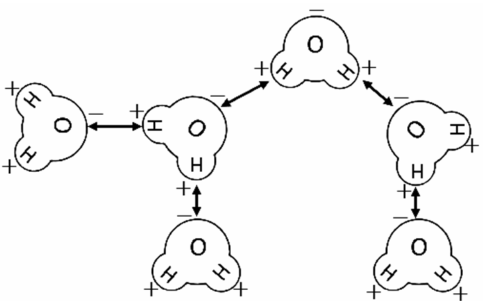


Fig.1-8 Dipole moment in each water molecule and the hydrogen bonds developed between neighboring molecules.

While correlating the physical properties with the bond character, one can assume a solid with atoms vibrating about their mean positions on fixed atomic sites. On melting, atoms have translational freedom causing continuous breaking and rebuilding of bonds between them; while the bonds are totally broken in gaseous state. The thermal energy required to break the interatomic bonds happens to be large for strongly bonded materials and this gives rise to a corresponding rise in melting and boiling temperatures. Since, covalent and ionic bonds are stronger than metallic bond, covalent and ionic solids possess high melting and boiling points. Thus, in case of silica (SiO_2) crystal, the three-dimensional network of Si-O-Si bonds of covalent nature becomes responsible for its high melting point of 1723°C. On the other hand, solids consisting of molecules held together by secondary bonds, exhibit melting and boiling points exclusively on the basis of strength of the secondary bonds playing between the molecules. Based on this fact, the strong C-H bond of covalent type has no relation with the melting point of CH_4; instead, the weaker van-der-Waals' force of attraction holding the CH_4 molecules in solid state are broken during melting at a very low temperature of -182°C. It is also interesting to note that the free electrons in a metal become responsible for good thermal and electrical conductivities. For want of free electrons, ionic and covalent solids are good thermal and electrical insulators. Besides, solids possessing secondary bonds of van-der-Waals type, wholly or partially with ionic or covalent bonds, also behave as good insulators.

Now, to understand the thermal expansion in materials, one can refer to the process of asymmetry as appearing in the potential energy versus interatomic separation curve in Fig.1-9. In comparison to shallow potential well, deep

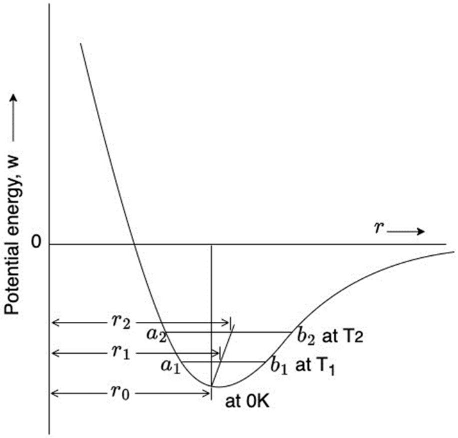


Fig.1-9 Effect of temperature on the mean spacing between atoms.

potential well is symmetrical with the equilibrium distance of separation, r_0, which corresponds to zero Kelvin, i.e., requiring no thermal energy. With increase in temperature, atoms vibrate about their mean positions with increased amplitude of vibration. Referring to Fig.1-9, the amplitude is a_1b_1 at temperature $T_1 >$ zero Kelvin and at $T_2 > T_1$, an increased amplitude of a_2b_2 is noted. The corresponding mean spacings between atoms are r_1 and r_2, respectively. Following the said variation in the amplitude with increase in temperature, the sequence of mean spacings between the atoms appear as $r_2 > r_1 > r_0$, which indicates an increase in the bond length equivalent to the thermal expansion. Similarly, the thermal expansion at a given temperature tends to be less for strongly bonded materials as compared to a weakly bonded one. Based on this, the room temperature data on bond strength and thermal expansion are presented in Table 1-4.

Also, the mechanical properties of solids correlate with the bond character. Solids with strong and directional bonds, namely, the covalently bonded diamond happens to be very hard and brittle. In contrast, relatively weak and non-directional metallic bonds make metals strong and ductile at room temperature and so they can be hammered or pressed into shapes permanently. Solids with ionic bond falls in between covalent and metallic type; however, a balance between covalent and ionic character becomes prevalent due to polarizability factor. As for example, lithium iodide is fairly covalent because the large I^-ion is strongly polarized by the smaller Li^+ ion. Metals used for engineering applications, usually, belong to transition series bearing partially filled d-orbitals. Here, bonds are formed by overlapping of s- and d-orbitals of directional nature, thus, resulting in their properties lying in between covalent solids and metals. Consequently, transition metals show relatively poor thermal and electrical conductivity in association with inadequate ductility as compared to that of typical metals.

Table 1-4 Thermal expansion of some materials at room temperature

Elements/metals	Bond energy, $kJmol^{-1}$	Thermal expansion x10^{-6}, K^{-1}
Silver	47.5	19.2
Copper	56.4	16.7
Gold	60.0	14.1
Nickel	71.6	12.7
Platinum	94.3	8.9

Exercises

1. What is meant by ground state electron configuration? Mention the factors that can deviate an electron from its ground state.

2. Why electrons are added in 4s orbital first than 3d and 5s orbital first than 4d?

3. Describe the significance of Δp and Δx in equation 1.3?

4. Enunciate the rules for anion packing around a cation in ionic solids.

5. There is decrease in bond strength between atoms with increase in atomic number. Why?

6. Specify the roles of primary bonding forces of attraction between atoms and also of secondary bonding forces of attraction between molecules towards building the physical properties of matter.

7. Correlate the phenomenon of thermal expansion in solids with the bond energies and the mean spacings between atoms.

CHAPTER 2

THERMODYNAMICS

2.1 Introduction

Assembly of atoms and molecules into a mass produces an object or, more precisely, a system, which can be isolated from external influences (say, temperature) by enclosing it in an adiabatic container. The system under such isolation may achieve a state of equilibrium and behave homogeneously in terms of composition, structure and properties apart from occasional deviation arising out of vibrating atoms. System may also assume heterogeneous equilibrium consisting of different regions, namely, ice and water meeting at a common boundary, but each being homogeneous by itself. Collection of regions of same kind gives rise to a phase behaving homogeneously.

The thermodynamic state of an equilibrium system can be specified using two thermodynamic variables, the pressure P and the volume V. Let us consider two isolated systems, each occurring in equilibrium at their respective pressure and volume, say, P_1, V_1 and P_2, V_2. The systems are then taken together by keeping a thermally conducting wall in between, so that pressure and volume in each system start changing with a subsequent flow of heat from the hotter to the colder as long as the two systems assume thermal equilibrium. At equilibrium, a system can, thus, be represented by its property called temperature, which happens to be function of the respective pressure and volume. This gives rise to the equation of state:

$$T = f(P, V) \tag{2.1}$$

In case of thermal equilibrium between systems 1, 2, 3 … etc. $f(P_1, V_1) = f(P_2, V_2) = f(P_3, V_3)$… etc.

2.2 Internal Energy and Enthalpy

The internal energy in a system usually represents the summation of individual kinetic energies of motion and energies of interaction of the