STRUCTURE AND PROPERTIES OF HIGH TEMPERATURE MELTS IN METALLURGY

Many liquids such as metal, slag, matte and salt melts are of importance in pyrometallurgical operations. Theories of the liquid state, however, are less developed as compared to those of the solid state. The understanding of the structure and properties of crystalline solids is based on the simple concept of atoms being more or less fixed at regular positions in a lattice. There is almost perfect order. On the other hand, the theories of the gaseous state are based on the concept of atoms or molecules of gas being in perfect disorder with little mutual interaction. The liquid state falls in between, being characterized neither by perfect order nor by perfect disorder. In this chapter, we will examine the liquid state in some detail with emphasis on non-aqueous high temperature melts.

The melting of a solid is generally accompanied by an increase in the molar volume. For a large number of salts, this may be in the range of 10 to 20 percent. Metals also generally expand on melting. The percentage volume increase is often in the range 2.5–6 percent. This increase in volume is attributed to creation of some voids in the bulk when the solid melts. These voids remain distributed in the bulk as what are popularly known as holes. Various theories of liquid structure make various postulates regarding the size and distribution of these holes.

Some other significant changes also take place during the process of melting. In the molten state, the atoms, molecules or ions are relatively free although interactions amongst them are not totally destroyed. The crystalline form of a solid vanishes when it melts and there is no longer any long range order. However, some localised order still persists approximately resembling the parent solid lattice. This is known as short range order. The process of melting should cause an increase in entropy due to addition of voids in the lattice. Disorder is further enhanced by disappearance of long range order. If, however, we ignore the latter, then the entropy of melting should be directly related to the volume change during melting. If several liquids expand by the same degree during melting, then the entropies of melting should also be identical. This is the basis of Richard's rule which states that for the fusion of a large number of solids.

$$\Delta S_m = \frac{\Delta H_m}{T_m} \approx 8.4 \ \text{J. mol}^{-1}\text{K}^{-1} \tag{8.1}$$

where the symbols have their usual meanings.

Again, a liquid, being a condensed phase, possesses much greater order than the corresponding vapour where molecules are entirely free. The boiling of a large number of liquids, therefore, is characterised by identical entropy changes. This provides the basis for Trouton's rule which states that for a large number of liquids.

$$\Delta S_v = \frac{\Delta H_v}{T_v} \approx 8.8 \text{ J. mol}^{-1} \text{ K}^{-1} \tag{8.2}$$

where, again, the symbols have their usual meanings.

These rules indicate that the entropy change during vapourization is generally about ten times that during melting. We may thus conclude that the liquid state is structurally much closer to the solid state than to the gaseous state.

The following is a simple classification of various nonaqueous melts.

Non–aqueous melts

Atomic solution (e.g. solution of Meltais)	Solution of undissociated molecules (e.g. solution of Molten sulphides)	Solutions containing ions and electroneutral entities (e.g. MgCl₂ NaCl, NaCl-MgO, metal-salt solutions etc.)

Ionic solutions
(e.g. molten salts)

Simple solutions with common ion and symmetric charge (e.g. NaCl-KCl, PbCl₂-CdCl₂, AgBr-AgCl etc.)	Solutions without common ion and/or with charge asymmetry (e.g. NaCl-KBr, NaCl- PbCl₂, AgBr-PbCl₂ etc.	Solutions with polymerized ionic groups (e.g. slags)

We will now discuss some of these types in detail.

8.1 STRUCTURE OF LIQUID METALS

As indicated previously, the structure of the liquid state is best understood with reference to the solid structure and the changes that are brought about by the phenomenon of melting. Table 8.1 lists the values of coordination number in the solid and liquid state of some metals at their melting points. The table also indicates interatomic distances in Å.

TABLE 8.1 Interatomic distances in Å and coordination numbers (C.N.) in metals at their melting points

	Solid		Liquid	
Metal	C.N.	Nearest neighbour distance (Å)	C.N.	Nearest neighbour distance (Å)
Na	8	3.72	9.5	3.70
K	8	4.52	9.5	4.70
Mg	12	3.20	10.0	3.35
Al	12	2.86	10.6	2.96
Pb	12	3.50	8.0	3.40
Cu	12	2.50	11.5	2.57
Ag	12	2.89	10.0	2.86
Au	12	2.88	8.5	2.85

From the data given in Table 8.1 and other available data, it has been concluded that those metals such as Al nad Au which have closepacked structures and high coordination number in the solid state have similar nearest-neighbour distances and first coordination numbers in the liquid. Metals which have complicated crystal structures change considerably on melting.

Upon melting, many metals expand by about 3 percent and gain in entropy by some 7-9 J mol^{-1} K^{-1}. Their resistivities and coefficients of thermal expansion increase by some 50-100 percent. The so-called semi-metals, e.g. Ga, Si, Ge, Sb, Bi etc. are exceptions. They contract on melting and their resistivities fall. Their entropies of fusion are two to three times those of normal metals because of profound changes in structure during melting. Table 8.2 lists some values of expansivity, entropy of fusion (ΔS), and resistivity change.

8.1.1 Short–Range Order

Our knowledge of atomic arrangements in liquid metals primarily comes from X-ray diffraction studies. Absence of long range order and constantly changing arrangements of the atoms do not allow sharp diffraction pattern, but lead to diffused halos. Figure 8.1 shows some results of X-ray studies on liquid gold.

The figures are drawn with any particular atom as origin. ρ_r is the probability of finding another atom in unit volume at distance r from the origin. ρ_o is the probability of finding another atom in any randomly selected unit volume, the ratio ρ_r/ρ_o being called W, the **radial-density function**. If W is plotted as a

TABLE 8.2 Changes in metals on melting

Metal	Structure	Atomic volume change, %	∇S of fusion, J. mol^{-1} K^{-1}	Resistivity ratio of liquid-to-solid
Na	Cubic, bc	2.5	7.1	1.45
K	Cubic, bc	2.5	7.1	1.56
Mg	Hexagonal, cp	3.1	9.4	1.78
Al	Cubic, fc	6.0	11.3	2.20
Pb	Cubic, fc	3.5	8.3	1.94
Cu	Cubic, fc	4.5	9.6	2.04
Ag	Cubic, fc	3.3	8.9	2.09
Au	Cubic, fc	3.1	9.6	2.28
Fe	Cubic, fc	·3.6	7.5	~1.0
Ga	Orthorhombic	−3.2	18.5	—
Si	Cubic, diamond	−9.6	27.2	~0.05
Ge	Cubic, diamond	−5.0	28.3	~0.06
Sb	Rhombohedral	−0.9	22.0	0.61
Bi	Rhombohedral	−3.4	20.0	—

[Source : Ref. 1, vol. 1, ch. 7]

function of r, then the plot shows how the probability of finding atoms at various distances from the origin varies with r. The inset in Fig. 4.1 shows the plot. The vertical lines in the figure in the inset represent the solid crystal, the heights

indicating the numbers of atoms in the coordination shells at the distances indicated (n_r, given by the R.H.S. scale).

The first peak for the liquid gives the most probable distance between nearest neighbours. This peak appears very nearly at the same position as the nearest-neighbour distance in the crystal. The similarity between the solid and the liquid diminishes with distance.

The function $4\pi r^2 \rho_r$, known as the **radial distribution function**, is plotted against r in Fig. 8.1. The broken line shows values for $4\pi r^2 \rho_o$. The area under any curve between two r values gives the number of atoms present between two spherical shells having these r values as radii. The peaks correspond to the radii where atomic densities are high. Therefore, the area under the curve from the origin to the first peak corresponds the number of nearest neighbours. The position of the first peak yields a mean atomic separation of about 3 A° which is close to that obtained in the solid metal. The other peaks are less prominent, that is, the distinction between nearest and next-nearest neighbours becomes blurred with distance. This suggests that there is a short-range order but no long-range order. We have already seen that **co-ordination numbers** in the liquid state are similar to those in the solid state. This observation also leads to the conclusion that the structures of metallic melts are basically distorted versions of those of the corresponding solids.
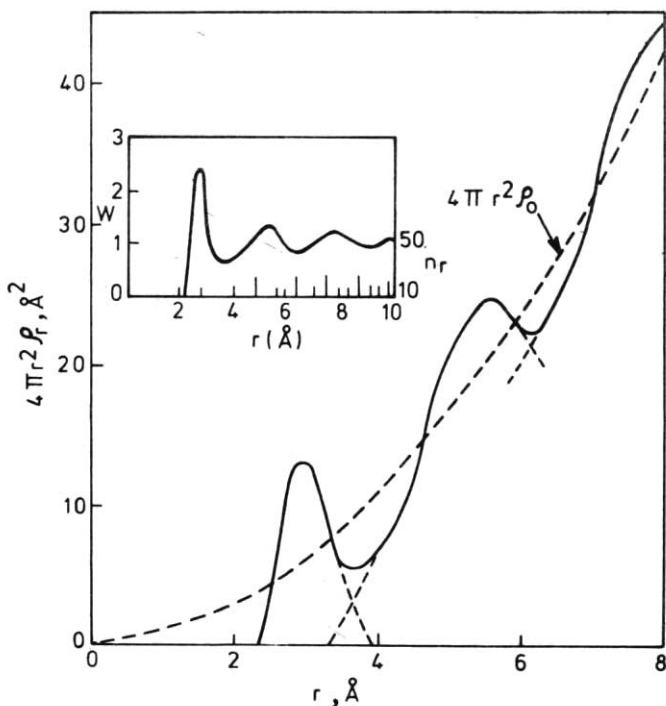

Fig. 8.1 Radial distribution function for liquid gold

Some X-ray studies have been carried out on liquid alloys also. The patterns are similar but quantitative interpretations are more difficult. From the above discussion on liquid metals, it is likely that liquid alloys are similar to the solid alloys but contain a significant fraction of holes. The nature of bonds are also probably retained above the melting point.

Figure 8.2 (a), (b) and (c) present plots to show the effect of alloying on gas solubility and viscosity in two systems. At approximately 50 atomic percent silicon, there is an abrupt change in the solubility of hydrogen in liquid Fe-Si alloy (Fig. 8.2a). This matches very well with the fact that the Fe-Si phase diagram shows a compoud Fe-Si at this composition in the solid state (Fig. 8.2b). Such abrupt changes are found in viscosity and some other properties as well. Figure 8.2c shows the phase diagram and viscosity isotherms for Mg-Sn system to illustrate this point.

Addition of alloying elements to liquid metals, therefore, alter physical properties. The changes are not significantly large so as to indicate gross changes in structure due to alloying additions. However, the atomic distribution in many alloy systems is far from random. Substantial interactions amongst dissimilar atoms may give rise to tendency for compound formation or the opposite repulsive effect tending towards immiscibility. Intermetallic bonds found in solid alloys tend to persist in the liquid state also.

8.2 PHYSICAL PROPERTIES OF LIQUID METALS

Table 8.3 lists some physical properties of common metals. The properties are melting point, boiling point as well as density, viscosity and surface tension values of liquid metals just above the melting point.
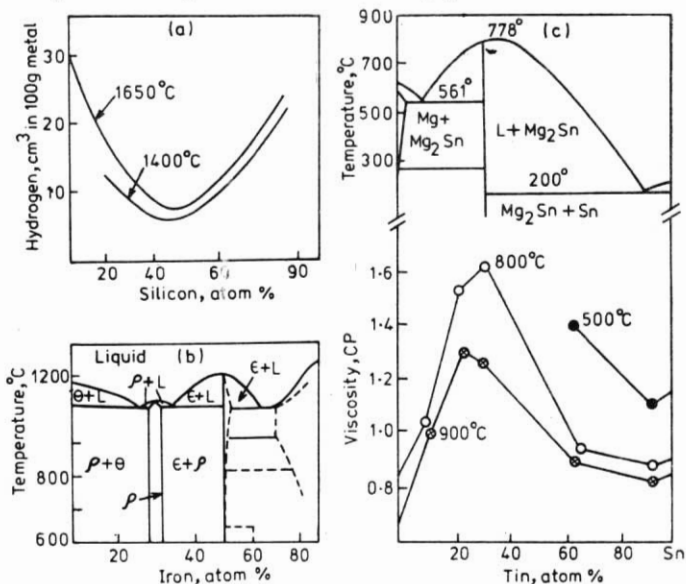
(a) Solbility of hydrogen in liquid Fe-Si solutions at 1 atm pressure
[Source: H. Liang, M.B. Baver and C.F. Floc Trans. TMS-AIME, vol., 167 (1946), 400]
(b) Fe-Si Phase diagram [Source : Metals, Handbook, The Am. Soc. Metals, USA, 7th Ed., 1948]
(c) Phase diagram and viscosity isotherms for the system Mg + Sn[1]

Fig. 8.2 Effect of alloy composition on solubility and viscosity

TABLE 8.3 Physical properties of some common liquid metals*

Metal	Melting Point (°C)	Physical Properties Just Above M.P.			
		Boiling Point (°C)	Density (gms/cc)	Viscosity (cp)	Surface Tension (Dynes/cm)
Aluminium	659	2467	2.37	4.5	915
Antimony	630	1634	6.50	–	387
Beryllium	1282	2477	1.56	–	1330
Bismuth	271.5	1559	10.06	2.5	–
Cadmium	321	765	8.02	3.0	55.0
Cerium	804	2927	6.6	0.2	610
Chromium	1893	2665	6.4	–	1880
Cobalt	1493	2877	7.8	4.0	1936
Copper	1083	2547	7.93	4.1	–
Gold	1063	2692	–	4.0	1124
Iron	1536	2870	7.21	6.7 (4.95)**	1835
Lead	327.5	1747	10.65	2.56	444-480
Magnesium	650	1117	1.585	1.32	556
Manganese	1243	2036	6.43	–	1293
Mercury	–39	357	13.55	1.55	465 (at 20°C)
Molybdenum	2607	4827	9.52	–	2500
Nickel	1453	3175	7.76	4.6	1924
Platinum	1769	3832	–	–	1770
Silver	961	2177	9.30	3.9	923
Tin	232	2687	–	2.71 (2.1)**	566
Titanium	1667	3252	4.11	–	1510
Tungsten	3377	5527	17.6	–	3200
Zinc	419.5	908	6.66	5.86 (3.79)**	824

[*See J.F. Elliott and M. Gleiser : Thermochemistry for Steelmaking, Addison–Wesley Publishing Co., Reading, Mass, U.S.A., Vol. I, 1960 pp. 4–12.] ** Controversial

8.2.1 Melting Point and Boiling Point

It should be noted that there is no apparent connection between melting point and boiling point of a metal. Thus a low value of the former does not necessarily mean a low value of the latter. Aluminium melts at 659°C, but boils at 2467°C. On the other hand, calcium has a higher melting point (850°C) but much lower boiling point (1492°C). The sublimation phenomenon, which is found in some non-metals and metalloids (e.g. P, C, As), is absent in metal. A metal exhibits an extensive liquid range and then boils.

The vapour pressure versus temperature relationship for liquid metals is approximately given by the **Clausius-Clapeyron** equation

$$\log p = - \frac{\Delta H^{O}_{v}}{2.303\ RT} + b \qquad (8.3)$$

where ΔH^{O}_{v} is the heat of vaporization assumed to be approximately independent of temperature. b is also another constant. At the boiling point (T_v), $p = 1$ atm. Hence

$$O = - \frac{\Delta H_v^O}{2.303 \, RT_v} + b \tag{8.4}$$

Combining Eqs. 8.3 and 8.4, one obtains

$$\log p = - \frac{\Delta H_v^O}{2.303 \, RT_v} \left[\frac{T_v}{T} - 1 \right] \tag{8.5}$$

We have seen before that, according to Trouton's rule, $(\Delta H_v^O / T_v)$, i.e. ΔS_v^O, is roughly the same for many metals because it essentially represents the disorder of one mole of gas. Therefore, if p is fixed at a given value (say $p = 10^{-2}$ mm Hg), then the ratio of T_v/T should also be approximately the same for many metals. That this is indeed the case is shown in Fig. 8.3.

The boiling point is an index of the binding energy of atoms in the liquid. The higher the binding energy, the higher is the boiling point. The heat of vaporization is to be supplied in order to break bonds and, hence, it is a measure of the binding energy. Melting and boiling points are crucial properties for extraction and refining of metals. A high melting metal (W, Mo), is extracted in the solid state. Smelting is widely practised for metals whose melting points are not too high. On the other hand, metals having high vapour pressures and, consequently, low boiling points may be extracted and refined in the gaseous state (Zn, Mg).
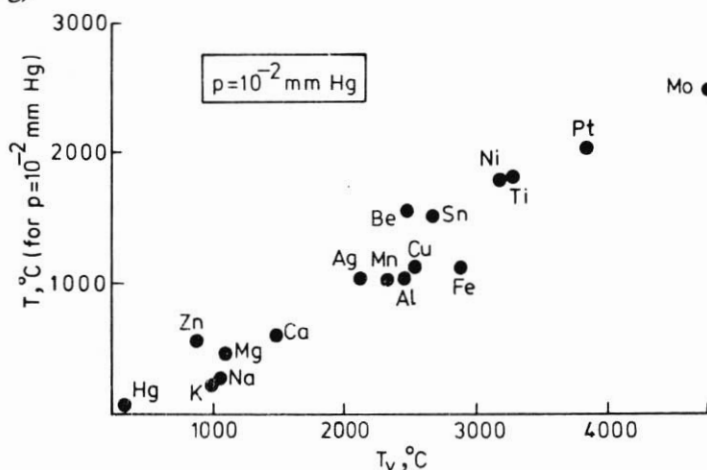

Fig. 8.3 T (for $P = 10^{-2}$ mm Hg) vs T_v for some metals

8.2.2 Density, Viscosity and Electrical Conductivity

The density of a liquid metal is not too different from that the solid. We have seen that for true metals, there is a slight decrease in density whereas for semi-metals, there is a slight increase.

Viscosity (η) is an important property of liquid metals in the context of flow, handling, pouring etc. The inverse of viscosity is called fluidity. Viscosities of molten metals are generally of the order of a few centipoise (1 cp = 10^{-3} kg m^{-1} s^{-1}) thus comparing well with that of liquid water (~ 1 cp). Kinematic viscosity (η/ρ) is a better guide to flow properties and in that respect many liquid metals have more fluidity than water. Thus, handling and pouring of liquid metals

is not a problem from this point of view. With rise in temperature, viscosity decreases rapidly just above the melting point and then shows only small variation with further rise in temperature. For example, viscosity of liquid aluminium is 3.0 cp at 660°C, 2.0 cp at 680°C and 1.5 cp at 800°C.
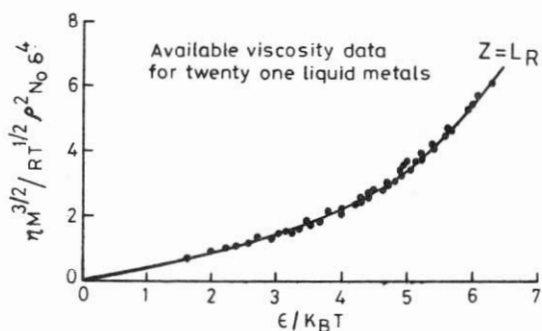

Fig. 8.4 Dimensionless viscosity vs dimensionless characteristic energy plot
[Source: T.W. Chapman, A.I. Ch. E.J. vol. 12 (1966), 395]

Estimation of viscosity of liquid metals may be done with the help of the theory and semiempirical correlation proposed by Chapman* and based on available viscosity data of several liquid metals. The dimensionless viscosity versus dimensionless characteristic energy plot is shown in Fig. 8.4.

Here ε is characteristic energy, K_B is Boltzmann's and T is absolute temperature.

Again empirically,

$$\frac{\varepsilon}{K_B} = 5.20 \, T_m \tag{8.6}$$

where T_m is melting point of the metal.

For the ordinate, M, denotes molecular weight, N_o denotes Avogadro's number and δ the atomic diameter in appropriate unit (for SI it should be in meter). δ is approximately equal to the nearest neighbour distance in Table 8.1

At constant pressure viscosity decreases exponentially with increase in temperature. This variation is expressed by the equation

$$\eta = \eta_o \cdot e^{E_\eta/RT} \tag{8.7}$$

where η_o is a constant and E_η is the Activation energy for viscous flow.

The electrical resistivity of metals does not increase drastically upon melting of metals, liquid metals being electronic conductors retain the high concentrations of free electrons characteristic of solid metals. The increase in resistivity is explained in terms of enhanced disorder in the melt structure. The temperature dependence of resistivity is discussed later in this chapter (see Sec. 8.3).

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*T.W. Chapman, A.I. Ch. E.J., ro' 12, (1966), pp. 395-400

8.2.3 Diffusivity

In simple melts, diffusion and viscous flow both depend on similar movements, viz. the movement of atoms with respect to one another. Thus the **activation energy for diffusion** (E_d) is generally close to that for viscous flow. There is also the Stokes-Einstein equation which relates diffusivity and viscosity for simple melts and relatively large particles which obey Stoke's law of settling. The equation is

$$D = \frac{K_B T}{6\pi r \eta} \tag{8.8}$$

where D is diffusivity, K_B is Boltzmann's constant, and r is particle radius.

The variation of diffusion coefficient with temperature at constant pressure is commonly represented by an equation similar in form to Equation 8.7, viz.

$$D = D_o \exp(-E_D/RT) \tag{8.9}$$

where D_o is a constant independent of temperature. The term E_D, the activation energy for diffusion, may be looked upon as the energy required for an atom to jump into a neighbouring hole which must be made available prior to motion. The hole theory has also been used* to derive an equation relating E_D with melting point. The equation is

$$E_D = 3.74 \, R \, T_m \tag{8.10}$$

There are experimental data to show that Eq. 8.10 is approximately valid for a large number of liquids. Yet, the hole theory of diffusion is no longer widely accepted. Also it is now known that Eq. 8.9 is not followed precisely.

8.2.4 Surface Tension

The surface tensions of liquid metals, as shown in Table 8.3, are very high compared to that of water ($\sim$76 dynes n at 0°C). This is not surprising. The binding energies of metal atoms are high as exemplified by their high boiling points and large heats of vaporisation. Hence, creation of free surfaces, which essentially involves breaking of some bonds, requires large energy. From the above discussion, it would appear that the higher the boiling point of a metal, the greater is its surface energy. This is borne out approximately by actual data as shown in Figure 8.5.

Measurement of surface tension is not always reliable since even very little concentration of surface active elements such as oxygen and sulphur lowers its value. It is not difficult to understand why small amount of impurities may sometimes profoundly influence surface properties. A surface has a structure different from the structure of the bulk. In the surface layers, atoms are bound to the bulk in two dimensions only. The bonds which are free often give rise to special surface properties. They also attract impurity elements. The so-called surface active agents are those which are preferentially adsorbed at the surface. This subject already has been discussed in Sec. 7.2.1

8.2.5 Non–Metals in Metals

Many alloys are solutions of non-metals in metals. Hydrogen, oxygen and sulphur are soluble in Pb, Sn, Ni, Fe etc. Many metals also dissolve nitrogen and

*L. Nanis and I.O.M. Bockris, J. Chem. Phys. Vol. 67 (1963), 2865

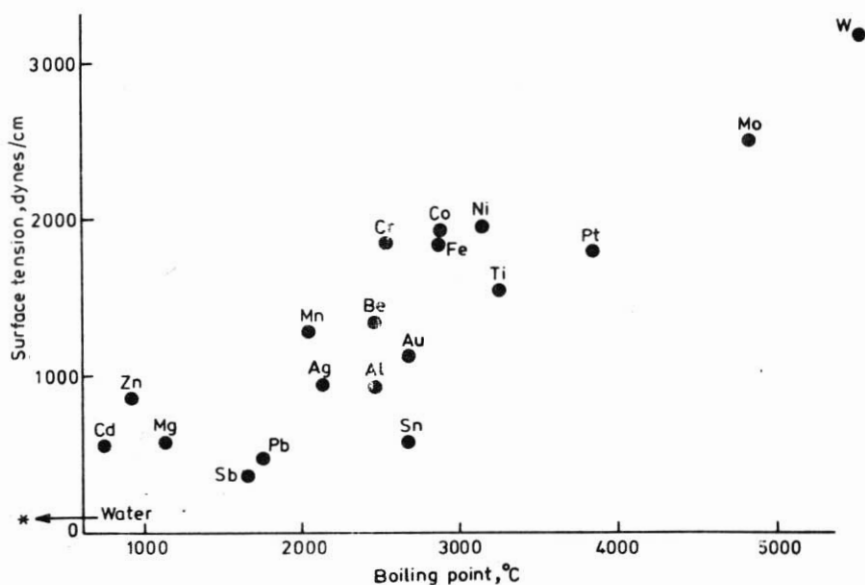carbon. The noble gases, however, are insoluble in metals and alloys.

Fig. 8.5 Surface tension (just above melting point) versus boiling points for some metals.

According to **Sieverts' law**, the solubility of diatomic gases, e.g. H_2 has the form (see also Section 4.10)

$$\text{wt.\% [H]} = K_H \, (P_{H_2})^{1/2} \qquad (8.11)$$

K_H is a constant which depends on temperature. This law follows directly from the consideration of the equilibrium

$$\tfrac{1}{2}H_2 = [H] \qquad (8.12)$$

If the solute is assumed to follow Henry's law at low concentration, then Eq. 8.11 is easily obtained by writing equilibrium relation for reaction 8.12 as follows.

$$K_H = \frac{[h_H]}{p_{H_2}^{1/2}} = \frac{[\text{wt.\%H}]}{p_{H_2}^{1/2}}$$

Nonmetallic solutes have significant effect on the properties of alloys. For example, oxygen and sulphur have profound effects on surface tension. Solubilities of all nonmetals increase substantially on melting. It is difficult to say as to what type of bonding exists between nonmetal solutes and surrounding metal atoms. For example, it was earlier believed that oxygen in liquid iron existed as dissolved FeO. However, it now seems more likely that oxygen dissolves atomically and each atom is strongly bonded to four or so nearest-neighbour metal atoms. At the same time, these metal atoms interact more weakly with neighbouring metal atoms than they would in pure metal or alloy.

8.3 SIMPLE IONIC MELT

We have seen a simple classification in introduction to this chapter and we have so far discussed structure of liquid metals and alloys which are atomic solutions. We shall consider simple melts which essentially consist of metal halides.

Halide salts form systems some of which remain liquid even at very high temperatures and some of which melt at very low temperatures. They constitute the largest class of nonaqueous inorganic solvents. Some salts have very small degree of dissociation and may be considered almost molecular (e.g. H_gCl_2) whereas some other, e.g. the alkali halides, are almost completely ionized. Some mixed salt systems may contain both ionic as well as molecular species (e.g. $MgCl_2 - NaCl_2$, $AlCl_3$, $- CaCl_2$, $ZnCl_2 - NaCl$) and some salts form polymeric melts (e.g. $ZnCl_2$).

Ionic melts are characterized by strong attractive forces between ions of opposite charge and repulsive forces between ions of similar charge. Because of this, a cation is always surrounded by **anions** as closest neighbours and vice versa. It has been calculated that the energy required to transfer a cation in NaCl melt from a position surrounded by arions to one surrounded by cations is exceedingly large. Heats of fusion and evaporation are very small (respectively, 1/30th and 1/5th) as compared to this. One may thus conclude that there can be no significant mix up of positive and negative ions. Each kind has a **sub-lattice** of its own. Thus, whereas all anions are free to occupy any configuration in the anion sub-lattice, all cations are free to occupy any configuration only in the cation sub-lattice. The anions and cations, however, can be freed from mutual interaction under an applied potential which causes ionic dissociation, migration and electrolysis. Ionic melts have high electrical conductivity due to mobility of ions.

The conductivity-temperature relationship generally takes the form.

$$\chi = A \exp (- E_{\chi}/RT) \tag{8.13}$$

where χ is specific conductivity and E_{χ} is the activation energy for specific conductance, similar equation applies for metals also (Sec. 8.2.2). It should be remembered that resistivity is the reciprocal of conductivity.

Ionic melts such as alkali halides generally are highly conducting. An exception is the fluorides of Na and K. It is believed that these halides form 'dimers' such as Na_2F_2 which dissociate according to the reaction

$$Na_2 F_2 = Na_2F^+ + F^- \tag{8.14}$$

Ions such as Na_2F^+ are relatively bulky and thus decrease the conductivity. When the salt has a molecular lattice where the elements of salt structure have few ions, then the fused salt conducts little current (e.g. $HgCl_2$). Where there is incomplete dissociation (e.g. $MgCl_2$), the conductivity value occupies an intermediate position.

Like other liquids, molten salts are also characterized by an expansion in volume and a positive entropy change upon melting. Table 8.4 presents some data on some alkali halides.

TABLE 8.4 Entropy change and volumetric expansion data for some alkali halides during melting

Alkali halide	Volume change, %	ΔS_m, J mol^{-1}K^{-1}
NaCl	+ 25.6	28.0
KCl	+ 20.2	26.0
KBr	+ 16.6	20.5
CsCl	+ 10.5	14.7

During melting of alkali halides, the nearest neighbour distance between anion and cation decreases considerably. The expansion in volume is, therefore accounted for not by an expansion of the lattice but by introduction of holes. Molten salts are often miscible in all proportions provided the temperatures are sufficiently high. At lower temperatures, there may be incomplete miscibility. Molten salt solutions are of considerable interest in the industry because of the preeminence of fused salt electrolysis for extraction and refining of rare and reactive metals. One interesting feature of molten salts is that they dissolve metals to varying degrees. This will be discussed later in this chapter in Sec. 8.3.2

8.3.1 Temkin's Model of Ionic Melts

In an ionized solution, e.g. a mixture of NaCl and KBr, the classical concept of the thermodynamic activity is rather ambiguous. There are few electroneutral molecules and, therefore, an activity term such as a NaCl has no clearcut physical meaning. However, one can define the thermodynamic activity of NaCl as the statistical probability of finding pairs of sodium and Chlorine ions.

According to the Temkin model[*], an ionized melt is a system of interlocked sublattices of anions and cations with short range order extending over a distance of a few ionic diameters. Anions are randomly distributed in the anion sublattice and cations are distributed in the cation sublattice. If the distribution is truly random and the solution is ideal then, according to Temkin, the activity is given by the product of ionic fraction. This is akin to the concept employed sometimes in aqueous solutions also.

Thus the activity of NaCl in any melt containing other ions is given by the equation

$$a_{NaCl} = X_{Na^+} \cdot X_{Cl^-} \tag{8.15}$$

where X stands for ionic fraction. The ionic fraction Na$^+$ is that amongst the cations only and the ionic fraction of Cl$^-$ is that amongst the anions only. Thus we have the following equations.

$$X_{Na^+} = \frac{\text{Moles of Na}^+ \text{ ions}}{\text{Moles of all cations}} \tag{8.16}$$

$$X_{Cl^-} = \frac{\text{Moles of Cl}^- \text{ ions}}{\text{Moles of all anions}} \tag{8.17}$$

Equation 8.15 is slightly modified when ions are not monovalent. Thus for a salt

[*]M. Temkin, Acta Phys-Chim. USSR, Vol. 20 (1945), 411.

$$M_m Z_n = (X_{M^{n+}})^m \, (X_{Z^{m-1}})^n \tag{8.18}$$

where m and n are respectively the valencies of species Z and M.

Example 8.1

Calculate activity values in a $1 : 1$ mole mixture of NaCl and CdBr$_2$.

Solution

Although the solution is made by mixing NaCl and CdBr$_2$, there are no such physical entities in the ionic melt. In fact a_{NaCl} and a_{CdBr_2}, as mentioned earlier, have only mathematical significance as have the terms a_{NaBr} and a_{CdCl_2}. Per mole of the mixture, number of moles of Na$^+$, Cd^{2+}, Cl$^-$ and Br$^-$ are respectively

$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and 1. Hence

$$X_{\text{Na}^+} = \frac{1/2}{1/2 + 1/2} = \frac{1}{2}$$

$$X_{\text{Cd}^{2+}} = \frac{1/2}{1/2 + 1/2} = \frac{1}{2}$$

$$X_{\text{Cl}^-} = \frac{1/2}{1/2 + 1} = \frac{1}{3}$$

$$X_{\text{Br}^-} = \frac{1/2}{1/2 + 1} = \frac{2}{3}$$

According to Eq. 8.18, therefore

$$a_{\text{NaCl}} = \frac{1}{2} \cdot \frac{1}{3} = \frac{1}{6}$$

$$a_{\text{NaBr}} = \frac{1}{2} \cdot \frac{2}{3} = \frac{1}{3}$$

$$a_{\text{CdBr}_2} = \frac{1}{2} \cdot \left[\frac{2}{3}\right]^2 = \frac{2}{9}$$

$$a_{\text{CdCl}_2} = \frac{1}{2} \cdot \left[\frac{1}{3}\right]^2 = \frac{2}{18} \qquad \text{(Answer)}$$

8.3.2 Metal–Salt Solutions

Fused salt are good solvents and amongst other thing, they dissolve metals also. Of course, if a metal dissolves in a salt, it can also reduce so that a new, more stable salt is produced and a less reactive metal is precipitated. This will be an ion exchange reaction. Of more importance to extraction is solubility of a metal in its own salts. In such an event, electrolytic extraction becomes difficult. There is immediate loss of liberated metal. Other operational problems also arise. *The dissolved metal may diffuse to the anode and recombine with the anode product* causing further decrease in current efficiency. It can also make the bath a partial electronic conductor thus causing still further loss of current efficiency.

It is now believed that such dissolution is a two-step process. In the first step, the metal dissolves in its own salt atomically.

$$M\ (l) = [M] \tag{8.19}$$

In the second step, a subhalide forms if this is possible. Considering subhalide formation in $CdCl_2$ we can think of the following possibilities.

$$Cd + CdCl_2 = 2\ CdCl \tag{8.20}$$

$$Cd + CdCl_2 = Cd_2Cl_2 \tag{8.21}$$

The solubility of alkali metals in their own salts is very limited because there are no subhalides. The solubility of alkaline earth metals is generally somewhat greater because here one subhalide can form. For transition metals with higher valencies, the solubilities are far greater because there can be several subhalides.

Metal solubilities are always lowered by a decrease in temperature. In many metal-salt systems, the metal solubility may be lowered by the addition of a second salt. Mixtures of salt are preferable also because they have lower melting points which allow electrolysis at lower temperatures as well.

8.4 POLYMERIC MELTS

We have noted earlier that in some liquids, ions combine together in large numbers to produce complex ions in melt. Melts with large complex ions are called **polymeric melts**. Metallurgical slags are generally polymeric multicomponent systems containing oxides such as CaO, Mgo, FeO, Al_2O_3, P_2O_5, SiO_2 etc. The first three are **basic** oxides, SiO_2 and P_2O_5 are **acidic**. Al_2O_3 and Fe_2O_3 are **amphoteric** oxides which exhibit acidic behaviour in combination with a strong base and basic behaviour when combined with a strong acid.

One way of classifying slags is on the basis of acidic groups, e.g. silicates, phosphates, alumino-silicates, borates etc. The silicate slags (copper smelting and lead smelting), alumino-silicate slags (iron blast furnace), and phospho-silicate slag (basic open hearth steel making) are the common variety. Considerable attention has been given to elucidate the structure and properties of binary silicates and attempts have been made to understand the nature of more complex slag systems based on observation on the simple binary systems.

8.4.1 Structure of Pure Oxides

The structure of pure oxides are generally simply characterized by a three dimensional crystalline network in which metallic cations are surrounded by oxygen ions. During melting, the crystalline network is destroyed and in the liquid phase, the bonds between ions are more disrupted by thermal agitation. However, every cation is still surrounded by anions and vice-versa, although the form and the coordination number may be different from those prevalent in the solid state. For silica, the bond between silicon and oxygen is very strong. Moreover, silicon exhibits tetrahedral co-ordination with oxygen atoms. The basic tetrahedral units remain unaltered on melting. The structures of solid and liquid silica are shown in Figure 8.6, which is a two-dimensional representation of three dimensional network.

The figure schematically shows how the long range order of the solid state is destroyed in the liquid state. The basic tetrahedral unit remains unaltered but many Si-O bonds are snapped thus loosening the crystal structure. Table 8.5 shows the values of the cationic radii in some metal oxides. The radius of O^{2-} is 1.40 Å.

The force of electrostatic attraction between a cation and an anion is

$\dfrac{2e.\,Ze}{(r_c + r_a)^2}$ where Z is valency of cation, e is electronic charge and r_c and r_a are,

respectively, radii of cation and anion. Table 8.5 also presents values of $Z/(r_c + r_a)^2$ which is proportional to this attractive force between ions.

TABLE 8.5 Ionic radii and ion-oxygen interaction

[Radius of O^Z ion = 1.40 Å]

Oxide	Cationic radius (Å)	$Z/(r_c + r_a)^2$	Remark
Na_2O	0.95	0.18	Basic oxides
CaO	0.99	0.35	(Network breakers)
MnO	0.80	0.42	
FeO	0.75	0.44	
MgO	0.65	0.48	
Cr_2O_3	0.64	0.72	
Fe_2O_3	0.60	0.75	Amphoteric oxides
Al_2O_3	0.50	0.83	
TiO_2	0.68	0.93	
SiO_2	0.41	1.22	
P_2O_5	0.34	1.66	Acid oxides (Network formers)

Oxygen ions, which are larger, are in closest packing and the smaller ions occupy the interstices. The coordinated polyhedron of anions around the cation is determined by the radius ratio of the cation and oxygen ions. From geometric reasoning, it has been derived that, if the ratio is less than 0.414, then the polyhedron is a tetrahedron with a coordination number of 4. Therefore CaO, FeO, etc. should have a coordination number if 6 corresponding to simple cubic lattice and Al_2O_3 SiO_2 etc. should have a coordination number of 4 corresponding to tetrahedron. These have been confirmed by X-ray studies.

8.4.2 Breakdown of Silicate Network

If a basic oxide such as CaO is added to silica, then calcium is unlikely to replace silicon in the tetrahedra because CaO shows a coordination number of 6. Therefore, calcium would stay outside and place itself between two tetrahedral units as shown in Figure 8.7.

The lower arrangement has one additional oxygen coming from CaO. Again $Z/(r_c + r_a)^2$ parameter of CaO is 0.35 only as against 1.22 for SiO_2. Therefore oxygen ions are expected to be weakly bonded to calcium ion in comparison to silicon ion and hence calcium ion is likely to remain free.
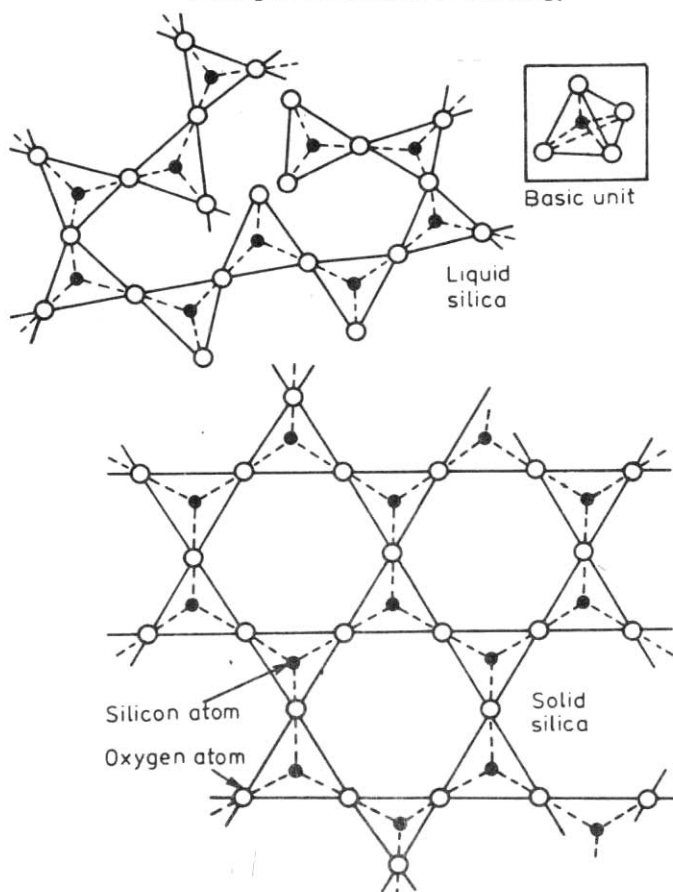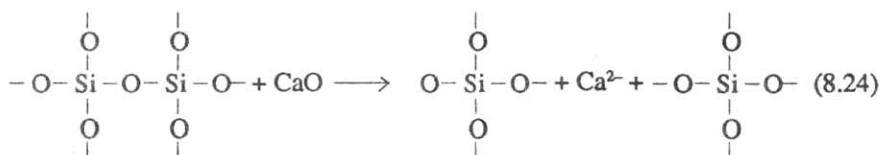
Fig. 8.6 Structure of silica

Addition of CaO thus causes a disruption of the silicate network. This is called **depolymerization**. With increasing addition of CaO, there is progressively increasing depolymerization. One evidence of this progressive breakdown of the network is gradual decrease of viscosity as well as the activation energy for viscous flow.

The ionization of CaO and Introduction O^{2-} into the three dimensional Si—O network and its breakdown may be represented by the following equations.

$$CaO \rightarrow (Ca^{2+} + Ca^{2-}) \qquad (8.23)$$

$$-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O- + CaO \longrightarrow O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O- + Ca^{2-} + -O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Si}}-O- \quad (8.24)$$
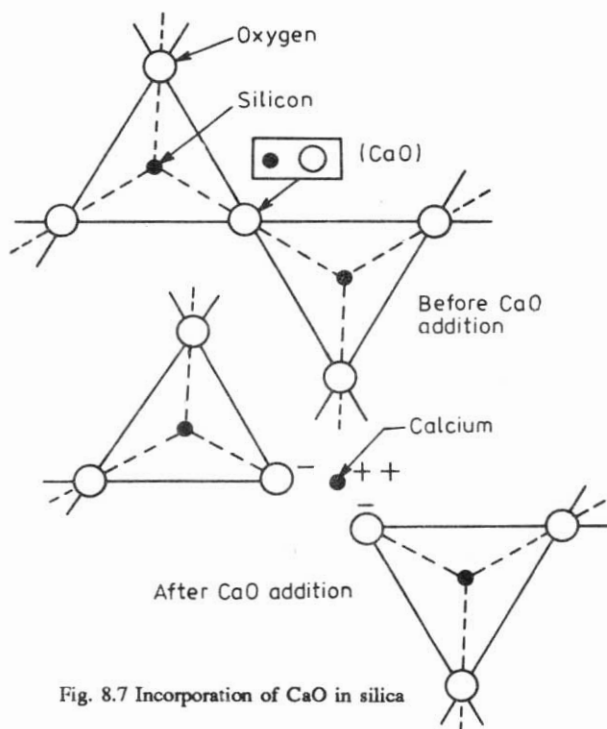
Fig. 8.7 Incorporation of CaO in silica

It has been conclusively proved that molten slags are ionic conductors. Some simple binary silicates obey Faraday'. .aws of electrolysis, a fact which confirms the ionic nature. However, some silicates e.g. FeO – SiO$_2$, CaO – SiO$_2$ exhibit electronic conduction as well. Transport number measurements have also been carried out in some silicate melts. It has been found that cations generally carry almost hundred percent of the total current. This observation agrees with the preceding discussion. Silicon and oxygen form complex anions which are less mobile because of their size. The relatively free metal cations are mobile and are free to carry current.

8.4.3 Structure of Liquid Binary Silicates

So far, we have discussed two important concepts regarding liquid silicates. Firstly, the silica network breaks down progressively as more and more basic oxides are added. Secondly, they are ionic liquids and the cations are free and mobile. Now the question comes up as to what exactly is the structure of a liquid silicate at a given composition.

According to the **Discrete Ion Theory,** the structure is rapidly depolymerized when basic oxide is added and above a certain concentration of basic oxide, it breaks down into discrete ions. There are experimental evidences to support this view. Figure 8.8 shows the experimentally determined activation energy for viscous flow (E_η) as a function of mole percent of metal oxide for some binary silicates. E_η decreases sharply upto approximately 10% M$_2$O and or 20% MO. Beyond this composition, E_η decreases more slowly. This has been interpreted as due to a marked change in structure around these compositions.

Figure 8.9 shows the variation of the coefficient of volume expansion (thermal)

with mole percent M_2O. The sudden rise of the curves beyond 10 mole % has been interpreted as a result of transition from three dimensional network to simple discrete ion structure. It matches excellently with similar conclusion drawn from Fig. 8.8. Similarly, the expansivity curves for MO type oxides also exhibit sudden rise at approximately 20 mole % oxide. At any given composition, a liquid silicate would contain relatively free metal cations Ca^{2+} Na^+ etc.), complex silicate anions (and some O^{2-} ions if the melt is sufficiently basic). Table 8.6 lists the likely silicate ions at some typical compositions.
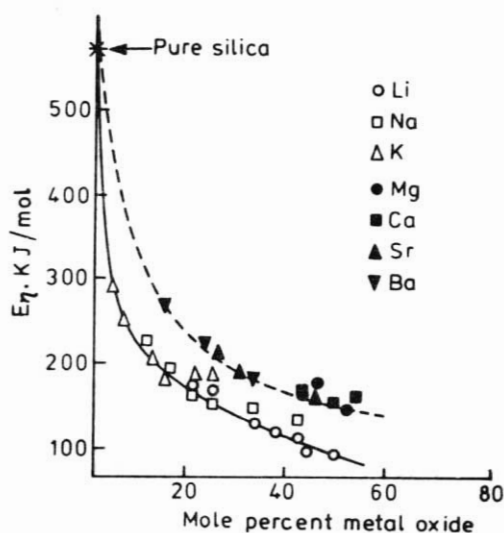
Fig. 8.8 Plot of E_η vs percent M_2O or MO (Source : J.D. Mackenzie, J. Chem. Rev. vol. 5 (56), 455)
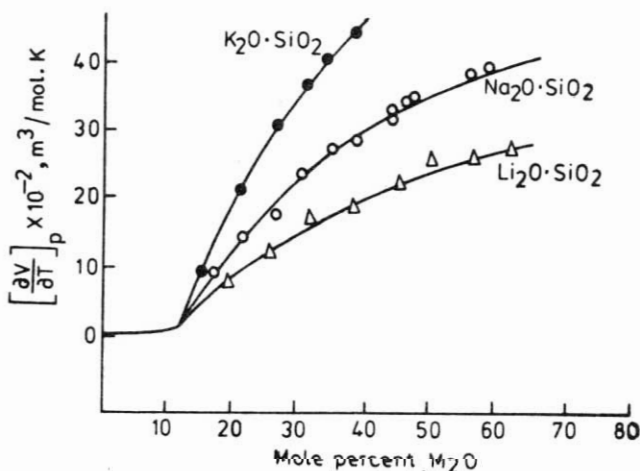

Fig. 8.9 Thermal expansivity vs percent M_2O (Source : same as for Fig. 8.8)

TABLE 8.6 Discrete silicate ions at some compositions

Composition	Molar % MO	Si/O	Discrete Ion
$2SiO_2 + MO$	33.3	2/5	$(Si_6O_{15})^{6-}$ or $(Si_6O_{20})^{8-}$
$SiO_2 + MO$	50.0	1/3	$(Si_3O_9)^{6-}$ or $(Si_4O_{12})^{8-}$
$SiO_2 + MO$	66.7	1/4	$(SiO_4)^{4-}$

These discrete ions have been postulated keeping the following viewpoints in mind

1. The silica tetrahedra are the basic units.
2. All the oxygen atoms are attached to the silicon atoms in discrete ions, and
3. The dihedral angle O-Si-O remains about the same as in silica. Figure 8.10 is a pictorial representation of some discrete ions. The discrete ions proposed in Table 8.6 are the only ones consistent with the foregoing observations.

Simple mass balance considerations show that the simplest ion $(SiO_4)^{4-}$ only occurs if the mole percent MO is greater than or equal to 66.7. If there is more than 66.7% MO, the excess oxygen from MO cannot cause any more depolymerization since $(SiO_4)^{4-}$, is the smallest tetrahedral unit possible. Therefore such a silicate would consist of free metal cations, $(SiO_4)^{4-}$, and O^{2-}. At compositions where % MO is less than 66.7, straight stoichiometric considerations do not envisage presence of free oxygen ions. However, we know that some free O^{2-} ions must be present to satisfy the equilibrium of the reaction of the type

$$MO = M^{2+} + O^2 \tag{8.25}$$

This O^{2-} would have to come from reactions of the type

$$2(Si_2O_7)^{6-} = (Si_4O_{12})^{8-} + 2O^{2-} \tag{8.26}$$

Therefore, thermodynamic consideration suggests that, at any composition, one particular discrete ion such as those cited in Table 8.6 may be predominant but other groups also are expected to be present to some extent. The present view of silicate melts is that there is a distribution of many kinds of silicate ions of various degrees of polymerization, some more predominant than others. The distribution changes with change of composition and temperature.

8.4.4 Structure of More Complex Silicates

So far, we have mainly discussed simple binary silicates and the question may be raised if the concepts discussed are valid for multicomponent silicate systems such as slags. No special considerations are involved if there are several cations (Ca^{2+}, Na^+, Fe^{2+} etc.) because all of them are network breakers and are expected to behave similarly. Experiments also point out that way. The netwrok formers like P_2O_5, B_2O_3 and sometimes Al_2O_3, if present in silicate, would also participate in creating anionic polymerized networks. Many alumino-silicates are based on a complete framework of linked tetrahedra similar to those of the various forms of silica, but involving some aluminium atoms. The anions with aluminium

and phosphorus are taken as $(AlO_4)^{5-}$ and $(PO_4)^{3-}$. Therefore, a complex slag having more than 66.7 mole % MO is expected to contain free metal cations and anions like $(SiO_4)^{4-}$, $(AlO_4)^{5-}$, $(PO_4)^{3-}$ and O^{2-}.
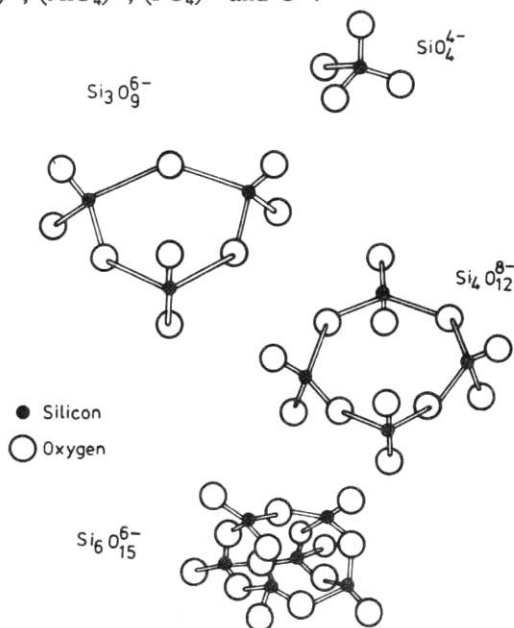

Fig. 8.10 Pictorial representation of some discrete ions

8.5 ACIDITY AND BASICITY OF SLAGS

In aqueous solutions, an acid is what provides H^+ ions and a base is what accepts H^+ ions. In liquid silicates, this type of definition does not work since there is insignificant concentration of H^+ ion. Here we proceed from the general definition of G.N. Lewis that an acid is an acceptor and the base is a donor of electrons. In slags, we think of oxygen ions rather than electrons and say that an acidic oxide absorbs O^{2-} ions, whereas a basic oxide provides O^{2-} ions. According to this definition and for a binary silicate, we may draw a dividing line at the composition corresponding to 2MO. SiO_2. When other acidic oxides such as P_2O_5, B_2O_3 are also present, then they may be lumped together with SiO_2. If the composition has more than 2/3 mole fraction of MO, then the concentration of free O^{2-} is high and the melt is basic. At mole fraction of MO less than 2/3, the concentration of free O^{2-} is rather small and acidic behaviour is to be expected.

This criterion of basicity and acidity has the disadvantage that the orthosilicate composition which divides the acid from the basic slags is not a unique composition if the slag analysis is expressed in weight percentage. For example, in simple FeO-SiO_2 the division occurs at 29.4 wt.% SiO_2 whereas in MgO–SiO_2 slag it is 45.5 wt.% SiO_2. When this definition is applied to more complex slags, the requirement of all acidic oxides (e.g. P_2O_5,SiO_2,Al_2O_3) for O^{2-} must be allowed for. In steelmaking slags, the neutral composition dividing acid from basic slags

frequently falls close to 33 wt. % SiO_2. Figure 8.11 shows schematically the approximate proportion of silica in some slags encountered in ferrous metallurgy.

The silica content of many slags encountered in nonferrous metallurgy is similar. Some typical slag compositions are as follows:
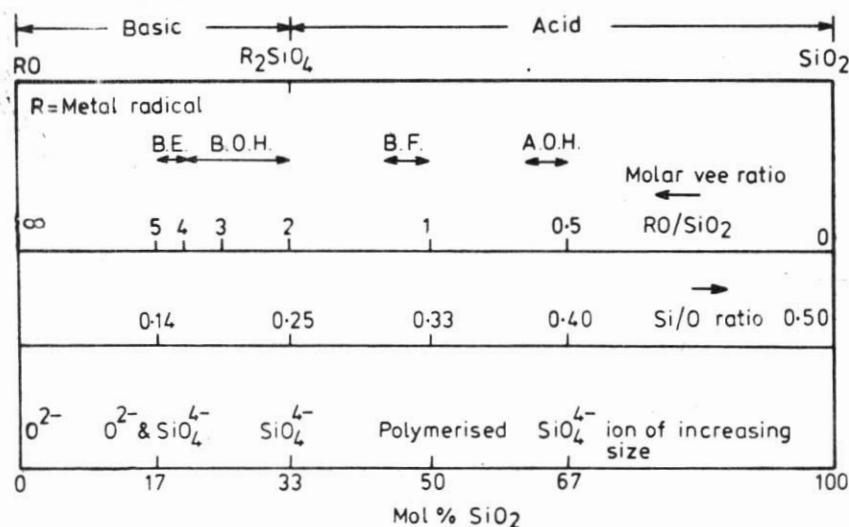

Fig. 8.11

Copper reverberatory slag : SiO_2~40, FeO~35, CaO~8
                            Al_2O_3~11, others — rest

Copper converter slag : SiO_2~30, FeO~50, Al_2O_3~5,
                        others — rest

Lead blast furnace slag : SiO_2 ~35, FeO~30, CaO ~22
                          others — rest.

In the industry, an index of basicity commonly used is the so called **Vee ratio** defined as

$$V = \frac{\text{wt. \% CaO}}{\text{wt. \% SiO}_2} \qquad (8.28)$$

Some modified V ratios are [wt. % CaO/(wt. % SiO_2 + wt. % Al_2O_3)] or [wt. % CaO/(wt. % SiO_2 + wt. % P_2O_5)]. When MgO is present then whole or part of it is added to CaO. Different ways of defining V-ratio have been in vogue to suit variety of process considerations. These are essentially empirical in nature.

Another way of describing the basicity makes use of the concept of excess base i.e. free oxygen ions available. In terms of **molecular theory**, this will correspond to the amount of free oxide present after the requirements of the acids for basic oxides have been met. For example, if lime is considered as the main base, then excess lime can be used as a basicity parameter by assuming the formation of $2CaO\ SiO_2$ and $3CaO\ P_2O_5$. For example, one formula proposed is* Excess base, (B) = wt. % CaO − 1.86 wt. % SiO_2 + 1.19 wt. % P_2O_5

$$(8.29)$$

*R.G. Ward, An Introduction to the Physical Chemistry of Iron and Steelmaking, Edward Arnold (Lond.) 1962. Ch. 5.

For a more complex slag, if one assumes formation of the compounds 2MO SiO₂, 4MO. P_2O_5, 2MO. Al_2O_3 and MO. Fe_2O_3 then in terms of gram molecules, the excess base* (B) is given as

$$B = MO - 2SiO_2 - 4P_2O_5 - 2Al_2O_3 - Fe_2O_3 \qquad (8.30)$$

, 8.6 OXIDISING POWER OF SLAGS

Since slag coexists with metal in pyrometallurgical operations, the slag- metal system often approaches thermodynamic equilibrium. It is then possible to oxidize or reduce the metal through controlling the slag composition. Similarly, it may be possible to control desulphurization of the metal by controlling the slag. The slag phase composition can be controlled by addition of basic or acidic oxides or by controlling the composition of the gas phase above it.

Suppose molten iron is in equilibrium with a slag containing FeO. The equilibrium between the oxygen dissolved in the metal and iron oxide in the slag can be written as

$$(FeO) = [Fe] + [O] \qquad (8.31)$$

There is, therefore, always some dissolved oxygen in the metal. This oxygen may be used to oxidize the impurity elements in iron and bring about refining. Assuming the activity of iron to be unity, the equilibrium constant may be written as

$$K_{e,31} = \frac{[h_o]}{(a_{FeO})} \; \alpha \; \frac{[\text{wt. \%, O}]}{(a_{FeO})} \qquad (8.32)$$

Obviously, the oxygen content of metal can be reduced by lowering the activity of FeO in slag and it can be increased by increasing FeO activity at a constant temperature. Therefore, FeO activity in slag can be taken as a measure of oxidising power of slag in iron and steel making under somewhat reducing condition when Fe_2O_3 does not form.

8.7 SULPHIDE CAPACITY OF SLAGS

Sulphide capacity or sulphur capacity of a slag (C_s) indicates the capacity to hold sulphur. Consider a simple equilibrium involving sulphur and oxygen in slag and gas phases

$$\tfrac{1}{2}S_2 \, (g) + (O^{2-}) = \tfrac{1}{2} O_2 \, (g) + (S^{2-}) \qquad (8.33)$$
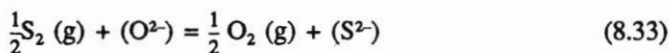
The equilibrium constant is written as

$$K_{e,33} = \frac{(a_s^{2-}). \, P_{O_2}^{1/2}}{(a_o^{2-}) \, ps_2^{1/2}} \qquad (8.34)$$

If Henrian behaviour is assumed for S^{2-} ions in slag, then Eq. 8.34 can be rewritten as

$$(\text{wt. \% S}). \, Po_2^{1/2}/Ps_2^{1/2} = K'_{e,33}. \, a_o^{2-} = C_s \qquad (8.35)$$

The L.H.S. of Eq. 8.35 depends solely on slag composition at a given temperature and, therefore, is a property of the slag. The sulphur capacity (C_s)

is thus a measure of the ability of slags to absorb sulphur from gases of given oxygen and sulphur partial pressures. The concept of sulphur capacity is very useful and with modification it is employed to make calculations on sulphur partition. In a similar fashion, concepts of phosphate capacity, carbonate capacity etc. have been developed and are being utilised for the study of equilibrium partitioning of respective species either between metal and slag or gas and slag.

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