

# 6

## General properties of the elements

### SIZE OF ATOMS AND IONS

#### Size of atoms

The size of atoms decreases from left to right across a period in the periodic table. For example, on moving from lithium to beryllium one extra positive charge is added to the nucleus, and an extra orbital electron is also added. Increasing the nuclear charge results in all of the orbital electrons being pulled closer to the nucleus. In a given period, the alkali metal is the largest atom and the halogen the smallest. When a horizontal period contains ten transition elements the contraction in size is larger, and when in addition there are 14 inner transition elements in a horizontal period, the contraction in size is even more marked.

On descending a group in the periodic table such as that containing lithium, sodium, potassium, rubidium and caesium, the sizes of the atoms increase due to the effect of extra shells of electrons being added: this outweighs the effect of increased nuclear charge.

#### Size of ions

Metals usually form positive ions. These are formed by removing one or more electrons from the metal atom. Metal ions are smaller than the atoms from which they were formed for two reasons:

1. The whole of the outer shell of electrons is usually ionized, i.e. removed. This is one reason why cations are much smaller than the original metal atom.
2. A second factor is the effective nuclear charge. In an atom, the number of positive charges on the nucleus is exactly the same as the number of orbital electrons. When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of orbital electrons, and the effective nuclear charge (which is the ratio of the number of charges on the nucleus to the number of electrons) is increased. This results in the remaining electrons being more strongly attracted by the nucleus. Thus the electrons are pulled in – further reducing the size.

**Table 6.1** Covalent radii of the elements

Group Period \	1	2											13	14	15	16	17	18		
1	H												H	He						
	.												.							
2	Li	Be											B	C	N	O	F	Ne		
	.												.	.	.	.	.	.		
													0.80	0.77	0.74	0.74	0.72	1.60*		
3	Na	Mg	Group										Al	Si	P	S	Cl	Ar		
	.												.	.	.	.	.	.		
			1.57	1.36	3	4	5	6	7	8	9	10	1.25	1.17	1.10	1.04	0.99	1.91*		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	.		2.03	1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.25	1.25	1.22	1.21	1.14	1.14	2.00*	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
	.		2.16	1.91	1.62	1.45	1.34	1.29	-	1.24	1.25	1.28	1.34	1.41	1.50	1.40	1.41	1.37	1.33	2.20*
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
	.		2.35	1.98	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44	1.55	1.46	1.52			
7	Fr	Ra	Ac																	
<b>Lanthanides</b>			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
			.	.	.	-	.	.	.	.	.	.	.	.	.	.				
			1.65	1.64	1.64		1.66	1.85	1.61	1.59	1.59	1.58	1.57	1.56	1.70	1.56				

**COVALENT RADII OF THE ELEMENTS**

(Numerical values are given in Ångström units. \* The values for the noble gases are atomic radii, i.e. non-bonded radii, and should be compared with van der Waals radii rather than with covalent bonded radii. Large circles indicate large radii and small circles small radii.)

After Moeller, T., *Inorganic Chemistry*, Wiley 1952

A positive ion is always smaller than the corresponding atom, and the more electrons which are removed (that is, the greater the charge on the ion), the smaller the ion becomes.

Metallic radius Na	1.86 Å	Atomic radius Fe	1.17 Å
Ionic radius $\text{Na}^+$	1.02 Å	Ionic radius $\text{Fe}^{2+}$	0.780 Å (high spin)
		Ionic radius $\text{Fe}^{3+}$	0.645 Å (high spin)

When a negative ion is formed, one or more electrons are added to an atom, the effective nuclear charge is reduced and hence the electron cloud expands. Negative ions are bigger than the corresponding atom.

Covalent radius Cl	0.99 Å
Ionic radius $\text{Cl}^-$	1.84 Å

### Problems with ionic radii

There are several problems in obtaining an accurate set of ionic radii.

1. Though it is possible to measure the internuclear distances in a crystal very accurately by X-ray diffraction, for example the distance between  $\text{Na}^+$  and  $\text{F}^-$  in  $\text{NaF}$ , there is no universally accepted formula for apportioning this to the two ions. Historically several different sets of ionic radii have been estimated. The main ones are by Goldschmidt, Pauling and Ahrens. These are all calculated from observed internuclear distances, but differ in the method used to split the distance between the ions. The most recent values, which are probably the most accurate, are by Shannon (1976).
2. Corrections to these radii are necessary if the charge on the ion is changed.
3. Corrections must also be made for the coordination number, and the geometry.
4. The assumption that ions are spherical is probably true for ions from the *s*- and *p*-blocks with a noble gas configuration, but is probably untrue for transition metal ions with an incomplete *d* shell.
5. In some cases there is extensive delocalization of *d* electrons, for example in  $\text{TiO}$  where they give rise to metallic conduction, or in cluster compounds. This also changes the radii.

Thus ionic radii are not absolute constants, and are best seen as a working approximation.

### Trends in ionic radii

Irrespective of which set of ionic radii are used, the following trends are observed:

1. In the main groups, radii increase on descending the group, e.g.  $\text{Li}^+ = 0.76 \text{ \AA}$ ,  $\text{Na}^+ = 1.02 \text{ \AA}$ ,  $\text{K}^+ = 1.38 \text{ \AA}$ , because extra shells of electrons are added.

2. The ionic radii decrease moving from left to right across any period in the periodic table, e.g.  $\text{Na}^+ = 1.02 \text{ \AA}$ ,  $\text{Mg}^{2+} = 0.720 \text{ \AA}$  and  $\text{Al}^{3+} = 0.535 \text{ \AA}$ . This is partly due to the increased number of charges on the nucleus, and also to the increasing charge on the ions.
3. The ionic radius decreases as more electrons are ionized off, that is as the valency increases, e.g.  $\text{Cr}^{2+} = 0.80 \text{ \AA}$  (high spin),  $\text{Cr}^{3+} = 0.615 \text{ \AA}$ ,  $\text{Cr}^{4+} = 0.55 \text{ \AA}$ ,  $\text{Cr}^{5+} = 0.49 \text{ \AA}$  and  $\text{Cr}^{6+} = 0.44 \text{ \AA}$ .
4. The *d* and *f* orbitals do not shield the nuclear charge very effectively. Thus there is a significant reduction in the size of ions just after  $10d$  or  $14f$  electrons have been filled in. The latter is called the lanthanide contraction, and results in the sizes of the second and third row transition elements being almost the same. This is discussed in Chapter 30.

### IONIZATION ENERGIES

If a small amount of energy is supplied to an atom, then an electron may be promoted to a higher energy level, but if the amount of energy supplied is sufficiently large the electron may be completely removed. The energy required to remove the most loosely bound electron from an isolated gaseous atom is called the ionization energy.

Ionization energies are determined from spectra and are measured in  $\text{kJ mol}^{-1}$ . It is possible to remove more than one electron from most atoms. The first ionization energy is the energy required to remove the first electron and convert  $\text{M}$  to  $\text{M}^+$ ; the second ionization energy is the energy required to remove the second electron and convert  $\text{M}^+$  to  $\text{M}^{2+}$ ; the third ionization energy converts  $\text{M}^{2+}$  to  $\text{M}^{3+}$ , and so on.

The factors that influence the ionization energy are:

1. The size of the atom.
2. The charge on the nucleus.
3. How effectively the inner electron shells screen the nuclear charge.
4. The type of electron involved (*s*, *p*, *d* or *f*).

These factors are usually interrelated. In a small atom the electrons are tightly held, whilst in a larger atom the electrons are less strongly held. Thus the ionization energy decreases as the size of the atoms increases.

**Table 6.2** Ionization energies for Group 1 and 2 elements ( $\text{kJ mol}^{-1}$ )

	1st	2nd		1st	2nd	3rd
Li	520	7296	Be	899	1757	14 847
Na	496	4563	Mg	737	1450	7 731
K	419	3069	Ca	590	1145	4 910
Rb	403	2650	Sr	549	1064	4 207
Cs	376	2420	Ba	503	965	
Fr			Ra	509	979	3 281*

\* Estimated value.

This trend is shown, for example, by Group 1 and Group 2 elements (see Table 6.2), and also by the other main groups.

Comparison of the first and second ionization energies for the Group 1 elements shows that removal of a second electron involves a great deal more energy, between 7 and 14 times more than the first ionization energy. Because the second ionization energy is so high, a second electron is not removed. The large difference between the first and second ionization energies is related to the structure of the Group 1 atoms. These atoms have just one electron in their outer shell. Whilst it is relatively easy to remove the single outer electron, it requires much more energy to remove a second electron, since this involves breaking into a filled shell of electrons.

The ionization energies for the Group 2 elements show that the first ionization energy is almost double the value for the corresponding Group 1 element. This is because the increased nuclear charge results in a smaller size for the Group 2 element. Once the first electron has been removed, the ratio of charges on the nucleus to the number of orbital electrons (the effective nuclear charge) is increased, and this reduces the size. For example,  $Mg^+$  is smaller than the Mg atom. Thus the remaining electrons in  $Mg^+$  are even more tightly held, and consequently the second ionization energy is greater than the first. Removal of a third electron from a Group 2 element is very much harder for two reasons:

1. The effective nuclear charge has increased, and hence the remaining electrons are more tightly held.
2. Removing another electron would involve breaking a completed shell of electrons.

The ionization energy also depends on the type of electron which is removed. *s*, *p*, *d* and *f* electrons have orbitals with different shapes. An *s* electron penetrates nearer to the nucleus, and is therefore more tightly held than a *p* electron. For similar reasons a *p* electron is more tightly held than a *d* electron, and a *d* electron is more tightly held than an *f* electron. Other factors being equal, the ionization energies are in the order *s* > *p* > *d* > *f*. Thus the increase in ionization energy is not quite smooth on moving from left to right in the periodic table. For example, the first ionization energy for a Group 13 element (where a *p* electron is being removed) is actually less than that for the adjacent Group 2 element (where an *s* electron is being removed).

In general, the ionization energy decreases on descending a group and increases on crossing a period. Removal of successive electrons becomes

**Table 6.3** Comparison of some first ionization energies ( $\text{kJ mol}^{-1}$ )

Li 520	Be 899	B 801	C 1086	N 1403	O 1410	F 1681	Ne 2080
Na 496	Mg 737	Al 577	Si 786	P 1012	S 999	Cl 1255	Ar 1521

**Table 6.4** First ionization energies of the elements

Group Period \ \diagdown	1	2											13	14	15	16	17	18
1	H																He	
		● 1311															● 2372	
2	Li	Be											B	C	N	O	F	Ne
	● 520	● 899											● 801	● 1086	● 1403	● 1410	● 1681	● 2080
3	Na	Mg	Group										Al	Si	P	S	Cl	Ar
	● 496	● 737	3	4	5	6	7	8	9	10	11	12	● 577	● 786	● 1012	● 999	● 1255	● 1521
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	● 419	● 590	631	656	650	652	717	762	758	736	745	906	● 579	● 760	● 947	● 941	● 1142	● 1351
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	● 403	● 549	616	674	664	685	703	711	720	804	731	876	● 558	● 708	● 834	● 869	● 1191	● 1170
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	● 376	● 503	541	760	760	770	759	840	900	870	889	1007	● 589	● 715	● 703	● 813	● 912	● 1037
7	Fr	Ra	Ac															

**FIRST IONIZATION ENERGIES OF THE ELEMENTS**

(Numerical values are given in  $\text{kJ mol}^{-1}$ .)

(Large circles indicate high values and small circles low values.)

After Sanderson, R.T., *Chemical Periodicity*, Reinhold, New York.

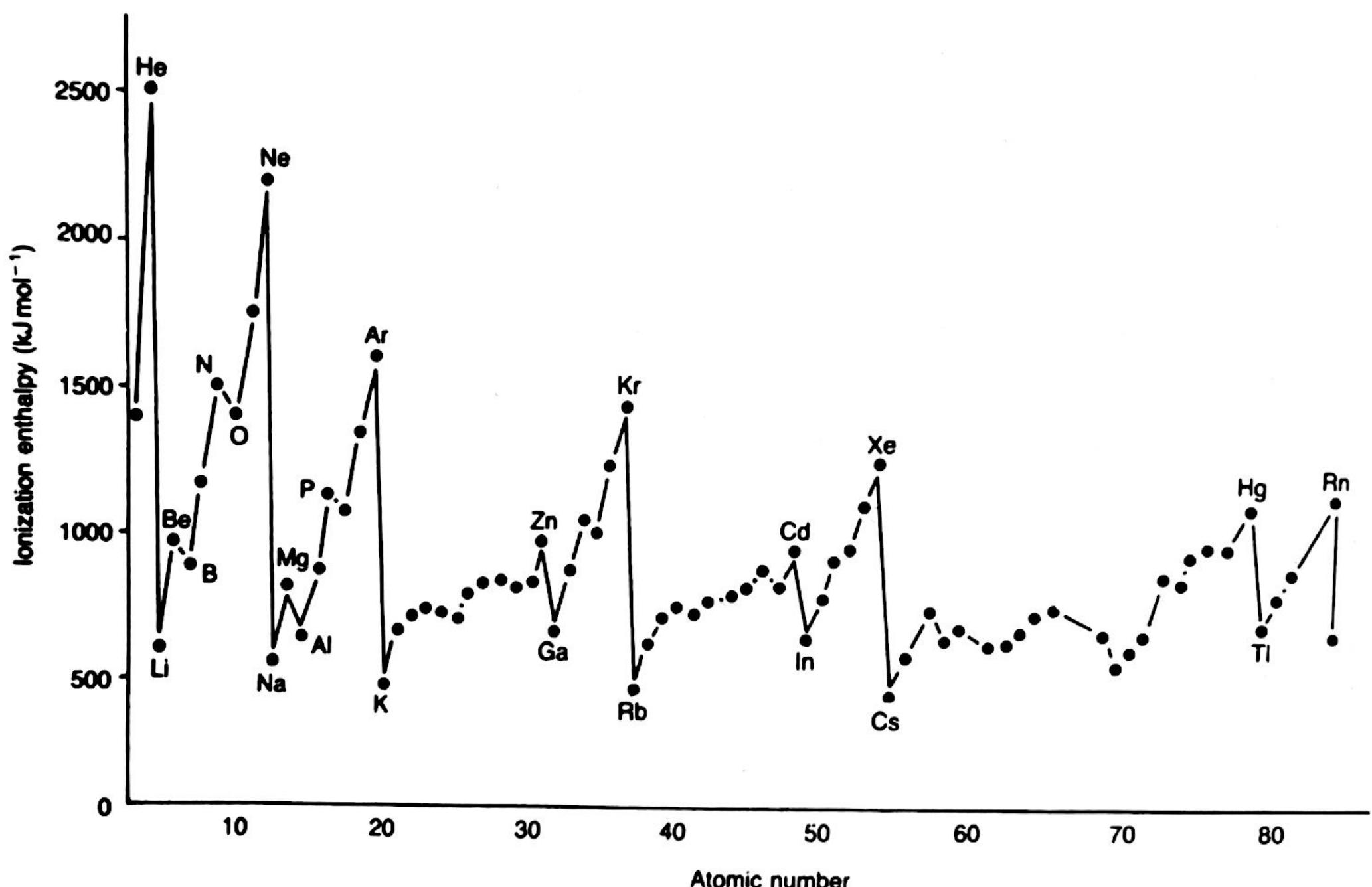


Figure 6.1 First ionization energies of the elements.

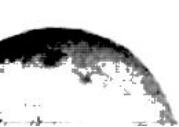
more difficult and first ionization energy < second ionization energy < third ionization energy. There are a number of deviations from these generalizations.

The variation in the first ionization energies of the elements are shown in Figure 6.1. The graph shows three features:

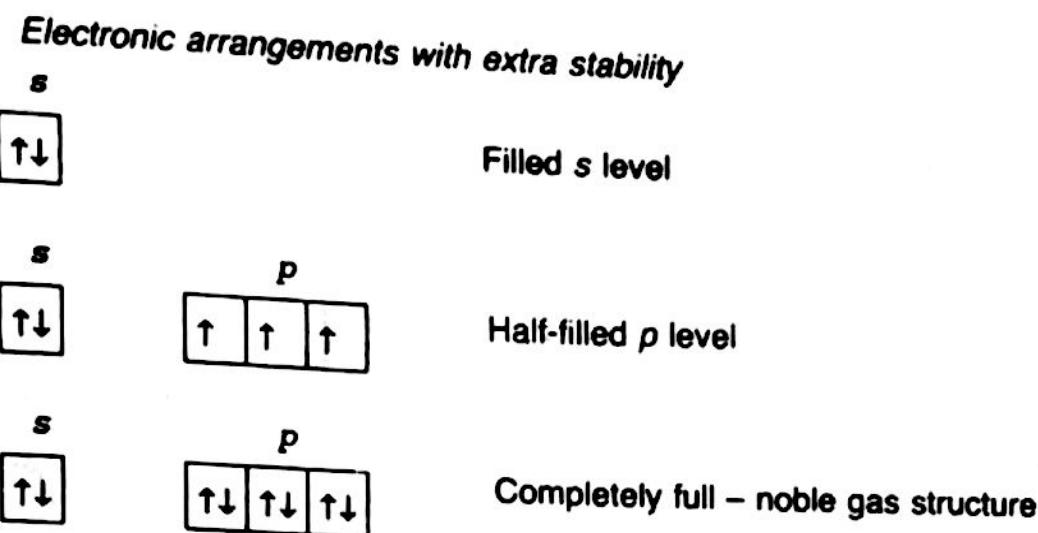
1. The noble gases He, Ne, Ar, Kr, Xe and Rn have the highest ionization energies in their respective periods.
2. The Group 1 metals Li, Na, K and Rb have the lowest ionization energies in their respective periods.
3. There is a general upward trend in ionization energy within a horizontal period, for example from Li to Ne or from Na to Ar.

The values for Ne and Ar are the highest in their periods because a great deal of energy is required to remove an electron from a stable filled shell of electrons.

The graph does not increase smoothly. The values for Be and Mg are high, and this is attributed to the stability of a filled s level. The values for N and P are also high, and this indicates that a half-filled p level is also particularly stable. The values for B and Al are lower because removal of



one electron leaves a stable filled *s* shell, and similarly with O and S a stable half-filled *p* shell is left.



In general the first ionization energy decreases in a regular way on descending the main groups. A departure from this trend occurs in Group 13, where the expected decrease occurs between B and Al, but the values for the remaining elements Ga, In and Tl do not continue the trend, and are irregular. The reason for the change at Ga is that it is preceded by ten elements of the first transition series (where the *3d* shell is being filled). This makes Ga smaller than it would otherwise be. A similar effect is observed with the second and third transition series, and the presence of the three transition series not only has a marked effect on the values for Ga, In and Tl, but the effect still shows in Groups 14 and 15.

**Table 6.5 Ionization energies for Group 13 elements ( $\text{kJ mol}^{-1}$ )**

	1st	2nd	3rd
B	801	2427	3659
Al	577	1816	2744
Ga	579	1979	2962
In	558	1820	2704
Tl	589	1971	2877

The ionization energies of the transition elements are slightly irregular, but the third row elements starting at Hf have lower values than would be expected due to the interpolation of the 14 lanthanide elements between La and Hf.

## ELECTRON AFFINITY

The energy released when an extra electron is added to a neutral gaseous atom is termed the electron affinity. Usually only one electron is added, forming a uninegative ion. Since energy is evolved these terms have a negative sign. Electron affinities depend on the size and effective nuclear

**Table 6.6** Some electron affinity values ( $\text{kJ mol}^{-1}$ )

$\text{H} \rightarrow \text{H}^-$	- 72
$\text{He} \rightarrow \text{He}^-$	54
$\text{Li} \rightarrow \text{Li}^-$	- 57
$\text{Be} \rightarrow \text{Be}^-$	66
$\text{B} \rightarrow \text{B}^-$	- 15
$\text{C} \rightarrow \text{C}^-$	- 121
$\text{N} \rightarrow \text{N}^-$	31
$\text{O} \rightarrow \text{O}^-$	- 142
$\text{O} \rightarrow \text{O}^{2-}$	702
$\text{F} \rightarrow \text{F}^-$	- 333
$\text{Ne} \rightarrow \text{Ne}^-$	99
$\text{Na} \rightarrow \text{Na}^-$	- 21
$\text{Mg} \rightarrow \text{Mg}^-$	67
$\text{Al} \rightarrow \text{Al}^-$	- 26
$\text{Si} \rightarrow \text{Si}^-$	- 135
$\text{P} \rightarrow \text{P}^-$	- 60
$\text{S} \rightarrow \text{S}^-$	- 200
$\text{S} \rightarrow \text{S}^{2-}$	332
$\text{Cl} \rightarrow \text{Cl}^-$	- 348
$\text{Br} \rightarrow \text{Br}^-$	- 324
$\text{I} \rightarrow \text{I}^-$	- 295

charge. They cannot be determined directly, but are obtained indirectly from the Born-Haber cycle.

Negative electron affinity values indicate that energy is given out when the atom accepts an electron. The above values show that the halogens all evolve a large amount of energy on forming negative halide ions, and it is not surprising that these ions occur in a large number of compounds.

Energy is evolved when one electron is added to an O or S atom, forming the species  $\text{O}^-$  and  $\text{S}^-$ , but a substantial amount of energy is absorbed when two electrons are added to form  $\text{O}^{2-}$  and  $\text{S}^{2-}$  ions. Thus the electron affinities for  $\text{O}-\text{O}^{2-}$  and  $\text{S}-\text{S}^{2-}$  have a positive sign. Even though it requires energy to form these divalent ions, compounds containing these ions are known. It follows that the energy required to form the ions must come from some other process, such as the lattice energy when the ions are packed together in a regular way to form a crystalline solid, or from solvation energy in solution. It is always dangerous to consider one energy term in isolation, and a complete energy cycle should be considered whenever possible.

### BORN-HABER CYCLE

This cycle devised by Born and Haber in 1919 relates the lattice energy of a crystal to other thermochemical data. The energy terms involved in building a crystal lattice such as sodium chloride may be taken in steps. The elements in their standard state are first converted to gaseous atoms, and then to ions, and finally packed into the crystal lattice.

The enthalpies of sublimation and dissociation and the ionization energy are positive since energy is supplied to the system. The electron affinity and lattice energy are negative since energy is evolved in these processes.

According to Hess's law, the overall energy change in a process depends only on the energy of the initial and final states and not on the route taken. As can be seen from Fig. 6.2 the enthalpy of formation of  $\Delta H_f$  is the algebraic sum of the terms going round the cycle (paying heed to the exothermic or endothermic nature of each step).

$$\Delta H_f = \Delta H_s + I + \frac{1}{2}\Delta H_d + E + U$$

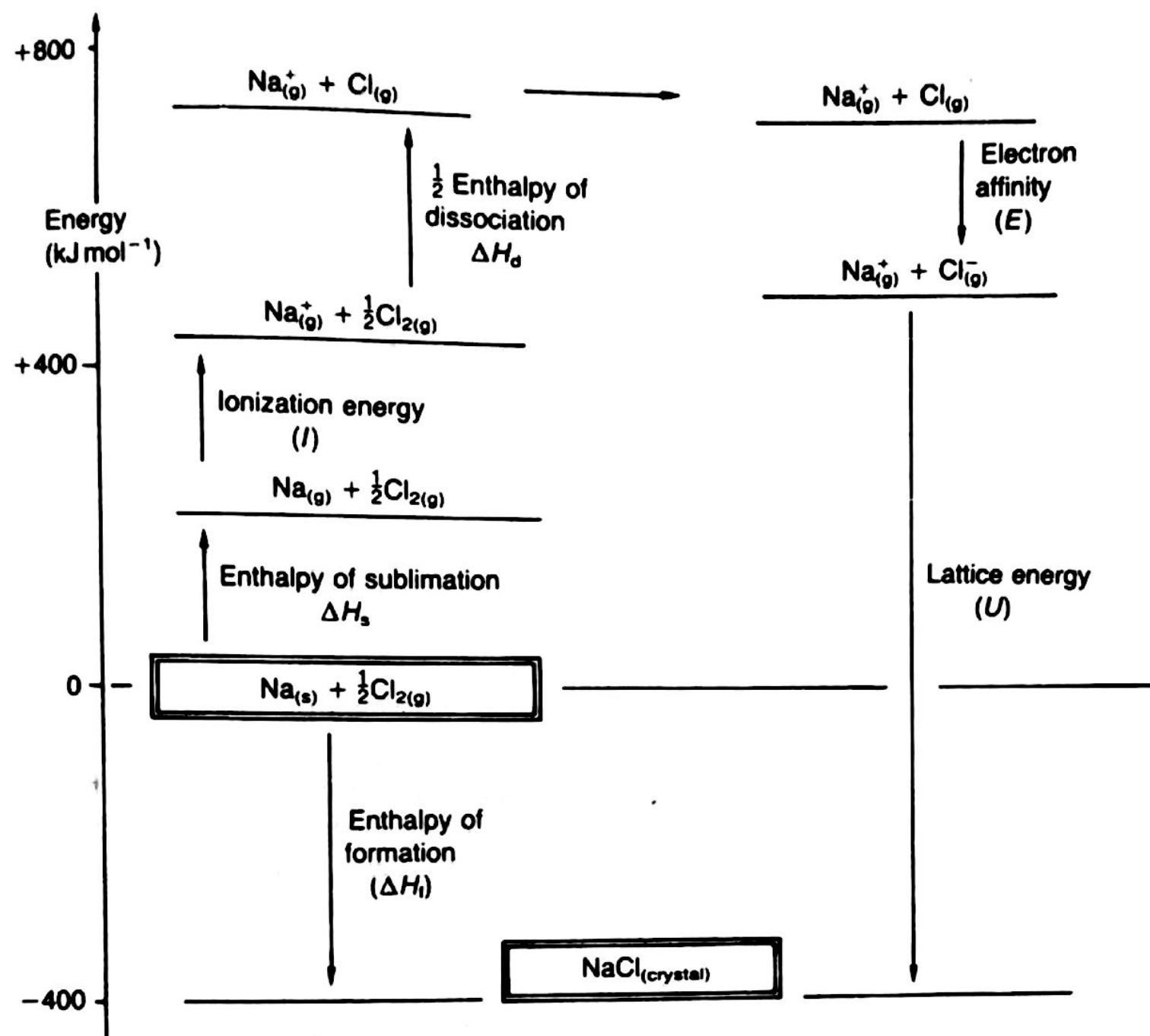


Figure 6.2 Born-Haber cycle for the formation of NaCl.

All the terms except the lattice energy and electron affinity can be measured. Originally the cycle was used to calculate electron affinities. By using known crystal structures, it was possible to calculate the lattice energy, and hence values were obtained for the electron affinity.

$$\Delta H_f = +\Delta H_s + I + \frac{1}{2}H_d + E + U$$

$$\text{For NaCl } 381.2 = +108.4 + 495.4 + 120.9 + E - 757.3$$

$$\text{hence } E = -348.6 \text{ kJ mol}^{-1}$$

Now that some electron affinity values are known, the cycle is used to calculate the lattice energy for unknown crystal structures.

It is useful to know the lattice energy, as a guide to the solubility of the crystal. When a solid dissolves, the crystal lattice must be broken up (which requires that energy is put in). The ions so formed are solvated (with the evolution of energy). When the lattice energy is high a large amount of energy is required to break the lattice. It is unlikely that the enthalpy of solvation will be big enough (and evolve sufficient energy to offset this), so the substance will probably be insoluble.

**Table 6.7** Comparison of theoretical and experimental lattice energies

	Theoretical lattice energy (kJ mol <sup>-1</sup> )	Born–Haber lattice energy (kJ mol <sup>-1</sup> )	% difference
LiCl	-825	-817	0.8
NaCl	-764	-764	0.0
KCl	-686	-679	1.0
KI	-617	-606	1.8
CaF <sub>2</sub>	-2584	-2611	1.0
CdI <sub>2</sub>	-1966	-2410	22.6

The ‘noble behaviour’ of many transition metals, that is their resistance to chemical attack, is related to a similar series of energy changes. Noble character is favoured by a high heat of sublimation, high ionization energy and low enthalpy of solvation of the ions.

Lattice energies may also provide some information about the ionic/covalent nature of the bonding. If the lattice energy is calculated theoretically assuming ionic bonding then the value can be compared with the experimental value for the lattice energy obtained from the experimentally measured quantities in the Born–Haber cycle. Close agreement indicates that the assumption that bonding is ionic is in fact true, whilst poor agreement may indicate that the bonding is not ionic. A number of lattice energies are compared in Table 6.7. The agreement is good for all the compounds listed except for CdI<sub>2</sub>, confirming that these are ionic. The large discrepancy for CdI<sub>2</sub> indicates that the structure is not ionic, and in fact it forms a layer structure which is appreciably covalent.

### POLARIZING POWER AND POLARIZABILITY – FAJANS’ RULES

Consider making a bond theoretically by bringing two ions A<sup>+</sup> and B<sup>-</sup> together to their equilibrium distance. Will the bond remain ionic, or will it become covalent? Ionic and covalent bonding are two extreme types of bonding, and almost always the bonds formed are intermediate in type, and this is explained in terms of polarizing (that is deforming) the shape of the ions.

The type of bond between A<sup>+</sup> and B<sup>-</sup> depends on the effect one ion has on the other. The positive ion attracts the electrons on the negative ion and at the same time it repels the nucleus, thus distorting or polarizing the negative ion. The negative ion will also polarize the positive ion, but since anions are usually large, and cations small, the effect of a large ion on a small one will be much less pronounced. If the degree of polarization is quite small, then the bond remains largely ionic. If the degree of polarization is large, electrons are drawn from the negative ion towards the positive ion, resulting in a high concentration of electrons between the two nuclei, and a large degree of covalent character results.

The extent to which ion distortion occurs depends on the power of an ion to distort the other ion (that is on its polarizing power) and also on how susceptible the ion is to distortion (that is on its polarizability). Generally the polarizing power increases as ions become smaller and more highly charged. The polarizability of a negative ion is greater than that of a positive ion since the electrons are less firmly bound because of the differences in effective nuclear charge. Large negative ions are more polarizable than small ones.

Fajans put forward four rules which summarize the factors favouring polarization and hence covalency.

1. *A small positive ion favours covalency.*

In small ions the positive charge is concentrated over a small area. This makes the ion highly polarizing, and very good at distorting the negative ion.

2. *A large negative ion favours covalency.*

Large ions are highly polarizable, that is easily distorted by the positive ion, because the outermost electrons are shielded from the charge on the nucleus by filled shells of electrons.

3. *Large charges on either ion, or on both ions, favour covalency.*

This is because a high charge increases the amount of polarization.

4. *Polarization, and hence covalency, is favoured if the positive ion does not have a noble gas configuration.*

Examples of ions which do not have a noble gas configuration include a few main group elements such as  $\text{Ti}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Bi}^{3+}$ , many transition metal ions such as  $\text{Ti}^{3+}$ ,  $\text{V}^{3+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cu}^+$ , and some lanthanide metal ions such as  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$ . A noble gas configuration is the most effective at shielding the nuclear charge, so ions without the noble gas configuration will have high charges at their surfaces, and thus be highly polarizing.

## ELECTRONEGATIVITY

In 1931, Pauling defined the electronegativity of an atom as the tendency of the atom to attract electrons to itself *when combined in a compound*.

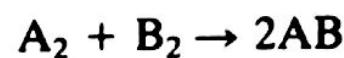
The implication of this is that when a covalent bond is formed, the electrons used for bonding need not be shared equally by both atoms. If the bonding electrons spend more time round one atom, that atom will have a  $\delta^-$  charge, and consequently the other atom will have a  $\delta^+$  charge. In the extreme case where the bonding electrons are round one atom all of the time, the bond is ionic. Pauling and others have attempted to relate the electronegativity difference between two atoms to the amount of ionic character in the bond between them.

Generally, small atoms attract electrons more strongly than large ones, and hence small atoms are more electronegative. Atoms with nearly filled shells of electrons tend to have higher electronegativities than those with sparsely occupied ones. Electronegativity values are very difficult to

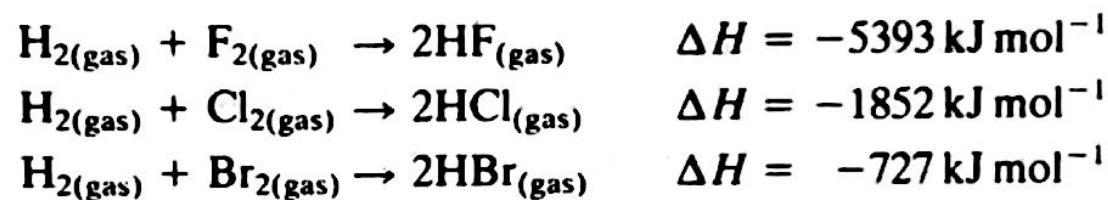
measure. Even worse, a particular type of atom in different molecules may well be in a different environment. It is unlikely that the electronegativity of an atom remains constant regardless of its environment, though it is invariably assumed that it is constant. Some of the more important approaches to obtaining electronegativity values are outlined below.

### Pauling

Pauling pointed out that since reactions of the type:



are almost always exothermic, the bond formed between the two atoms A and B must be stronger than the average of the single bond energies of A—A and B—B molecules. For example:



The bonding molecular orbital for AB ( $\phi_{AB}$ ) is made up from contributions from the wave functions for the appropriate atomic orbitals ( $\psi_A$  and  $\psi_B$ ).

$$\phi_{AB} = (\psi_A) + \text{constant } (\psi_B)$$

If the constant is greater than 1, the molecular orbital is concentrated on the B atom, which therefore acquires a partial negative charge, and the bond is partly polar.



Conversely, if the constant is less than 1, atom A gains a partial negative charge. Because of this partial ionic character, the A—B bond is stronger than would be expected for a pure covalent bond. The extra bond energy is called delta  $\Delta$ .

$$\Delta = (\text{actual bond energy}) - (\text{energy for 100% covalent bond})$$

The bond energy can be measured, but the energy of a 100% covalent bond must be calculated. Pauling suggested the 100% covalent bond energy be calculated as the geometric mean of the covalent energies of A—A and B—B molecules.

$$E_{100\% \text{ covalent } A-B} = \sqrt{(E_{A-A} \cdot E_{B-B})}$$

The bond energy in A—A and B—B molecules can be measured and so:

$$\Delta = (\text{actual bond energy}) - \sqrt{(E_{A-A} \cdot E_{B-B})}$$

Pauling states that the electronegativity difference between two atoms is equal to  $0.208/\Delta$ , where  $\Delta$  is the extra bond energy in  $\text{kcal mol}^{-1}$ .



(Converting the equation to SI units gives  $0.1017/\Delta$ , where  $\Delta$  is measured in  $\text{kJ mol}^{-1}$ .)

Pauling evaluated  $0.208/\Delta$  for a number of bonds and called this the electronegativity difference between A and B. Repeating Pauling's calculation with SI units for energy, we can evaluate  $0.1017/\Delta$ :

Bond	$\Delta(\text{kJ mol}^{-1})$	$0.1017/\Delta$	
C—H	24.3	0.50	i.e. $\chi_C - \chi_H = 0.50$
H—Cl	102.3	1.02	i.e. $\chi_{\text{Cl}} - \chi_H = 1.02$
N—H	105.9	1.04	i.e. $\chi_N - \chi_H = 1.04$

( $\chi$  (chi) = electronegativity of atom)

If  $\chi_H = 0$  then the electronegativity values for C, Cl and N would be 0.50, 1.02 and 1.04 respectively. Pauling changed the origin of the scale from  $\chi_H = 0$  to  $\chi_H = 2.05$  to avoid having any negative values in the table of values, and this made the value for C become 2.5 and the value for F become 4.0. At the same time the values for a number of other elements approximated to whole numbers: Li = 1.0, B = 2.0, N = 3.0. Thus by adding 2.05 to the values calculated in this way we can obtain the usually accepted electronegativity values (Table 6.8).

If two atoms have similar electronegativities, that is a similar tendency to attract electrons, the bond between them will be predominantly covalent. Conversely a large difference in electronegativity leads to a bond with a high degree of polar character, that is a bond that is predominantly ionic.

Rather than have two extreme forms of bond (ionic and covalent), Pauling introduced the idea that the ionic character of a bond varies with

**Table 6.8** Pauling's electronegativity coefficients (for the most common oxidation states of the elements)

						H
						2.1
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na						Cl
0.9						3.0
K						Br
0.8						2.8
Rb						I
0.8						2.5
Cs						
0.7						

**Table 6.9 Pauling's electronegativity values**

Period \ Group	1	2											13	14	15	16	17	18
1	H ● 2.1																	
2	Li ● 1.0	Be ● 1.5											B ● 2.0	C ● 2.5	N ● 3.0	O ● 3.5	F ● 4.0	Ne
3	Na ● 0.9	Mg ● 1.2											Al ● 1.5	Si ● 1.8	P ● 2.1	S ● 2.5	Cl ● 3.0	Ar
4	K ● 0.8	Ca ● 1.0	Sc ● 1.3	Ti ● 1.5	V ● 1.6	Cr ● 1.6	Mn ● 1.5	Fe ● 1.8	Co ● 1.8	Ni ● 1.8	Cu ● 1.9	Zn ● 1.6	Ga ● 1.6	Ge ● 1.8	As ● 2.0	Se ● 2.4	Br ● 2.8	Kr
5	Rb ● 0.8	Sr ● 1.0	Y ● 1.2	Zr ● 1.4	Nb ● 1.6	Mo ● 1.8	Tc ● 1.9	Ru ● 2.2	Rh ● 2.2	Pd ● 2.2	Ag ● 1.9	Cd ● 1.7	In ● 1.7	Sn ● 1.8	Sb ● 1.9	Te ● 2.1	I ● 2.5	Xe
6	Cs ● 0.7	Ba ● 0.9	La ● 1.1	Hf ● 1.3	Ta ● 1.5	W ● 1.7	Re ● 1.9	Os ● 2.2	Ir ● 2.2	Pt ● 2.2	Au ● 2.4	Hg ● 1.9	Tl ● 1.8	Pb ● 1.8	Bi ● 1.9	Po ● 2.0	At ● 2.2	Rn
7	Fr ● 0.7	Ra ● 0.9	Ac ● 1.1															

**PAULING'S ELECTRONEGATIVITY VALUES**

Electronegativity varies with the oxidation state of the element. The values given are for the most common oxidation states.  
(Large circles indicate high values and small circles small values.)

Copyright 1960, Cornell University. Adapted by permission of Cornell University Press.

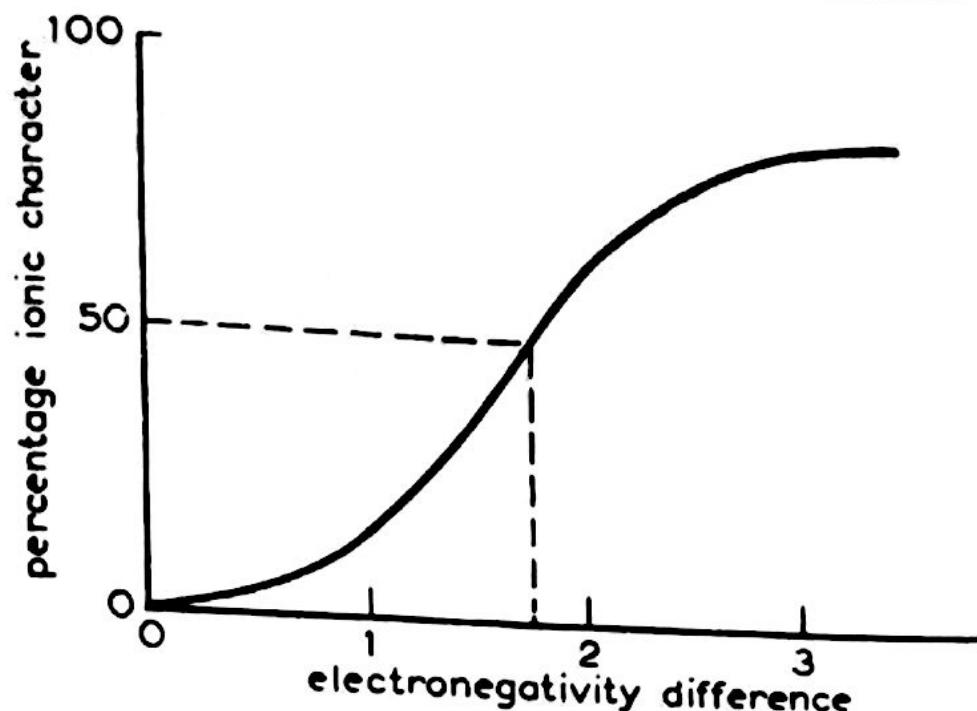


Figure 6.3 Electronegativity difference.

the difference in electronegativity as shown in Figure 6.3. This graph is based on the ionic characters HI 4% ionic, HBr 11%, HCl 19% and HF 45%, which are known from dipole measurements. Fifty per cent ionic character occurs when the electronegativity difference between the atoms is about 1.7, so for a larger difference than this a bond is more ionic than covalent. Similarly, if the electronegativity difference is less than 1.7, the bond is more covalent than ionic. It is better to describe a bond such as one of those in  $\text{BF}_3$  as 63% ionic, rather than just ionic.

### Mulliken

In 1934, Mulliken suggested an alternative approach to electronegativity based on the ionization energy and electron affinity of an atom. Consider two atoms A and B. If an electron is transferred from A to B, forming ions  $\text{A}^+$  and  $\text{B}^-$ , then the energy change is the ionization energy of atom A ( $I_A$ ) minus the electron affinity of atom B ( $E_B$ ), that is  $I_A - E_B$ . Alternatively, if the electron was transferred the other way to give  $\text{B}^+$  and  $\text{A}^-$  ions, then the energy change would be  $I_B - E_A$ . If  $\text{A}^+$  and  $\text{B}^-$  are actually formed, then this process requires less energy, and

$$(I_A - E_B) < (I_B - E_A)$$

### Rearranging

$$(I_A + E_A) < (I_B + E_B)$$

Thus Mulliken suggested that electronegativity could be regarded as the average of the ionization energy and the electron affinity of an atom.

$$\text{Electronegativity} = \frac{(I + E)}{2}$$

Mulliken used  $I$  and  $E$  values measured in electron volts, and the values were about 2.8 times larger than the Pauling values. We now measure  $I$  and

$E$  in  $\text{kJ mol}^{-1}$ . The energy  $1\text{eV}/\text{molecule} = 96.48 \text{ kJ mol}^{-1}$ , so the commonly accepted Pauling values are more nearly obtained by performing this calculation  $(I + E)/(2 \times 2.8 \times 96.48)$  or  $(I + E)/540$ .

This method has a simple theoretical basis, and also has the advantage that different values can be obtained for different oxidation states of the same element. It suffers from the limitation that only a few electron affinities are known. It is more usual to use the approach based on bond energies.

### Allred and Rochow

In 1958 Allred and Rochow considered electronegativity in a different way, and worked out values for 69 elements. (See Further Reading.) They defined electronegativity as the attractive force between a nucleus and an electron at a distance equal to the covalent radius. This force  $F$  is electrostatic, and is given by:

$$F = \frac{e^2 \cdot Z_{\text{effective}}}{r^2}$$

where  $e$  is the charge on an electron,  $r$  is the covalent radius, and  $Z_{\text{effective}}$  is the effective nuclear charge. The latter is the nuclear charge modified by screening factors for the orbital electrons. The screening factors vary depending on the principal quantum number (the shell that the electron occupies), and the type of electron,  $s$ ,  $p$ ,  $d$  or  $f$ . Screening factors have been worked out by Slater, so this provides a convenient method of calculating electronegativity values. These  $F$  values may be converted to electronegativity values on the Pauling scale of values using an empirical relationship:

$$\chi = 0.744 + \frac{0.359 Z_{\text{effective}}}{r^2}$$

The electronegativity values so obtained agree quite closely with those obtained by Pauling and Mulliken.

As the oxidation number of an atom increases, the attraction for the electrons increases, so the electronegativity should also increase. Allred and Rochow's method gives slightly different values:

Mo(II)	2.18	Fe(II)	1.83	Tl(I)	1.62	Sn(II)	1.80
Mo(III)	2.19	Fe(III)	1.96	Tl(III)	2.04	Sn(IV)	1.96
Mo(IV)	2.24						
Mo(V)	2.27						
Mo(VI)	2.35						

Allred and Rochow's method depends on measuring covalent radii (and these are obtained with great accuracy by X-ray crystallography) so it might be expected to yield very accurate electronegativity values. This is not so, because although the interatomic distances can be measured very

precisely, covalent radii are much less well known because the multiplicity of the bond is not known for certain, that is the bond may possess some double bond character.

The electronegativity values given in this book are those due to Pauling, but others have been calculated from different theoretical assumptions by Mulliken, Allred and Rochow and Sanderson. For details of these and several modern reviews of electronegativity values see Further Reading. *It is now considered that attempts to measure very accurate values for electronegativity are unjustified, and it is better to retain a loose definition of electronegativity, and use it for a more qualitative description of bonds.* For this purpose, it is worth remembering a few electronegativity values (see Table 6.8). From these it is possible to make a reasonable guess at the values for other elements, and hence predict the nature of the bonds formed. Bonds between atoms with similar electronegativity values will be largely non-polar (covalent), and bonds between atoms with a large electronegativity difference will be largely polar (ionic). Predictions using electronegativity in general agree with those made using Fajans' rules.

The basic properties of elements are inversely related to the electronegativity. Thus on descending one of the main groups, the electronegativity decreases, and basic properties increase. Similarly, on going across a period the elements become more electronegative, and less basic.

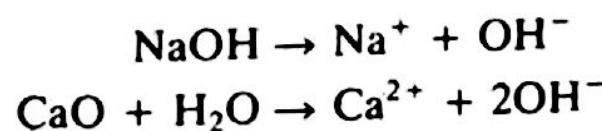
## METALLIC CHARACTER

Metals are electropositive and have a tendency to lose electrons, if supplied with energy:



The stronger this tendency, the more electropositive and more metallic an element is. The tendency to lose electrons depends on the ionization energy. It is easier to remove an electron from a large atom than from a small one, so metallic character increases as we descend the groups in the periodic table. Thus in Group 14, carbon is a non-metal, germanium shows some metallic properties, and tin and lead are metals. Similarly, metallic character decreases from left to right across the periodic table because the size of the atoms decreases and the ionization energy increases. Thus sodium and magnesium are more metallic than silicon, which, in turn, is more metallic than chlorine. The most electropositive elements are found in the lower left of the periodic table and the most non-metallic in the top right.

Electropositivity is really the converse of electronegativity, but it is convenient to use the concept of electropositivity when describing metals. Strongly electropositive elements give ionic compounds. Metallic oxides and hydroxides are basic since they ionize, and give hydroxyl ions:



Oxides which are insoluble in water cannot produce  $\text{OH}^-$  in this way, and these are regarded as basic if they react with acids to form salts. Thus in the main groups of the periodic table, basic properties increase on descending a group because the elements become more electropositive and more ionic. However, this generalization does not hold for the *d*-block, and particularly for the central groups of transition elements (Cr, Mn, Fe, Co, Ni) where basicity and the ability to form simple ions decreases on descending the group.

The degree of electropositivity is shown in a variety of ways. Strongly electropositive elements react with water and acids. They form strongly basic oxides and hydroxides, and they react with oxoacids to give stable salts such as carbonates, nitrates and sulphates. Weakly electropositive elements are unaffected by water and are much less readily attacked by acids. Their oxides are frequently amphoteric, and react with both acids and alkalis. They are not basic enough to form stable carbonates.

The electropositive nature of a metal is also shown in the degree of hydration of the ions. In the change  $\text{M}^+$  to  $[(\text{H}_2\text{O})_n \rightarrow \text{M}]^+$  the positive charge becomes spread over the whole complex ion. Since the charge is no longer localized on the metal, this is almost the same as the change  $\text{M}^+ \rightarrow \text{M}$ . Strongly electropositive metals have a great tendency to the opposite change,  $\text{M} \rightarrow \text{M}^+$ , so that they are not readily hydrated. The less electropositive the metal, the weaker the tendency  $\text{M} \rightarrow \text{M}^+$  and the stronger the degree of hydration. Thus the elements in Group 2 are less electropositive than those of Group 1, and Group 2 ions are more heavily hydrated than those in Group 1. The degree of hydration also decreases down a group, e.g.  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

Salts of strongly electropositive metals have little tendency to hydrolyse and form oxosalts. Since the metal ion is large, it has little tendency to form complexes. On the other hand, salts of weakly electropositive elements hydrolyse and may form oxosalts. Because they are smaller, the metal ions have a greater tendency to form complexes.

### VARIABLE VALENCY AND OXIDATION STATES

In the *s*-block the oxidation state is always the same as the group number. For *p*-block elements, the oxidation state is normally (the group number – 10) or (18 – the group number). Variable valency does occur to a limited extent in the *p*-block. In these cases the oxidation state always changes by two, e.g.  $\text{TiCl}_3$  and  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  and  $\text{SnCl}_2$ ,  $\text{PCl}_5$  and  $\text{PCl}_3$ , and is due to a pair of electrons remaining paired and not taking part in bonding (the inert pair effect). The term oxidation state is preferred to valency. The oxidation state may be defined as the charge left on the central atom when all the other atoms of the compound have been removed in their usual oxidation states. Thus Ti shows oxidation states of (+III) and (+I), Sn of (+IV) and (+II), and P of (+V) and (+III). The oxidation number can be calculated equally well for ionic or covalent compounds, and without knowing the types of bonds. The oxidation number of S in  $\text{H}_2\text{SO}_4$  can be worked out as

follows. O usually has an oxidation state of (-II) (except in  $O_2$  and  $O_2^{2-}$ ). H usually has an oxidation state of (+I) (except in  $H_2$  and  $H^-$ ). The sum of the oxidation numbers of all the atoms in  $H_2SO_4$  is zero, so:

$$(2 \times 1) + (S^x) + (4 \times -2) = 0$$

Thus  $x$ , the oxidation state of S, is (+VI). In the case of the oxidation state of Mn in  $KMnO_4$ , the compound ionizes into  $K^+$  and  $MnO_4^-$  ions. In  $MnO_4^-$  the sum of the oxidation states is equal to the charge on the ion, so:

$$Mn^x + (4 \times -2) = -1$$

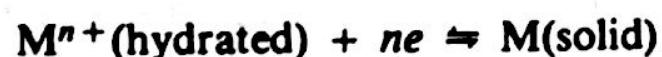
Thus  $x$ , the oxidation state of Mn, is 7, i.e. (+VII).

One of the most striking features of the transition elements is that the elements usually exist in several different oxidation states. Furthermore, the oxidation states change in units of 1, e.g.  $Fe^{3+}$  and  $Fe^{2+}$ ,  $Cu^{2+}$  and  $Cu^+$ . This is in contrast to the s-block and p-block elements. The reason why this occurs is that a different number of  $d$  electrons may take part in bonding.

Though the oxidation number is the same as the charge on the ion for ions such as  $Tl^+$  and  $Tl^{3+}$ , the two are not necessarily the same. Thus Mn exists in the oxidation state (+VII) but  $Mn^{7+}$  does not exist, as  $KMnO_4$  ionizes into  $K^+$  and  $MnO_4^-$ .

### STANDARD ELECTRODE POTENTIALS AND ELECTROCHEMICAL SERIES

When a metal is immersed in water, or a solution containing its own ions, the metal tends to lose positive metal ions into the solution. Thus the metal acquires a negative charge.



The size of the electric potential  $E$  set up between the two depends on the particular metal, the number of electrons involved, the activity of the ions in solution, and the temperature.  $E^\circ$  is the standard electrode potential, which is a constant for any particular metal and is in fact the electrode potential measured under standard conditions of temperature and with unit activity. These terms are related by the equation:

$$E = E^\circ + \frac{RT}{nF} \ln (1/a_M n^+)$$

(where  $R$  is the gas constant,  $T$  the absolute temperature,  $a_M n^+$  the activity of the ions in solution,  $n$  the valency of the ion and  $F$  the Faraday). For most purposes, the activity,  $a_M n^+$ , may be replaced by the concentration of ions in solution.

The potential of a single electrode cannot be measured, but if a second electrode of known potential is placed in the solution, the potential difference between the two electrodes can be measured. The standard against which all electrode potentials are compared is the hydrogen electrode.

**Table 6.10** Standard electrode potentials  
(volts at 25 °C)

Li <sup>+</sup>	Li	-3.05
K <sup>+</sup>	K	-2.93
Ca <sup>2+</sup>	Ca	-2.84
Al <sup>3+</sup>	Al	-1.66
Mn <sup>2+</sup>	Mn	-1.08
Zn <sup>2+</sup>	Zn	-0.76
Fe <sup>2+</sup>	Fe	-0.44
Cd <sup>2+</sup>	Cd	-0.40
Co <sup>2+</sup>	Co	-0.27
Ni <sup>2+</sup>	Ni	-0.23
Sn <sup>2+</sup>	Sn	-0.14
Pb <sup>2+</sup>	Pb	-0.13
H <sup>+</sup>	H <sub>2</sub>	0.00
Cu <sup>2+</sup>	Cu	+0.35
Ag <sup>+</sup>	Ag	+0.80
Au <sup>3+</sup>	Au	+1.38

**Table 6.11** Standard electrode potentials (V)

O <sub>2</sub>   OH <sup>-</sup>	+0.40
I <sub>2</sub>   I <sup>-</sup>	+0.57
Br <sub>2</sub>   Br <sup>-</sup>	+1.07
Cl <sub>2</sub>   Cl <sup>-</sup>	+1.36
F <sub>2</sub>   F <sup>-</sup>	+2.85

(This comprises a platinized platinum electrode, which is saturated with hydrogen at one atmosphere pressure and immersed in a solution of H<sub>3</sub>O<sup>+</sup> at unit activity. The potential developed by this electrode is arbitrarily fixed as zero.)

If the elements are arranged in order of increasing standard electrode potentials, the resulting Table 6.10 is called the electrochemical series.

Electrode potentials can also be measured for elements such as oxygen and the halogens which form negative ions (Table 6.11).

In the electrochemical series the most electropositive elements are at the top and the least electropositive at the bottom. The greater the negative value of the potential, the greater is the tendency for a metal to ionize. Thus a metal high in the electrochemical series will displace another metal lower down the series from solution. For example, iron is above copper in the electrochemical series, and scrap iron is sacrificed to displace Cu<sup>2+</sup> ions from solution of CuSO<sub>4</sub> in the recovery of metallic copper.



In the Daniell cell zinc displaces copper from copper salts in solution. This causes the potential difference between the plates.

**Table 6.12** Some standard reduction potentials in acid solution at 25 °C (volts)

<i>Group 1</i>	$E^\circ$	<i>Group 15</i>	$E^\circ$	<i>Group 17</i>	$E^\circ$
$\text{Li}^+ + \text{e} \rightarrow \text{Li}$	-3.05	$\text{As} + 3\text{e} \rightarrow \text{AsH}_3$	-0.60	$\text{I}_3^- + 2\text{e} \rightarrow 3\text{I}^-$	+0.54
$\text{K}^+ + \text{e} \rightarrow \text{K}$	-2.93	$\text{Sb} + 3\text{e} \rightarrow \text{SbH}_3$	-0.51	$\text{Br}_3^- + 2\text{e} \rightarrow 3\text{Br}^-$	+1.05
$\text{Rb}^+ + \text{e} \rightarrow \text{Rb}$	-2.93	$\text{H}_3\text{PO}_2 + \text{e} \rightarrow \text{P}$	-0.51	$2\text{ICl}_2^- + 2\text{e} \rightarrow \text{I}_2$	+1.06
$\text{Cs}^+ + \text{e} \rightarrow \text{Cs}$	-2.92	$\text{H}_3\text{PO}_3 + 2\text{e} \rightarrow \text{H}_3\text{PO}_2$	-0.50	$\text{Br}_2 + 2\text{e} \rightarrow 2\text{Br}^-$	+1.07
$\text{Na}^+ + \text{e} \rightarrow \text{Na}$	-2.71	$\text{H}_3\text{PO}_4 + 2\text{e} \rightarrow \text{H}_3\text{PO}_3$	-0.28	$2\text{IO}_3^- + 10\text{e} \rightarrow \text{I}_2$	+1.20
$\frac{1}{2}\text{N}_2 + 3\text{e} \rightarrow \text{NH}_4^+$					
$\frac{1}{2}\text{N}_2 + 2\text{e} \rightarrow \frac{1}{2}\text{N}_2\text{H}_5^+$					
$\text{Ba}^{2+} + 2\text{e} \rightarrow \text{Ba}$	-2.90	$\text{P} + 3\text{e} \rightarrow \text{PH}_3$	+0.06	$\text{H}_5\text{IO}_6 + 2\text{e} \rightarrow \text{IO}_3^-$	+1.60
$\text{Sr}^{2+} + 2\text{e} \rightarrow \text{Sr}$	-2.89	$\frac{1}{2}\text{Sb}_2\text{O}_3 + 3\text{e} \rightarrow \text{Sb}$	+0.15	$2\text{HOCl} + 2\text{e} \rightarrow \text{Cl}_2$	+1.63
$\text{Ca}^{2+} + 2\text{e} \rightarrow \text{Ca}$	-2.87	$\text{HAsO}_2 + 3\text{e} \rightarrow \text{As}$	+0.25	$\text{F}_2 + 2\text{e} \rightarrow 2\text{F}^-$	+2.65
$\text{Mg}^{2+} + 2\text{e} \rightarrow \text{Mg}$	-2.37	$\text{H}_3\text{AsO}_4 + 2\text{e} \rightarrow \text{HAsO}_2$	+0.56		
$\text{Be}^{2+} + 2\text{e} \rightarrow \text{Be}$	-1.85	$\text{HN}_3 + 8\text{e} \rightarrow 3\text{NH}_4^+$	+0.69	<i>Transition Metals</i>	
$\text{NO}_3^- + 3\text{e} \rightarrow \text{NO}$					
$\text{HNO}_2 + \text{e} \rightarrow \text{NO}$					
$\text{Al}^{3+} + 3\text{e} \rightarrow \text{Al}$	-1.66	$\frac{1}{2}\text{N}_2\text{O}_4 + 2\text{e} \rightarrow \text{NO}$	+1.03	$\text{Mn}^{2+} + 2\text{e} \rightarrow \text{Mn}$	-1.18
$\text{Ga}^{3+} + 3\text{e} \rightarrow \text{Ga}$	-0.53	$\frac{1}{2}\text{N}_2\text{H}_5^+ + 2\text{e} \rightarrow \text{NH}_4^+$	+1.28	$\text{Zn}^{2+} + 2\text{e} \rightarrow \text{Zn}$	-0.76
$\text{In}^{3+} + 3\text{e} \rightarrow \text{In}$	-0.34	$\text{NH}_3\text{OH} + 2\text{e} \rightarrow \text{NH}_4^+$	+1.35	$\text{Cr}^{3+} + 3\text{e} \rightarrow \text{Cr}$	-0.74
$\text{Tl}^+ + \text{e} \rightarrow \text{Tl}$	-0.34			$\text{Fe}^{2+} + 2\text{e} \rightarrow \text{Fe}$	-0.44
$\text{Tl}^{3+} + 2\text{e} \rightarrow \text{Tl}^+$	+1.25	<i>Group 16</i>		$\text{Cr}^{3+} + \text{e} \rightarrow \text{Cr}^{2+}$	-0.41
$\text{Te} + 2\text{e} \rightarrow \text{H}_2\text{Te}$					
$\text{Se} + 2\text{e} \rightarrow \text{H}_2\text{Se}$					
$\text{SiO}_2 + 4\text{e} \rightarrow \text{Si}$	-0.86	$\text{S}_4\text{O}_6^{2-} + 2\text{e} \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+0.08	$\text{Cu}^{2+} + \text{e} \rightarrow \text{Cu}^+$	+0.15
$\text{PbSO}_4 + 2\text{e} \rightarrow \text{Pb}$	-0.36	$\text{S} + 2\text{e} \rightarrow \text{H}_2\text{S}$	+0.14	$\text{Hg}_2\text{Cl}_2 + 2\text{e} \rightarrow 2\text{Hg}$	+0.27
$\text{CO}_2 + 4\text{e} \rightarrow \text{C}$	-0.20	$\text{HSO}_4^- + 2\text{e} \rightarrow \text{H}_2\text{SO}_3$	+0.17	$\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$	+0.35
$\text{GeO}_2 + 4\text{e} \rightarrow \text{Ge}$	-0.15	$\text{H}_2\text{SO}_3 + 2\text{e} \rightarrow \frac{1}{2}\text{S}_2\text{O}_3^{2-}$	+0.40	$[\text{Fe}(\text{CN})_6]^{4-} + \text{e} \rightarrow [\text{Fe}(\text{CN})_6]^{3-}$	+0.36
$\text{Sn}^{2+} + 2\text{e} \rightarrow \text{Sn}$	-0.14	$\text{H}_2\text{SO}_3 + 4\text{e} \rightarrow \text{S}$	+0.45	$\text{Cu}^+ + \text{e} \rightarrow \text{Cu}$	+0.50
$\text{Pb}^{2+} + 2\text{e} \rightarrow \text{Pb}$	-0.13	$4\text{H}_2\text{SO}_3 + 6\text{e} \rightarrow \text{S}_4\text{O}_6^{2-}$	+0.51	$\text{Cu}^{2+} + \text{e} \rightarrow \text{CuCl}$	+0.54
$\text{Si} + 4\text{e} \rightarrow \text{SiH}_4$	+0.10	$\text{S}_2\text{O}_6^{2-} + 2\text{e} \rightarrow 2\text{H}_2\text{SO}_4$	+0.57	$\text{MnO}_4^- + \text{e} \rightarrow \text{MnO}_4^{2-}$	+0.56
$\text{C} + 4\text{e} \rightarrow \text{CH}_4$	+0.13	$\text{O}_2 + 2\text{e} \rightarrow \text{H}_2\text{O}_2$	+0.68	$\text{Fe}^{3+} + \text{e} \rightarrow \text{Fe}^{2+}$	+0.77
$\text{Sn}^{4+} + 2\text{e} \rightarrow \text{Sn}^{2+}$	+0.15	$\text{H}_2\text{SeO}_3 + 4\text{e} \rightarrow \text{Se}$	+0.74	$\text{Hg}_2^{2+} + 2\text{e} \rightarrow 2\text{Hg}$	+0.79
$\text{PbO}_2 + 2\text{e} \rightarrow \text{PbSO}_4$	+1.69	$\text{SeO}_4^{2-} + 2\text{e} \rightarrow \text{H}_2\text{SeO}_3$	+1.15	$2\text{Hg}^{2+} + 2\text{e} \rightarrow \text{Hg}_2^{2+}$	+0.92
$\frac{1}{2}\text{O}_2 + 2\text{e} \rightarrow \text{H}_2\text{O}$					
$\text{H}_2\text{O}_2 + 2\text{e} \rightarrow 2\text{H}_2\text{O}$					
$\text{S}_2\text{O}_8^{2-} + 2\text{e} \rightarrow 2\text{SO}_4^{2-}$					
$\text{O}_3 + 2\text{e} \rightarrow \text{O}_2$					
$\text{MnO}_4^- + 3\text{e} \rightarrow \text{MnO}_4^{2-}$					

Table 6.12 is a table of standard reduction potentials. From this table we can see that the standard reduction potential for  $\text{Cu}^{2+}/\text{Cu}$  is 0.35 V. What does this mean?

$\text{Cu}^{2+}/\text{Cu}$  is referred to as a redox couple and as written it refers to the half reaction (or electrode reaction)



In general, redox couples are written *ox/red* where *ox* is the oxidized form and is written on the left and *red* is the reduced form and is written on the right.

Standard reduction potential values are determined relative to a hydrogen electrode, that is the redox couple  $\text{H}^+/\text{H}_2$  at 25°C for 1 M concentrations (or one atmosphere pressure) of all chemical species in the equations. (The concentration of water is included in the constant.)

Thus,  $\text{Cu}^{2+}/\text{Cu} E^\circ = +0.35 \text{ V}$  really means that the standard reduction potential of the reaction is 0.35 V.



Similarly the standard reduction potential of the couple  $\text{Zn}^{2+}/\text{Zn}$  is -0.76 V.



Subtracting equation (6.2) from (6.1) gives



Both of the standard potentials are relative to the  $\text{H}^+/\text{H}_2$  couple and therefore  $\text{H}^+$  and  $\text{H}_2$  disappear when the  $\text{Cu}^{2+}/\text{Cu}$  couple is combined with the  $\text{Zn}^{2+}/\text{Zn}$  couple.

From experience the oxidized forms of couples of high positive potential, for example  $\text{MnO}_4 + 5\text{e}^- \rightarrow \text{Mn}^{2+} E^\circ = +1.54 \text{ V}$ , are termed strong oxidizing agents. Conversely the reduced forms of couples of high negative potential, for example  $\text{Li}^+ + \text{e}^- \rightarrow \text{Li} E^\circ = -3.05 \text{ V}$ , are termed strong reducing agents. It follows that at some intermediate potential the oxidizing power of the oxidized form and the reducing power of the reduced form are similar. What is the value of this potential at which there is a change-over from oxidizing to reducing properties? The first point to note is that it is not at 0 V, the value assigned arbitrarily to the  $\text{H}^+/\text{H}$  couple: hydrogen is known to be a reducing agent. A group of chemical species which are used in classical (analytical) chemistry as weak reducing agents (e.g. sulphite and tin(II)) are the reduced forms of couples with potentials between 0 and about +0.6 V. On the other hand  $\text{VO}^{2+}$  is the stable form of vanadium and  $\text{VO}_2^+$  is a weak oxidizing agent: the potential  $\text{VO}_2^+/\text{VO}^{2+}$  is +1.00 V. Thus from experience, as a general rule of thumb we can say that if  $E^\circ \approx 0.8 \text{ V}$ , then the oxidized and reduced forms are of about equal stability in redox processes.

It is not very discriminating to term a metal a reducing agent: most metals may be called reducing agents. It is useful to divide metals into four groups in regard to the ease of reduction of their metal ions.

1. The noble metals (with  $E^\circ$  more positive than 0 V).
2. Metals which are easily reduced (e.g. with coke) ( $E^\circ 0 - (-0.5)$  V).
3. Typically reactive transition metals ( $E^\circ (-0.5) - (-1.5)$  V) which are often prepared by reduction with electropositive metals.
4. The electropositive metals ( $E^\circ$  more negative than  $-1.5$  V) which can be prepared by electrochemical reduction.

When a solution is electrolysed the externally applied potential must overcome the electrode potential. The minimum voltage necessary to cause deposition is equal and opposite in sign to the potential between the solution and the electrode. Elements low down in the series discharge first; thus  $\text{Cu}^{2+}$  discharges before  $\text{H}^+$ , so copper may be electrolysed in aqueous solution. However, hydrogen and other gases often require a considerably higher voltage than the theoretical potential before they discharge. For hydrogen, this extra or over-voltage may be 0.8 volts, and thus it is possible to electrolyse zinc salts in aqueous solution.

Several factors affect the value of the standard potential. The conversion of M to  $\text{M}^+$  in aqueous solution may be considered in a series of steps:

1. sublimation of a solid metal
2. ionization of a gaseous metal atom
3. hydration of a gaseous ion

These are best considered in a Born–Haber type of cycle (Figure 6.4).

The enthalpy of sublimation and the ionization energy are positive since energy must be put into the system, and the enthalpy of hydration is negative since energy is evolved. Thus

$$E = +\Delta H_s + I + \Delta H_h$$

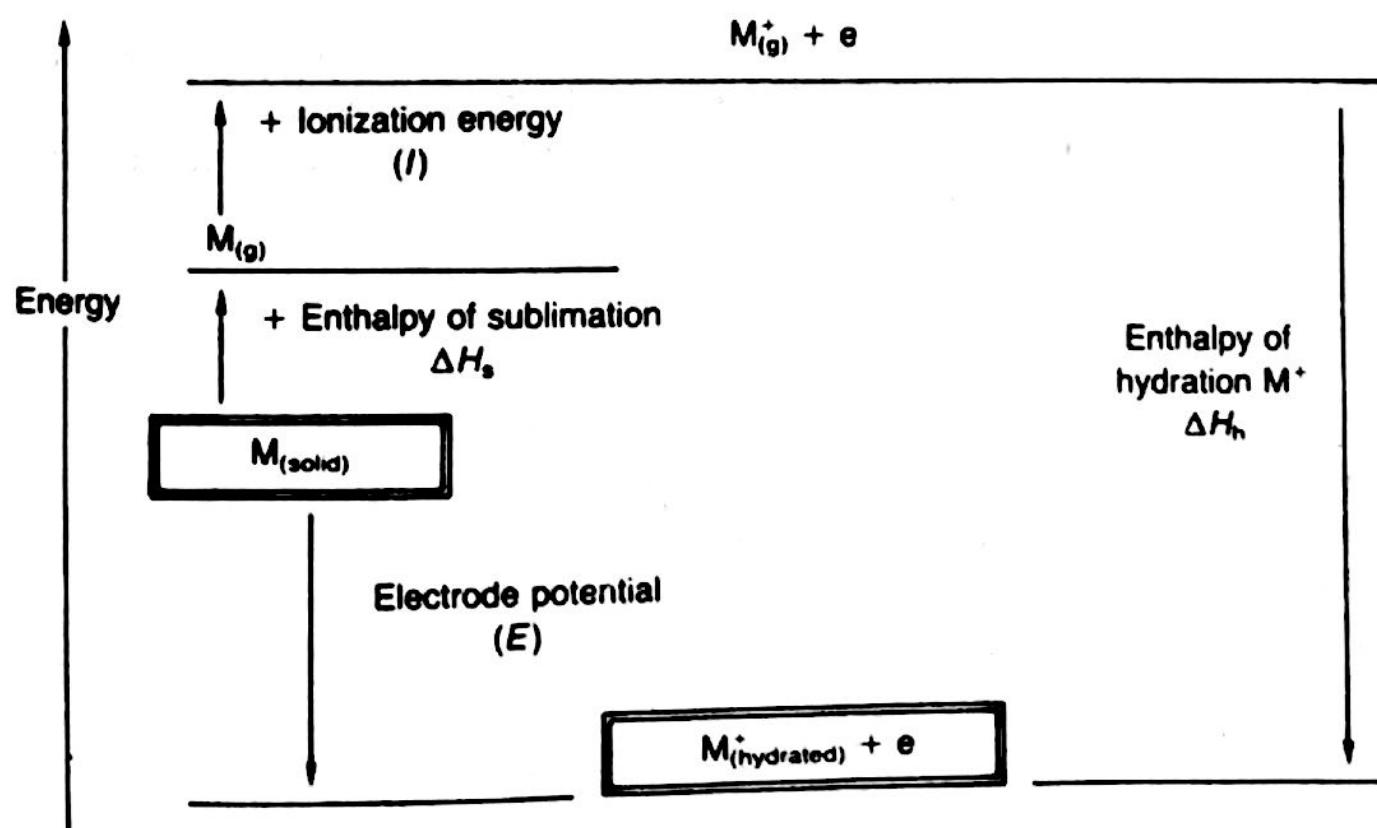


Figure 6.4 Energy cycle for electrode potentials. (Strictly E is the free energy change associated with electrode potential)

Consider first a transition metal. Most transition metals have high melting points: hence the enthalpy of sublimation is high. Similarly they are fairly small atoms and have high ionization energies. Thus the value for the electrode potential  $E$  is low, and the metal has little tendency to form ions: hence it is unreactive or noble.

In contrast the s-block metals (Groups 1 and 2) have low melting points (hence low enthalpies of sublimation), and the atoms are large and therefore have low ionization energies. Thus the electrode potential  $E$  is high and the metals are reactive.

Electrons are lost when a substance is oxidized and electrons are gained when it is reduced. A reducing agent must therefore supply electrons, and elements having large negative electrode potentials are strong reducing agents. The strengths of oxidizing and reducing agents may be measured by the size of the potential between a solution and an inert electrode. Standard reduction potentials are obtained when the concentrations of oxidized and reduced forms are 1 M, and the potential developed is measured against a standard hydrogen electrode. The most powerful oxidizing agents have a large positive oxidation potential and strong reducing agents have a large negative potential. Standard oxidation potentials allow us to predict which ions should oxidize or reduce other ions. The potentials indicate if the energy changes for the process are favourable or unfavourable. It is important to realize that though the potentials may suggest that a reaction is possible, they do not give any kinetic information concerning the rate of the reaction. The rate of the reaction may be very fast or slow, and in some cases a catalyst may be required for it to occur at all – for example in the oxidation of sodium arsenite by ceric sulphate.

### OXIDATION–REDUCTION REACTIONS

Oxidation is the removal of electrons from an atom, and reduction is the addition of electrons to an atom. The standard electrode potentials given in Table 6.10 are written by convention with the oxidized species on the left, and the reduced species on the right.



or



The potential developed by the half cell is therefore written as a reduction potential, since electron(s) are being added. A fuller list of reduction potentials in acid solution is given in Table 6.12.

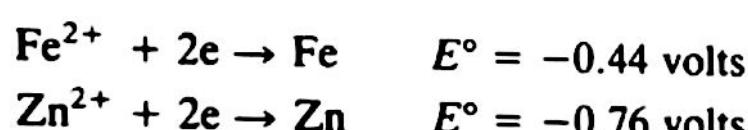
Oxidation–reduction (redox) potentials can be used to great advantage in explaining oxidation–reduction reactions in aqueous solution. The reduction potential is related to energy by the equation:

$$\Delta G = -nFE^\circ$$

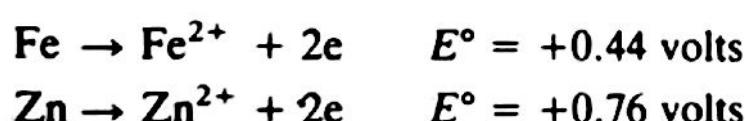
(where  $\Delta G$  is the change in Gibbs free energy,  $n$  the valency of the ion,  $F$  the Faraday and  $E^\circ$  the standard electrode potential). This is really an

application of thermodynamics. Ultimately whether a reaction occurs or not depends on energy. A reaction will not proceed if the free energy change  $\Delta G$  is positive, and thus thermodynamics saves us the trouble of trying the reaction. If  $\Delta G$  is negative, then the reaction is thermodynamically possible. It does not follow that because a reaction is thermodynamically possible, it will necessarily occur. Thermodynamics does not give any information on the rate of a reaction, which may be fast, slow, or infinitely slow, nor does it indicate if another reaction is even more favourable.

Consider the corrosion that may occur when a sheet of galvanized iron is scratched. (Galvanized iron is iron which has been coated with zinc to prevent rusting.) Half reactions and the corresponding reduction potentials are shown below.

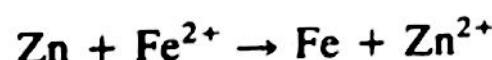


When in contact with water, either metal might be oxidized and lose metal ions, so we require the reverse reactions, and the potentials for these are called oxidation potentials, and have the same magnitude but the opposite sign to the reduction potentials.



Plainly, since  $\text{Zn} \rightarrow \text{Zn}^{2+}$  produces the largest positive  $E^\circ$  value, and since  $\Delta G = -nFE^\circ$ , it will produce the largest negative  $\Delta G$  value. Thus it is energetically more favourable for the Zn to dissolve, and hence the Zn will corrode away in preference to the Fe.

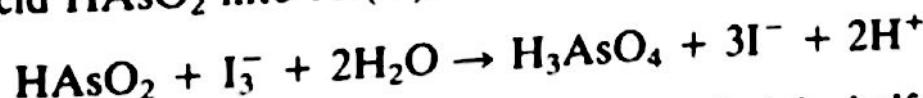
It is possible that when the galvanized steel is scratched, the air may oxidize some iron. The  $\text{Fe}^{2+}$  so produced is immediately reduced to iron by the zinc, and rusting does not occur.



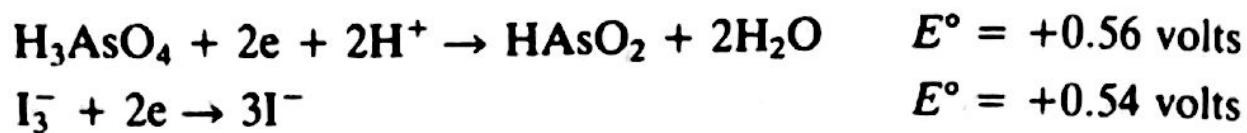
Similar applications in which one metal is sacrificed to protect another are the attaching of sacrificial blocks of magnesium to underground steel pipelines and the hulls of ships to prevent the rusting of iron.

Thus the coating of zinc serves two purposes – first it covers the iron and prevents its oxidation (rather like a coat of paint) and second it provides anodic protection.

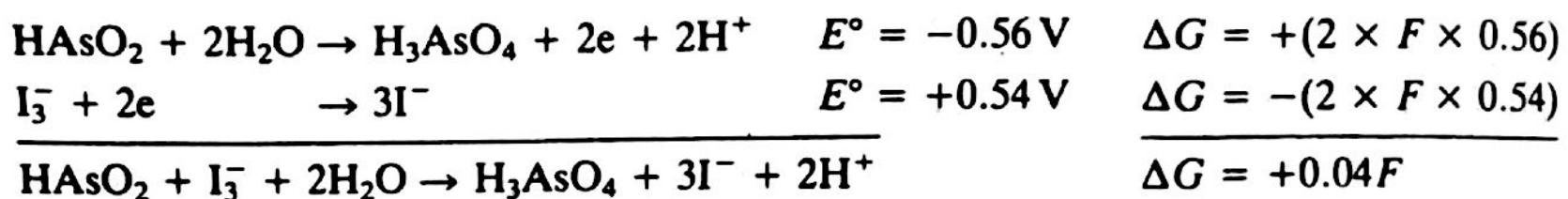
A table of standard reduction potentials (Table 6.12) may be used to predict if a reaction is possible, and what the equilibrium constant will be. Consider for example if the triiodide ion  $\text{I}_3^-$  will oxidize As(III) in arsenious acid  $\text{HAsO}_2$  into As(V).



Since the table lists reduction potentials, we must find the half reactions for  $\text{H}_3\text{AsO}_4 + 2e \rightarrow$  products, and  $\text{I}_3^- + 2e \rightarrow$  products.



The reaction we are investigating requires the first half reaction in the reverse direction, added to the second half reaction.  $E^\circ$  values for half reactions must not be added together, since they do not take account of the number of electrons involved. However,  $E^\circ$  values may be converted to the corresponding  $\Delta G$  values, which may be added to give  $\Delta G$  for the overall reaction.

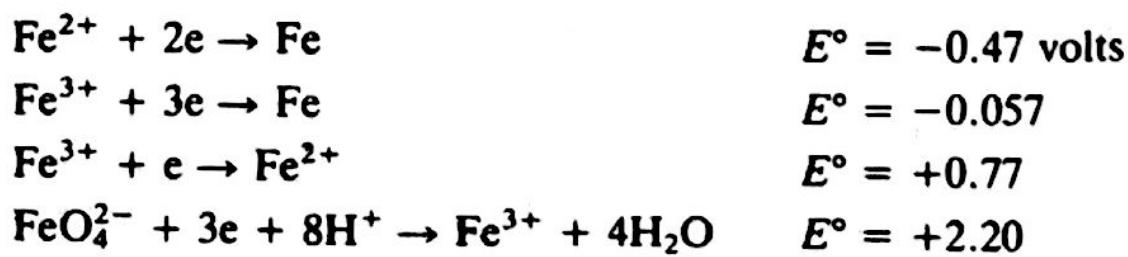


The  $\Delta G$  free energy change so calculated is positive, which indicates that the reaction will not proceed spontaneously in the forward direction, and suggests that it is energetically feasible for the reaction to proceed in the reverse direction. It should be noted that the value of  $\Delta G$  is very small, and thus it is unwise to draw very firm conclusions. The  $E^\circ$  values relate to standard conditions, and since  $\Delta G$  is small, a small change in conditions, such as varying the concentration, or the pH, or the temperature, could change the potentials and hence change  $\Delta G$  sufficiently to make the reaction proceed in either direction. There are volumetric methods of analysis for reducing arsenic acid with iodide ions in 5M acid, and for oxidizing arsenious acid by triiodide ion at pH 7.

### THE USE OF REDUCTION POTENTIALS

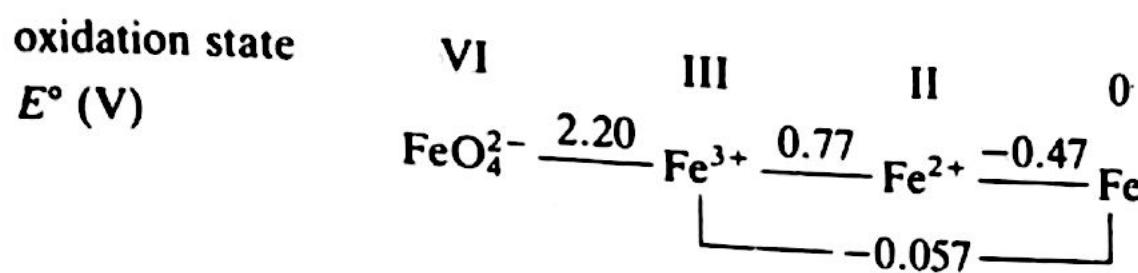
Enormous use may be made of reduction potentials for summarizing what species will oxidize or reduce something else, what the products of the reaction will be, and what oxidation states are stable with respect to the solvent, and also with respect to disproportionation. This topic is often insufficiently understood, so a number of examples are given.

A great deal of useful information about an element can be shown by the appropriate half reactions and reduction potentials. Consider some half reactions involving iron:



Where an element exists in several different oxidation states (in this case Fe(VI), Fe(III), Fe(II), and Fe(0)), it is convenient to display all of the reduction potentials for the half reactions in a single reduction potential diagram. In this the highest oxidation state is written at the left, and the

lowest state at the right, and species such as electrons,  $H^+$  and  $H_2O$  are omitted.



The potential for the reduction of  $FeO_4^{2-}$  to  $Fe^{3+}$  is +2.20 volts. Since  $\Delta G = -nFE^\circ$ , it follows that  $\Delta G$  for this change will be large and negative. This means that the reaction is thermodynamically possible since it releases a large amount of energy, and  $FeO_4^{2-}$  is a strong oxidizing agent.

Standard electrode potentials are measured on a scale with

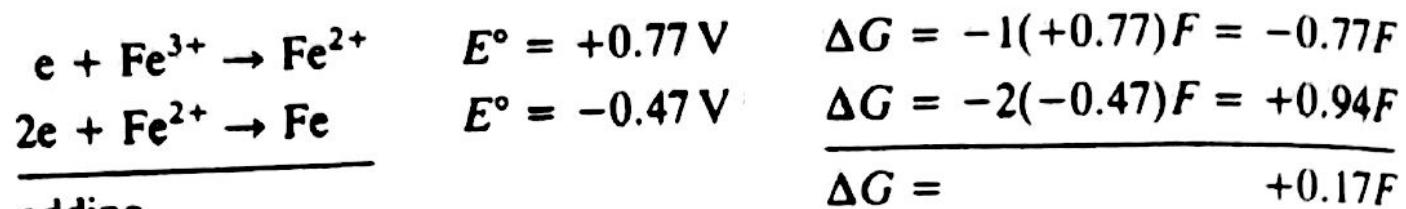


Since hydrogen is normally regarded as a reducing agent, reactions with negative value for  $E^\circ$  are more strongly reducing than hydrogen, that is they are strongly reducing. Materials which are generally accepted as oxidizing agents have  $E^\circ$  values above +0.8 volts, those such as  $Fe^{3+} \rightarrow Fe^{2+}$  of about 0.8 volts are stable (equally oxidizing and reducing), and those below +0.8 volts become increasingly reducing.

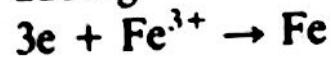
For the change  $Fe^{3+}/Fe^{2+}$ ,  $E^\circ$  is +0.77 V. This is close to the value of 0.8 V, and therefore  $Fe^{3+}$  and  $Fe^{2+}$  are of almost equal stability with respect to oxidation and reduction. The  $E^\circ$  values for the changes  $Fe^3 \rightarrow Fe$  and for  $Fe^{2+} \rightarrow Fe$  are both negative: hence  $\Delta G$  is positive, so neither  $Fe^{3+}$  nor  $Fe^{2+}$  have any tendency to reduce to Fe.

One of the most important facts which can be obtained from a reduction potential diagram is whether any of the oxidation states are unstable with regard to disproportionation. Disproportionation is where one oxidation state decomposes, forming some ions in a higher oxidation state, and some in a lower oxidation state. This happens when a given oxidation state is a stronger oxidizing agent than the next highest oxidation state, and this situation occurs when a reduction potential on the right is more positive than one on the left. In the diagram of iron reduction potentials, the values become progressively more negative on moving from left to right, and hence  $Fe^{3+}$  and  $Fe^{2+}$  are stable with respect to disproportionation.

At first sight the potential of -0.057 V for  $Fe^{3+} \rightarrow Fe$  seems wrong since the potentials for  $Fe^{3+} \rightarrow Fe^{2+}$  and  $Fe^{2+} \rightarrow Fe$  are 0.77 V and -0.47 V respectively, and adding 0.77 and -0.47 does not give -0.057. Potentials for complete reactions may be added since there are no electrons left over in the process. Potentials may not be added for half reactions since the electrons may not balance. However, potentials can always be converted into free energies using the equation  $\Delta G = -nFE^\circ$  where  $n$  is the number of electrons involved and  $F$  is the Faraday. Since the Gibbs free energy  $G$  is a thermodynamic function, free energies may be added, and the final total free energy converted back to an  $E^\circ$  value:



**adding**



Hence  $E^\circ$  can be calculated for the reaction  $\text{Fe}^{3+} \rightarrow \text{Fe}$

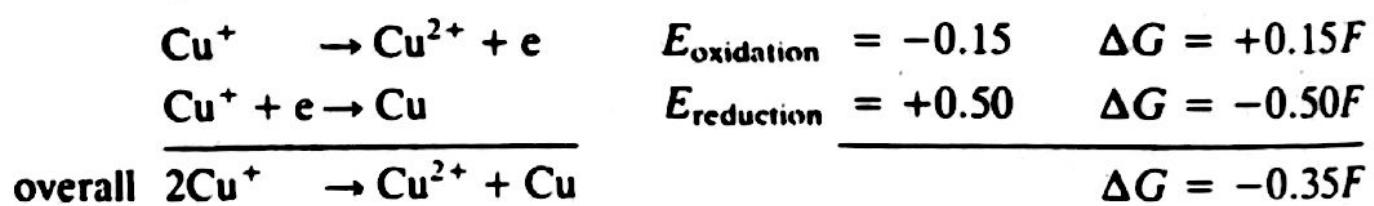
$$E^\circ = \frac{\Delta G}{-nF} = \frac{0.17F}{-3F} = -0.057 \text{ V}$$

The reduction potential diagram for copper in acid solution is

oxidation state	II	I	0
$E^\circ(V)$	$\text{Cu}^{2+} \xrightarrow{+0.15^*} \text{Cu}^+ \xrightarrow{+0.50} \text{Cu}$		
	$+0.35$		

## \*Disproportionates

The potential, and hence the energy released when  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$ , are both very small, and so  $\text{Cu}^{2+}$  is not an oxidizing agent but is stable. On moving from left to right the potentials  $\text{Cu}^{2+}-\text{Cu}^+-\text{Cu}$  become more positive. Whenever this is found, the species in the middle ( $\text{Cu}^+$  in this case) disproportionates, that is it behaves as both a self-oxidizing and self-reducing agent because it is energetically favourable for the following two changes to occur together



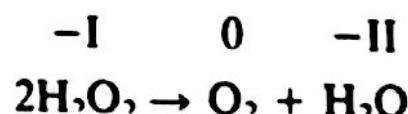
Thus in solution  $\text{Cu}^+$  disproportionates into  $\text{Cu}^{2+}$  and  $\text{Cu}$ , and hence  $\text{Cu}^+$  is only found in the solid state.

**The reduction potential diagram for oxygen is shown.**

<b>oxidation state</b>	0	-I	-II
<b><math>E^\circ(V)</math></b>			
$O_2$	+0.682 *	$H_2O_2$	+1.776
			$H_2O$
		+1.229	

## \* Disproportionates

On moving from left to right, the reduction potentials increase, and hence  $\text{H}_2\text{O}_2$  is unstable with respect to disproportionation.



It must be remembered that the solvent may impose a limitation on what species are stable, or exist at all. Very strong oxidizing reagents will oxidize

water to  $O_2$ , whilst strong reducing agents will reduce it to  $H_2$ . Thus very strong oxidizing or reducing agents can not exist in aqueous solution. The following half reactions are of special importance:

*Reduction of water*

neutral solution	$H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2$	$E^\circ = -0.414 V$
1.0 M acid solution	$H_3O^+ + e^- \rightarrow H_2O + \frac{1}{2}H_2$	$E^\circ = 0.000 V$
1.0 M base solution	$H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2$	$E^\circ = -0.828 V$

*Oxidation of water*

neutral solution	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$E^\circ = +0.185 V$
1.0 M acid solution	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$E^\circ = +1.229 V$
1.0 M base solution	$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$E^\circ = +0.401 V$

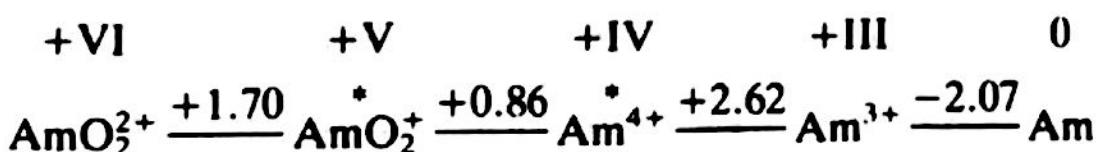
These reactions limit the *thermodynamic stability* of any species in aqueous solution.

Thus the minimum reduction potentials required to oxidize water to dioxygen is  $E^\circ > +0.185 V$  in neutral solution,  $E^\circ > +1.229 V$  in 1.0M acid solution and  $E^\circ > +0.401 V$  in 1.0 M basic solution.

In the same way half reactions with  $E^\circ$  potentials less than zero (that is negative values) should reduce water to  $H_2$  in 1.0 M acid solution, whilst an  $E^\circ < -0.414 V$  is required in neutral solution, and  $E^\circ < -0.828 V$  in 1.0 M basic solution.

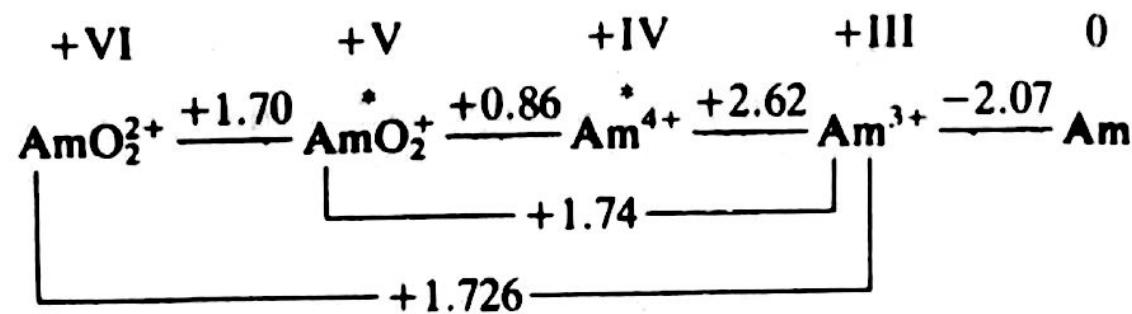
Often when the  $E^\circ$  values are just large enough to suggest that a reaction is thermodynamically possible, we find that it does not appear to happen. It must be remembered that a substance may be thermodynamically unstable, but kinetically stable, since the activation energy for the reaction is high. This means that the rates of these reactions are very slow. If the potentials are appreciably more positive or negative than these limits then reaction with the solvent is usually observed.

The reduction potentials for americium show that  $Am^{4+}$  is unstable with regard to disproportionation.



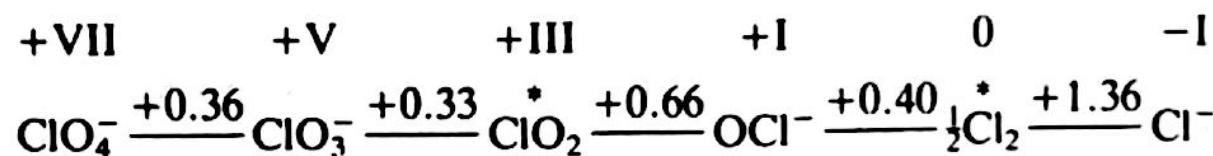
\* Disproportionates

The potential for the couple  $AmO_2^+ \rightarrow Am^{3+}$  can be calculated by converting the values of 0.86 and 2.62 volts into free energies, adding them, then converting back to give a potential of 1.74 volts. When this step is added to the diagram it becomes apparent that the potentials do not decrease from  $AmO_2^{2+}$  to  $AmO_2^+$  to  $Am^{3+}$ , and hence  $AmO_2^+$  is unstable with regard to disproportionation to  $AmO_2^{2+}$  and  $Am^{3+}$ . Finally, the potential for the couple  $AmO_2^{2+} \rightarrow Am^{3+}$  can be worked out to be +1.726 volts. Thus considering  $AmO_2^{2+} \rightarrow Am^{3+} \rightarrow Am$ ,  $Am^{3+}$  is stable:



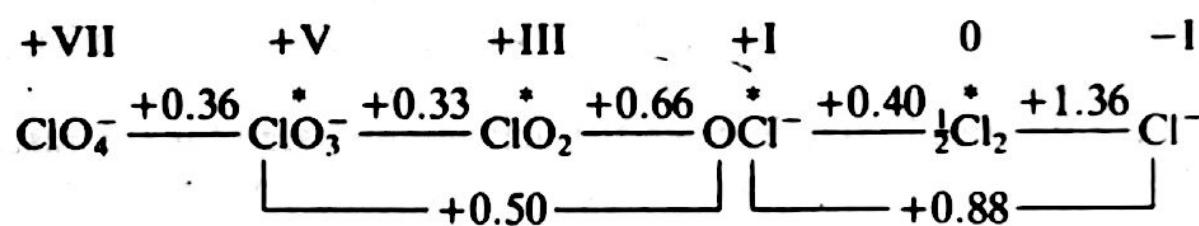
\* Disproportionates

It is important to include all the possible half reactions in a reduction potential diagram, or incorrect conclusions may be drawn. Examination of the incomplete diagram for chlorine in basic solution would indicate that  $\text{ClO}_2^-$  should disproportionate into  $\text{ClO}_3^-$  and  $\text{OCl}^-$ , and that  $\text{Cl}_2$  should disproportionate into  $\text{OCl}^-$  and  $\text{Cl}^-$ . Both of these deductions are correct.



\* Disproportionates

The incomplete data also suggest that  $\text{OCl}^-$  should be stable with regard to disproportionation, but this is not true. The species which disproportionate are 'ignored', and a single potential calculated for the change  $\text{ClO}_3^- \rightarrow \text{OCl}^-$  to replace the values  $+0.33\text{ V}$  and  $+0.66\text{ V}$ . Similarly a single potential is calculated for  $\text{OCl}^- \rightarrow \text{Cl}^-$



\* Disproportionates

When the complete diagram is examined, it is apparent that the potentials around  $\text{OCl}^-$  do not decrease from left to right, and hence  $\text{OCl}^-$  is unstable with respect to disproportionation into  $\text{ClO}_3^-$  and  $\text{Cl}^-$

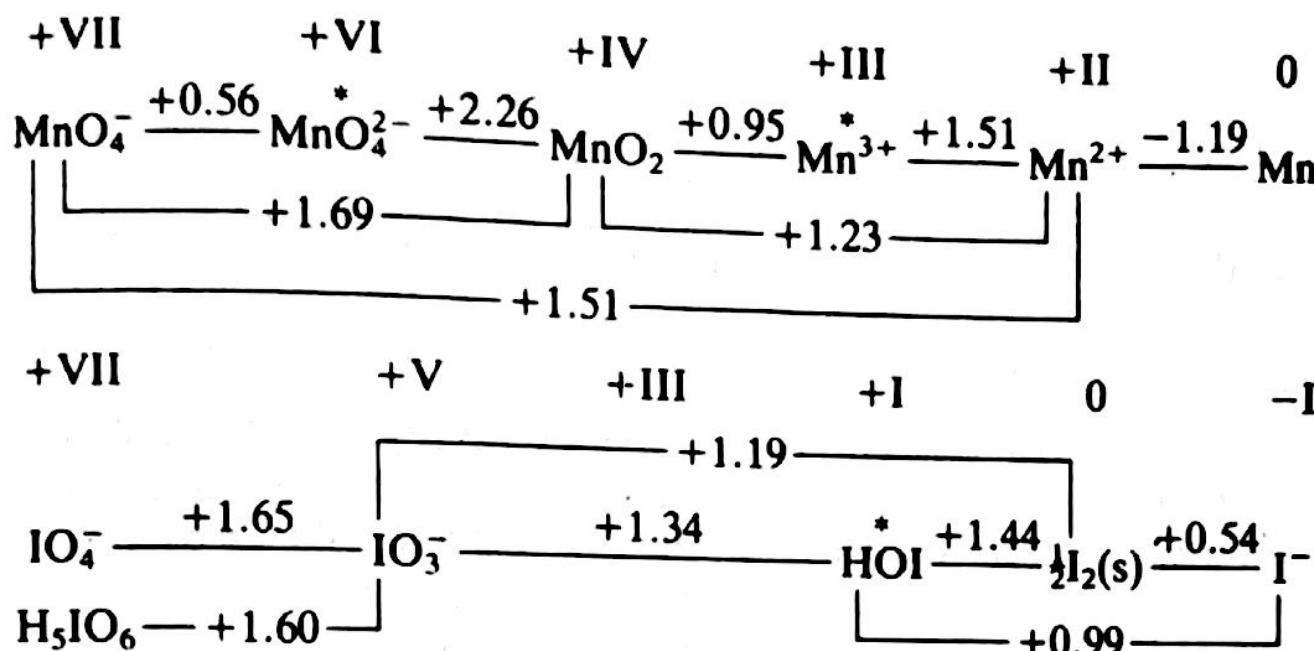


In the same way, the potentials round  $\text{ClO}_3^-$  do not decrease from left to right



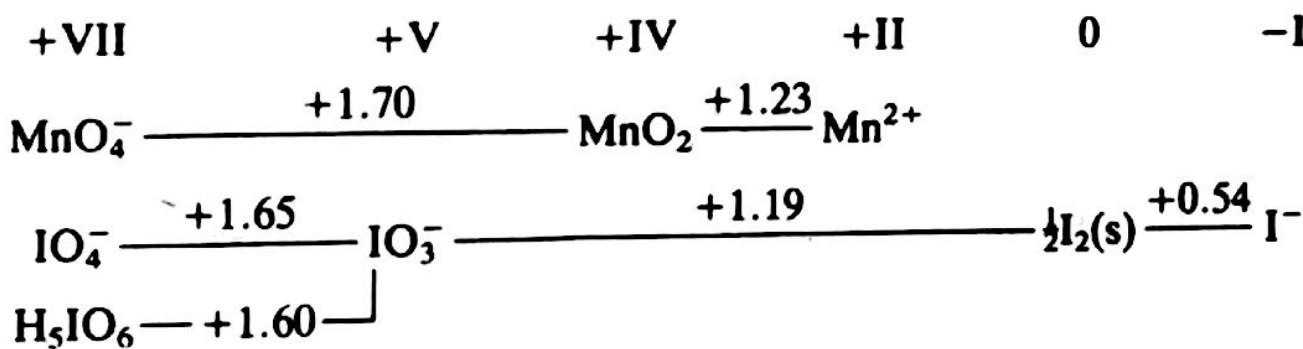
Similarly  $\text{ClO}_3^-$  should disproportionate into  $\text{ClO}_4^-$  and  $\text{OCl}^-$ , and  $\text{OCl}^-$  should disproportionate to give  $\text{Cl}^-$  and more  $\text{ClO}_3^-$ .

Reduction potential diagrams may also be used to predict the products of reactions in which the elements have several oxidation states. Consider for example the reaction between an acidified solution of  $\text{KMnO}_4$  and  $\text{KI}$ . The reduction potential diagrams are:

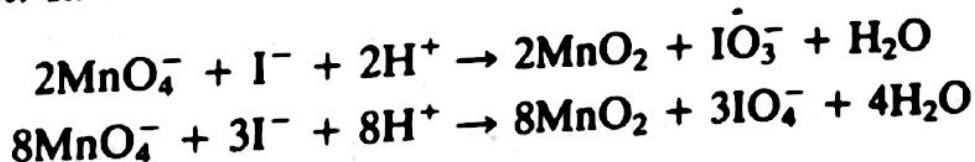


\* Disproportionates

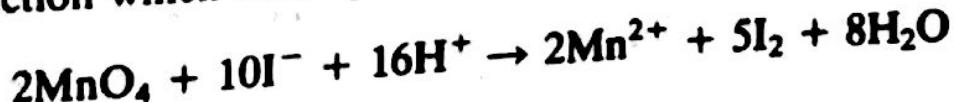
If we assume that the reactions are thermodynamically controlled, that is equilibrium is reached fairly quickly, then since  $\text{MnO}_4^{2-}$ ,  $\text{Mn}^{3+}$  and  $\text{HOI}$  disproportionate, they need not be considered. The half reaction  $\text{Mn}^{2+} \rightarrow \text{Mn}$  has a large negative  $E^\circ$  value, and hence  $\Delta G$  will have a large positive value, so this will not occur, and can be ignored. Thus the reduction potential diagrams may be simplified:



If the reaction is carried out by adding KI solution dropwise to an acidified solution of  $\text{KMnO}_4$ , the products of the reaction must be stable in the presence of  $\text{KMnO}_4$ . Thus  $\text{Mn}^{2+}$  cannot be formed, since  $\text{KMnO}_4$  would oxidize it to  $\text{MnO}_2$ . In a similar way,  $\text{I}_2$  cannot be formed, since  $\text{KMnO}_4$  would oxidize it. The fact that the half reaction potentials for  $\text{IO}_4^- \rightarrow \text{IO}_3^-$  and  $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}$  are close to the  $\text{MnO}_4^- \rightarrow \text{MnO}_2$  potential is a complication, and it is not obvious whether  $\text{IO}_3^-$ ,  $\text{IO}_4^-$  or  $\text{H}_2\text{O}_2$  will be the product. In fact  $\text{I}^-$  is oxidized to a mixture of  $\text{IO}_3^-$  and  $\text{IO}_4^-$ .



If the reaction is carried out in a different way, by adding the  $\text{KMnO}_4$  dropwise to the KI solution, then the products formed must be stable in the presence of  $\text{I}^-$ . Thus  $\text{MnO}_2$  cannot be formed, since it would oxidize  $\text{I}^-$  to  $\text{I}_2$ . Similarly,  $\text{IO}_3^-$  cannot be formed since it would oxidize any excess  $\text{I}^-$  to  $\text{I}_2$ . The reaction which takes place is



Since there is an excess of  $I^-$  ions, any  $I^2$  formed will dissolve as the triiodide ion  $I_3^-$ , but this does not affect the reaction



Note that the products formed depend on which reactant is in excess.

### THE OCCURRENCE AND ISOLATION OF THE ELEMENTS

The most abundant elements in the earth's crust (by weight) are shown in Table 6.13. It is worth noting that the first five elements comprise almost 92% by weight of the earth's crust, that the first ten make up over 99.5%, and the first twenty make up 99.97%. Thus a few elements are very abundant but most of the elements are very scarce.

**Table 6.13** The most abundant elements

	Parts per million of earth's crust	% of earth's crust
1. oxygen	455 000	45.5
2. silicon	272 000	27.2
3. aluminium	83 000	8.3
4. iron	62 000	6.2
5. calcium	46 000	4.66
6. magnesium	27 640	2.764
7. sodium	22 700	2.27
8. potassium	18 400	1.84
9. titanium	6 320	0.632
10. hydrogen	1 520	0.152
11. phosphorus	1 120	0.112
12. manganese	1 060	0.106

A full table of abundances is given in Appendix A.

Other very abundant elements are nitrogen (78% of the atmosphere) and hydrogen, which occurs as water in the oceans. The chemistry of these abundant elements is well known, but some elements which are rare are also well known, because they occur in concentrated deposits – for example, lead as PbS (galena) and boron as  $Na_2B_4O_7 \cdot 10H_2O$  (borax).

The different methods for separating and extracting elements may be divided into five classes (see Ives, D.J.G. in Further Reading).

#### Mechanical separation of elements that exist in the native form

A surprisingly large number of elements occur in the free elemental state. They have remained in the native form because they are unreactive. Only the least reactive of the metals, those of Group 11 (copper/silver/gold) and the platinum metals, occur in significant amounts as native elements.

1. Gold is found in the native form, as grains in quartz, as nuggets and in the silt of river beds. Gold has a density of  $19.3\text{ g cm}^{-3}$ , which is very

- much higher than that of the rocks or silt it is mixed with, and gold can be separated by 'panning'. (In recent times it has been more commonly extracted by amalgamating with mercury.) Silver and copper are some times found in the native form as 'nuggets'. All three metals are noble or unreactive, and this is associated with their position in the electro-chemical series below hydrogen, and with the non-metals.
2. Palladium and platinum are also found as native metals. In addition natural alloys of the Pt group are found.

The platinum metals are      Ru   Rh   Pd  
    Os   Ir   Pt

The names of these natural alloys indicate their composition: osmidium, iridosmine.

3. Liquid droplets of mercury are found associated with cinnabar  $HgS$ . Non-metals which occur as native elements in the earth's crust are from the carbon and sulphur groups, but the atmosphere comprises  $N_2$ ,  $O_2$  and the noble gases.
4. Diamonds are found in the earth, and are obtained by mechanical separation of large amounts of earth and rock. The largest deposits are in Australia, Zaire, Botswana, the USSR and South Africa. Diamonds are mostly used for making cutting tools, and some for jewellery. Graphite is mined mainly in China, South Korea, the USSR, Brazil and Mexico. It is used for making electrodes, in steel making, as a lubricant, and in pencils, brake linings and brushes for electric motors. It is also used as the moderator in the cores of gas cooled nuclear reactors.
5. Deposits of sulphur are also found deep underground in Louisiana (USA), Poland, Mexico and the USSR. These are extracted by the *Frasch process*. Small amounts of selenium and tellurium are often present in sulphur.
6. The atmosphere is made up of about 78% nitrogen, 22% oxygen and traces of the noble gases argon, helium and neon. These may be separated by fractional distillation of liquid air. Helium is also obtained from some natural gas deposits.

### Thermal decomposition methods

A few compounds will decompose into their constituent elements simply by heating.

1. A number of hydrides will decompose in this way, but since hydrides are usually made from the metal itself, the process is of no commercial significance. The hydrides arsine  $AsH_3$  and stibine  $SbH_3$  are produced in Marsh's test, where an arsenic or antimony compound is converted to the hydride with  $Zn/H_2SO_4$  and the gaseous hydrides are decomposed to give a silvery mirror of metal by passing the hydride through a heated tube.
2. Sodium azide  $NaN_3$  decomposes to give sodium and pure dinitrogen on

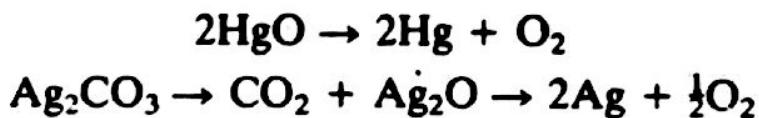
*gentle heating.* Considerable care is needed as azides are often explosive. This method is not used commercially, but it is useful for making small quantities of very pure dinitrogen in the laboratory.



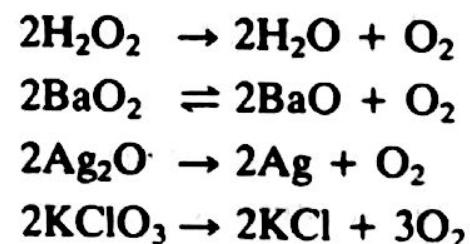
3. Nickel carbonyl  $\text{Ni}(\text{CO})_4$  is gaseous and may be produced by warming Ni with CO at  $50^\circ\text{C}$ . Any impurities in the Ni sample remain solid and the gas is heated to  $230^\circ\text{C}$ , when it decomposes to give pure metal and CO which is recycled. This was the basis of the *Mond process* for purifying nickel which was used in South Wales from 1899 until the 1960s. A new plant in Canada uses the same principle but uses  $150^\circ\text{C}$  and 20 atmospheres pressure to form  $\text{Ni}(\text{CO})_4$ .



4. The iodides are the least stable of the halides, and the *van Arkel-de Boer process* has been used to purify small quantities of zirconium and boron. The impure element is heated with iodine, producing a volatile iodide  $\text{ZrI}_4$  or  $\text{BI}_3$ . These are decomposed by passing the gas over an electrically heated filament of tungsten or tantalum which is white hot. The element is deposited on the filament and the iodine is recycled. The filament grows fatter, and is eventually removed. The tungsten core is drilled out of the centre, and a small amount of high purity Zr or B is obtained.
5. Most oxides are thermally stable at temperatures up to  $1000^\circ\text{C}$  but the metals below hydrogen in the electrochemical series decompose fairly easily. Thus  $\text{HgO}$  and  $\text{Ag}_2\text{O}$  decompose on heating. The mineral cinnabar  $\text{HgS}$  is roasted in air to give the oxide, which then decomposes on heating. Silver residues from the laboratory and photographic processing are collected as  $\text{AgCl}$  and treated with  $\text{Na}_2\text{CO}_3$ , giving  $\text{Ag}_2\text{CO}_3$ , which decomposes on heating, first to  $\text{Ag}_2\text{O}$  and then to Ag..



6. Dioxygen may be produced by heating hydrogen peroxide  $\text{H}_2\text{O}_2$ , barium peroxide  $\text{BaO}_2$ , silver oxide  $\text{Ag}_2\text{O}$  or potassium chlorate  $\text{KClO}_3$ .

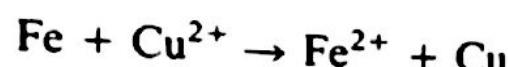


#### Displacement of one element by another

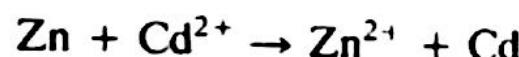
In principle any element may be displaced from solution by another element which is higher in the electrochemical series. The method is in-

applicable to elements which react with water, and to be economic must involve sacrificing a cheap element to obtain a more expensive element.

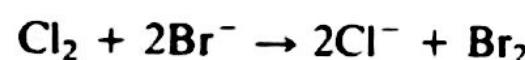
- Copper ores which are too lean in CuS for the Cu to be extracted by roasting in air are left to be weathered by air and rain to form a solution of CuSO<sub>4</sub>. The Cu<sup>2+</sup> ions are displaced as Cu metal by sacrificing scrap iron which turns into Fe<sup>2+</sup> because iron is above copper in the electrochemical series.



- Cadmium occurs in small amounts with zinc ores. The Zn is recovered by electrolysis of a solution of ZnSO<sub>4</sub> which contains traces of CdSO<sub>4</sub>. After a time the amount of Cd<sup>2+</sup> has concentrated, and since Zn is above Cd in the electrochemical series some Zn metal is sacrificed to displace the Cd<sup>2+</sup> from solution as Cd metal. The Zn which was sacrificed is subsequently recovered by electrolysis.



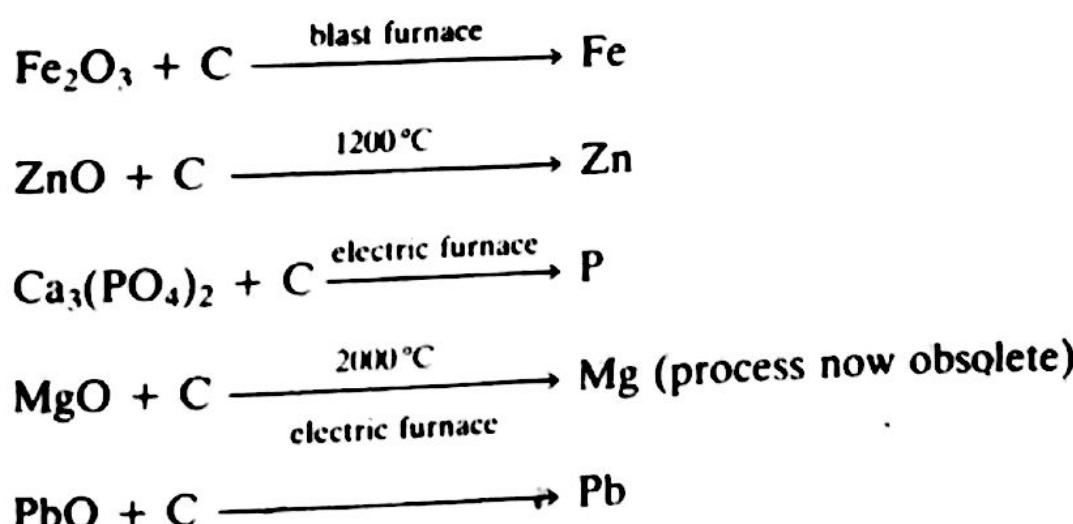
- Sea water contains Br<sup>-</sup> ions. Chlorine is above bromine in the electrochemical series, and bromine is obtained by passing chlorine into sea water.



### High temperature chemical reduction methods

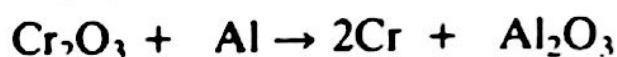
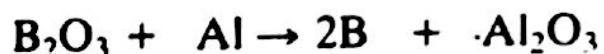
A large number of commercial processes come into this group. Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke this method is widely used. The disadvantages are that a high temperature is needed, which is expensive and necessitates the use of a blast furnace, and many metals combine with carbon, forming carbides. Some examples are:

#### *Reduction by carbon*

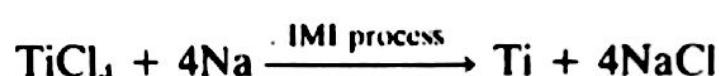
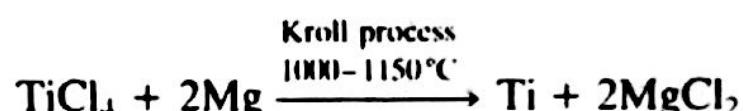


***Reduction by another metal***

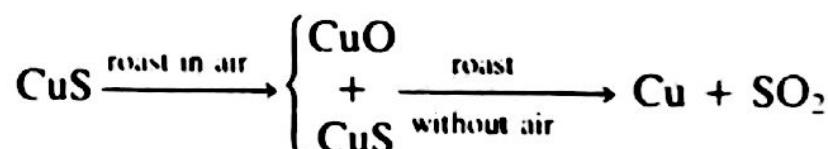
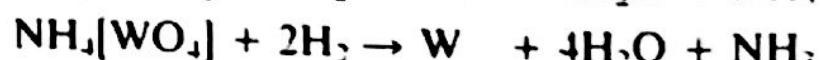
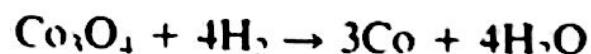
If the temperature needed for carbon to reduce an oxide is too high for economic or practical purposes, the reduction may be effected by another highly electropositive metal such as aluminium, which liberates a large amount of energy ( $1675 \text{ kJ mol}^{-1}$ ) on oxidation to  $\text{Al}_2\text{O}_3$ . This is the basis of the *Thermite process*:



Magnesium is used in a similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.

***Self-reduction***

A number of metals occur as sulphide ores (for example  $\text{PbS}$ ,  $\text{CuS}$  and  $\text{Sb}_2\text{S}_3$ ) which may be roasted first in air to partially convert them to the oxide, and then further roasted in the absence of air, causing self-reduction:

***Reduction of oxides with hydrogen***

This method is not widely used, because many metals react with hydrogen at elevated temperatures, forming hydrides. There is also a risk of explosion from hydrogen and dioxygen in the air.

***Electrolytic reduction***

The strongest possible reducing agent is an electron. Any ionic material may be electrolysed, and reduction occurs at the cathode. This is an excellent method, and gives very pure products, but electricity is expensive. Electrolysis may be performed:

*In aqueous solution*

Provided that the products do not react with water, electrolysis can be carried out conveniently and cheaply in aqueous solution. Copper and zinc are obtained by electrolysis of aqueous solutions of their sulphates.

*In other solvents*

Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water, and it is produced by electrolysis of  $\text{KHF}_2$  dissolved in anhydrous HF. (The reaction has many technical difficulties in that HF is corrosive, the hydrogen produced at the cathode must be kept separate from the fluorine produced at the anode or an explosion will occur, water must be rigorously excluded, and the fluorine produced attacks the anode and the reaction vessel.)

*In fused melts*

Elements that react with water are often extracted from fused melts of their ionic salts. These melts are frequently corrosive, and involve large fuel bills to maintain the high temperatures required. Aluminium is obtained by electrolysis of a fused mixture of  $\text{Al}_2\text{O}_3$  and cryolite  $\text{Na}_3[\text{AlF}_6]$ . Both sodium and chlorine are obtained from the electrolysis of fused  $\text{NaCl}$ : in this case up to two thirds by weight of  $\text{CaCl}_2$  is added as an impurity to lower the melting point from  $803^\circ\text{C}$  to  $505^\circ\text{C}$ .

**Factors influencing the choice of extraction process**

The type of process used commercially for any particular element depends on a number of factors.

1. Is the element unreactive enough to exist in the free state?
2. Are any of its compounds unstable to heat?
3. Does the element exist as an ionic compound, and is the element stable in water? If both are true, is there a cheap element above it in the electrochemical series which can be sacrificed to displace it from solution?
4. Does the element occur as sulphide ores which can be roasted, or oxide ores which can be reduced – using carbon is the cheapest whilst the use of Mg, Al and Na as reducing agents is more expensive.
5. If all other methods fail, electrolysis usually works for ionic materials, but is expensive. If the element is stable in water, electrolysing aqueous solutions is cheaper than using fused melts.

**Thermodynamics of reduction processes**

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition, involves a number of points which merit detailed discussion.

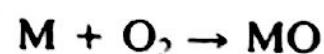
Table 6.14 Reduction potentials and extraction methods

Element	$E^\circ$ (V)	Materials	Extraction method
Lithium	$\text{Li}^+   \text{Li}$	-3.05 LiCl	Electrolysis of fused salts, usually chlorides
Potassium	$\text{K}^+   \text{K}$	-2.93 $\text{KCl}, [\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}]$	
Calcium	$\text{Ca}^{2+}   \text{Ca}$	-2.84 $\text{CaCl}_2$	
Sodium	$\text{Na}^+   \text{Na}$	-2.71 NaCl	
Magnesium	$\text{Mg}^{2+}   \text{Mg}$	-2.37 $\text{MgCl}_2, \text{MgO}$	Electrolysis of $\text{MgCl}_2$ , High temperature reduction with C
Aluminium	$\text{Al}^{3+}   \text{Al}$	-1.66 $\text{Al}_2\text{O}_3$	Electrolysis of $\text{Al}_2\text{O}_3$ dissolved in molten $\text{Na}_3[\text{AlF}_6]$
Manganese	$\text{Mn}^{2+}   \text{Mn}$	-1.08 $\text{Mn}_3\text{O}_4, \text{MnO}_2$	Reduction with Al Thermite process
Chromium	$\text{Cr}^{3+}   \text{Cr}$	-0.74 $\text{FeCr}_2\text{O}_4$	
Zinc	$\text{Zn}^{2+}   \text{Zn}$	-0.76 ZnS	Chemical reduction of oxides by C Sulphides are converted to oxides then reduced by C, or sometimes $\text{H}_2$
Iron	$\text{Fe}^{2+}   \text{Fe}$	-0.44 $\text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4$	
Cobalt	$\text{Co}^{2+}   \text{Co}$	-0.27 CoS	
Nickel	$\text{Ni}^{2+}   \text{Ni}$	-0.23 NiS, NiAs <sub>2</sub>	
Tin	$\text{Sn}^{2+}   \text{Sn}$	-0.14 SnO <sub>2</sub>	
Lead	$\text{Pb}^{2+}   \text{Pb}$	-0.13 PbS	
Copper	$\text{Cu}^{2+}   \text{Cu}$	+0.35 Cu(metal), CuS	Found as native metal, or compounds easily decomposed by heat. (Also cyanide extraction)
Silver	$\text{Ag}^+   \text{Ag}$	+0.80 Ag(metal), Ag <sub>2</sub> S, AgCl	
Mercury	$\text{Hg}^{2+}   \text{Hg}$	+0.85 HgS	
Gold	$\text{Au}^{3+}   \text{Au}$	+1.38 Au(metal)	

For a spontaneous reaction, the free energy change  $\Delta G$  must be negative.

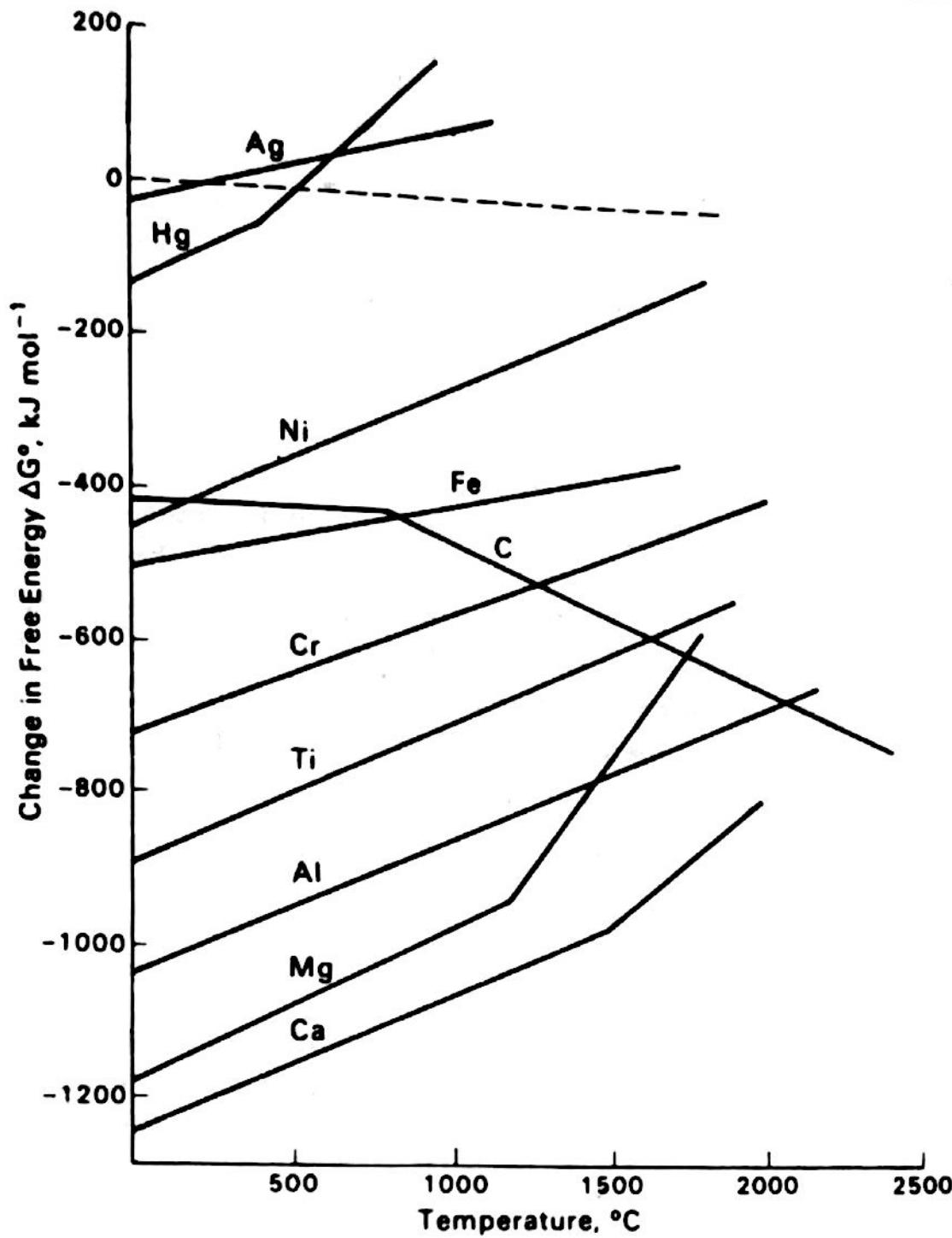
$$\Delta G = \Delta H - T\Delta S$$

$\Delta H$  is the enthalpy change during the reaction,  $T$  is the absolute temperature, and  $\Delta S$  is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:



Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently gases have a higher entropy than liquids or solids. In this reaction  $S$  the entropy or randomness decreases, and hence  $\Delta S$  is negative. Thus if the temperature is raised then  $T\Delta S$  becomes more negative. Since  $T\Delta S$  is subtracted in the equation, then  $\Delta G$  becomes less negative. *Thus the free energy change increases with an increase of temperature.*

The free energy changes that occur when one gram molecule of a



**Figure 6.5** Ellingham diagram showing the change in free energy  $\Delta G$  with temperature for oxides (based on 1 g mol of dioxygen in each case).

common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals to their oxides. This graph is shown in Figure 6.5 and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

The Ellingham diagram for oxides shows several important features:

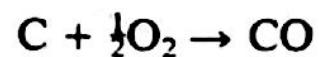
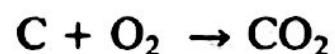
1. The graphs for metal to metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.
2. The free energy changes all follow a straight line unless the materials melt or vaporize, when there is a large change in entropy associated with the change of state, which changes the slope of the line (for example the Hg–HgO line changes slope at  $356^\circ\text{C}$  when Hg boils, and similarly Mg–MgO changes at  $1120^\circ\text{C}$ ).

3. When the temperature is raised, a point will be reached where the graph crosses the  $\Delta G = 0$  line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen.

Theoretically all oxides can be decomposed to give the metal and dioxygen if a sufficiently high temperature can be attained. In practice the oxides of Ag, Au and Hg are the only oxides which can be decomposed at temperatures which are easily attainable, and these metals can therefore be extracted by thermal decomposition of their oxides.

4. In a number of processes, one metal is used to reduce the oxide of another metal. Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the difference between the two graphs at that particular temperature. Thus Al reduces FeO, CrO and NiO in the well known Thermite reaction, but Al will not reduce MgO at temperatures below 1500°C.

In the case of carbon reacting with dioxygen, two reactions are possible:



In the first reaction, the volume of  $CO_2$  produced is the same as the volume of  $O_2$  used, so the change in entropy is very small, and  $\Delta G$  hardly changes with temperature. Thus the graph of  $\Delta G$  against  $T$  is almost horizontal.

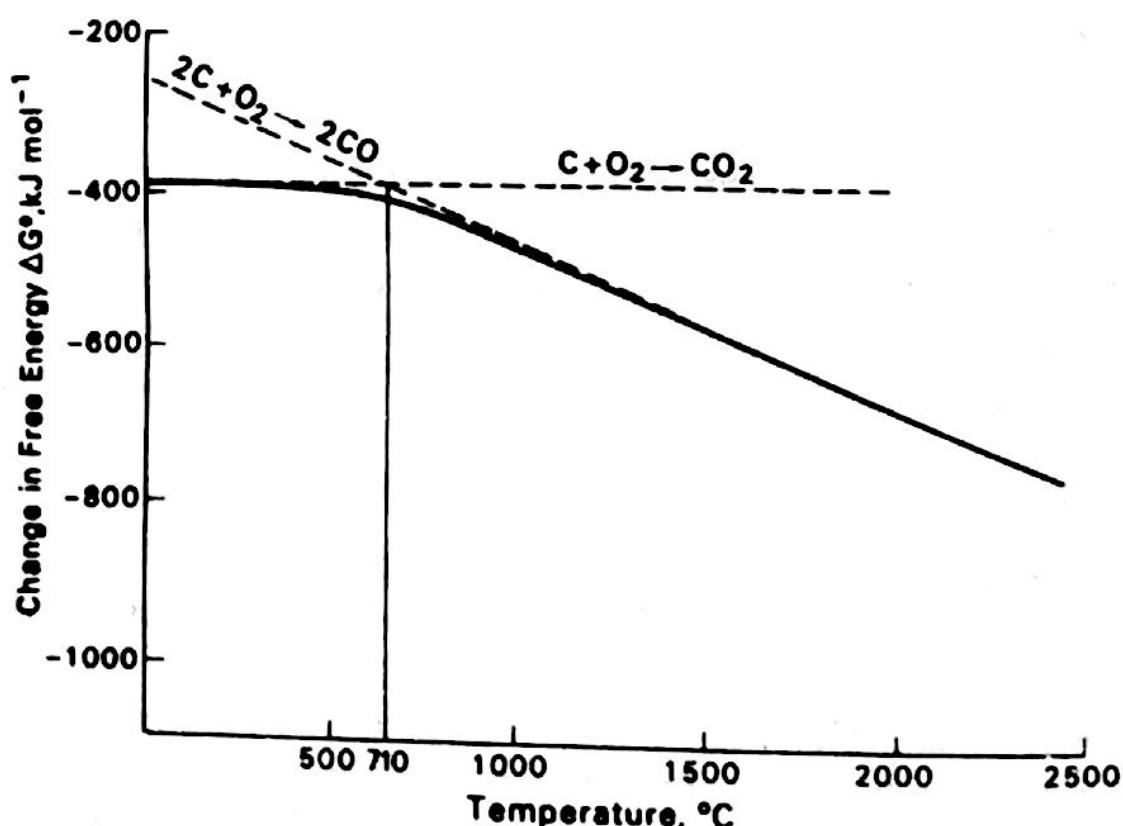
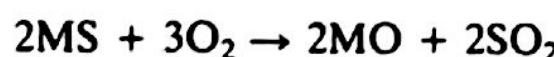


Figure 6.6 Ellingham diagram for carbon. (The composite curve is the solid line.)

The second reaction produces two volumes of CO for every one volume of dioxygen used. Thus  $\Delta S$  is positive, and hence  $\Delta G$  becomes increasingly negative as  $T$  increases. Consequently the line on the Ellingham diagram slopes downwards (Figure 6.6). The two lines for  $C \rightarrow CO_2$  and  $C \rightarrow CO$  cross at about  $710^\circ C$ . Below this temperature the reaction to form  $CO_2$  is energetically more favourable, but above  $710^\circ C$  the formation of CO is preferred.

Carbon is extensively used to reduce iron oxide in the extraction of iron, but it may also be used to reduce any other of the oxides above it on the Ellingham diagram. Since the  $\Delta G$  line slopes downwards it will eventually cross and lie below all the other graphs for metal/metal oxide. Thus in principle carbon could be used to reduce any metal oxide if a sufficiently high temperature were used. At one time  $MgO$  was reduced by C at  $2000^\circ C$ , followed by shock (i.e. rapid) cooling, though this process is now obsolete. Similarly the reduction of very stable oxides like  $TiO_2$ ,  $Al_2O_3$  and  $MgO$  is theoretically possible, but is not attempted because of the high cost and practical difficulties of using extremely high temperatures. A further limitation on the use of carbon for extracting metals is that at high temperatures many metals react with carbon, forming carbides.

Many metals occur as sulphide ores. Though carbon is a good reducing agent for oxides, it is a poor reducing agent for sulphides. The reason why carbon reduces so many oxides at elevated temperatures is that the  $\Delta G^\circ/T$  line for CO has a negative slope. There is no compound CS analogous to CO with a steep negative  $\Delta G^\circ/T$  line. Thus sulphides are normally roasted in air to form oxides before reducing with carbon.



In a similar way hydrogen is of limited use as a reducing agent for extracting metals from their oxides since the  $\Delta G^\circ/T$  line has a positive slope, and runs parallel to many metal oxide lines.



Thus only those metals with metal  $\rightarrow$  metal oxide lines above the hydrogen line will be reduced, and this does not change with temperature. A further problem with  $H_2$  is that many metals react with hydrogen, forming hydrides, and if hydrogen remains dissolved in the metal (interstitial hydrides) it significantly affects the properties of the metal.

Thermodynamic arguments about what will reduce a given compound have two limitations. They assume that the reactants and products are in equilibrium, which is often untrue, and they indicate whether a reaction is possible but do not predict the rate of reaction, or if some alternative reaction is even more favourable.

Further details of extraction processes and Ellingham diagrams for halides and sulphides are given in Further Reading (see Ives D.J.G., and Ellingham, H.J.T.).

**Table 6.15 Extraction methods and the periodic table**

	s-block												p-block					
Group \ Period	1	2											13	14	15	16	17	18
1															Fractional distillation of liquid air			
	<sup>1</sup> H												<sup>3</sup> He	<sup>4</sup> He				
2	<sup>3</sup> Li	<sup>4</sup> Be	d-block										<sup>5</sup> B	<sup>6</sup> C	<sup>7</sup> N	<sup>8</sup> S	<sup>9</sup> F	<sup>10</sup> Ne
3	<sup>11</sup> Na	<sup>12</sup> Mg	3	4	5	6	7	8	9	10	11	12	<sup>13</sup> Al	<sup>14</sup> Si	<sup>15</sup> P	<sup>16</sup> S	<sup>17</sup> Cl	<sup>18</sup> Ar
4	<sup>19</sup> K	<sup>20</sup> Ca	<sup>21</sup> Sc	<sup>22</sup> Tl	<sup>23</sup> V	<sup>24</sup> Cr	<sup>25</sup> Mn	<sup>26</sup> Fe	<sup>27</sup> Co	<sup>28</sup> Ni	<sup>29</sup> Cu	<sup>30</sup> Zn	<sup>31</sup> Ga	<sup>32</sup> Ge	<sup>33</sup> As	<sup>34</sup> Se	<sup>35</sup> Br	<sup>36</sup> Kr
5	<sup>37</sup> Rb	<sup>38</sup> Sr	<sup>39</sup> Y	<sup>40</sup> Zr	<sup>41</sup> Nb	<sup>42</sup> Mo	<sup>43</sup> Tc	<sup>44</sup> Ru	<sup>45</sup> Rh	<sup>46</sup> Pd	<sup>47</sup> Ag	<sup>48</sup> Cd	<sup>49</sup> In	<sup>50</sup> Sn	<sup>51</sup> Sb	<sup>52</sup> Te	<sup>53</sup> I	<sup>54</sup> Xe
6	<sup>55</sup> Cs	<sup>56</sup> Ba	<sup>57</sup> La	<sup>72</sup> Hf	<sup>73</sup> Ta	<sup>74</sup> W	<sup>75</sup> Re	<sup>76</sup> Os	<sup>77</sup> Ir	<sup>78</sup> Pt	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> Tl	<sup>82</sup> Pb	<sup>83</sup> Bi			
	Electrolysis of fused salts (often chlorides)			Electrolysis or chemical reduction			Found free in nature or compounds easily decomposed by heat											
	Oxides reduced by carbon or sulphides converted to oxides then reduced by carbon																	

**Notes**

1. Al, F and Cl are obtained by electrolysis of solutions
2. Br is obtained by displacement
3. I is obtained by reduction
4. Tc does not occur in nature

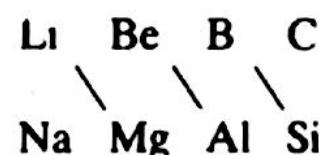
## HORIZONTAL, VERTICAL AND DIAGONAL RELATIONSHIPS IN THE PERIODIC TABLE

On moving across a period in the periodic table, the number of electrons in the outer shell increases from one to eight. Thus Group 1 elements all have one electron in their outer shell. When they react they are univalent, because the loss of one electron leaves a noble gas structure. Similarly Group 2 elements have two electrons in their outer shell and are divalent. The valency of an *s*-block element is the group number. For *p*-block elements, the valency is normally (the group number - 10) or (18 - the group number). This is the same as the number of *s* and *p* electrons in the outer shell, or (8 - this number of electrons). Group 15 elements (e.g. nitrogen) have five outer electrons. If three of these are shared in covalent bonds with other atoms, the nitrogen atom has a share in eight electrons and has a stable configuration. Thus nitrogen is trivalent, for example in ammonia NH<sub>3</sub>. The halogens are in Group 17 and have seven outer electrons. The valency should be 18 - 17 = 1. A stable structure is attained by gaining one electron either by forming an ionic or a covalent bond. The number of outer electrons thus determines the valency of the element.

On moving from left to right across a period, the size of the atoms decreases because of the additional nuclear charge. Thus the orbital electrons are more tightly held, and the ionization energy increases. The metallic character of the element also decreases, and the oxides of the elements become less basic. Thus Na<sub>2</sub>O is strongly basic; Al<sub>2</sub>O<sub>3</sub> is amphoteric and reacts with both acids and bases; SO<sub>2</sub> is an acidic oxide since it dissolves in water to form sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) and reacts with bases to form sulphites. Generally, metallic oxides are basic, whilst non-metallic oxides are acidic.

On descending a group in the periodic table, the elements all have the same number of outer electrons and the same valency, but the size increases. Thus the ionization energy decreases and the metallic character increases. This is particularly apparent in Groups 14 and 15, which begin with the non-metals carbon and nitrogen and end with the metals lead and bismuth. The oxides become increasingly basic on descending the group.

On moving diagonally across the periodic table the elements show certain similarities. These are usually weaker than the similarities within a group, but are quite pronounced in the following pairs of elements:



On moving across a period, the charge on the ions increases and the size decreases, causing the polarizing power to increase. On moving down a group, the size increases and the polarizing power decreases. On moving diagonally these two effects partly cancel each other, so that there is no marked change in properties. The type and strength of bond formed and

the properties of the compounds are often similar, although the valency is different. Thus lithium is similar to magnesium in many of its properties and beryllium is similar to aluminium. These similarities are examined in more detail in the chapters on Groups 1, 2 and 13. Diagonal similarities are most important among the lighter elements, but the line separating the metals from the non-metals also runs diagonally.

### FURTHER READING

#### Size, ionization energy, electron affinity, energetics and Born–Haber cycle, electronegativity

- Allred, A.L. and Rochow, E.G. (1958) *J. Inorg. Nucl. Chem.*, **5**, 264. (Original paper on Allred and Rochow scale of electronegativity values.)  
 Allred, A.L. (1961) *J. Inorg. Nucl. Chem.*, **17**, 215. (More on electronegativity values.)  
 Ashcroft, S.J. and Beech, G. (1973) *Inorganic Thermodynamics*. Van Nostrand.  
 Bratsch, S.G. (1988) Revised Mulliken electronegativities, *J. Chem. Ed.*, Part I: **65**, 34–41; Part II: **65**, 223–226.  
 Blustin, P.H. and Raynes, W.T. (1981) An electronegativity scale based on geometry changes on ionization, *J. Chem. Soc. (Dalton)*, 1237.  
 Emeléus, H.J. and Sharpe A.G. (1973) *Modern Aspects of Inorganic Chemistry*, 4th ed., (Chapter 5: Structures and energetics of inorganic molecules; Chapter 6: Inorganic chemistry in aqueous media). Routledge and Kegan Paul, London.  
 Huheey, J.E. (1972) *Inorganic Chemistry*, Harper and Row, New York. (Discussion on electronegativity.)  
 Lieberman, J.F. (1973) Ionization enthalpies and electron attachment enthalpies, *J. Chem. Ed.*, **50**, 831.  
 Mulliken, R.S. (1934, 1935) *J. Chem. Phys.*, **2**, 782; **3**, 573. (Mulliken electronegativity scale.)  
 Pauling, L. (1960) *The Nature of the Chemical Bond*, 3rd ed., Oxford University Press, London. (An old but classic text.)  
 Sanderson, R.T. (1945) A scale of electronegativity, *J. Chem. Ed.*, **31**, 2. (Original paper on Sanderson electronegativity scale.)  
 Sanderson, R.T. (1986) The Inert Pair Effect and Electronegativity, *Inorganic Chemistry*, **25**, 1856–1858.  
 Sanderson, R.T. (1988) Principles of electronegativity, *J. Chem. Ed.*, Part I: **65**, 112–118; Part II: **65**, 227–231.  
 Shannon, R.D. (1976) Revised effective ionic radii, *Acta Cryst.*, **A32**, 751–767. (The most recent and widely accepted values for ionic radii.)  
 Sharpe, A.G. (1981) *Inorganic Chemistry* (Chapter 3: Electronic configurations and some physical properties of atoms.), Longmans, London.  
 Zhang, Y. (1982) Electronegativities of elements in valence states, *Inorganic Chemistry*, **21**, 3886–3889.

#### Standard electrode potentials, redox reactions

- Baes, C.F. and Mesmer, R.E. (1976) *The Hydrolysis of Cations*. Wiley-Interscience, London, 1976. (Comprehensive but understandable.)  
 Bard, A.J., Parsons, R. and Jordan, J. (1985) *Standard Potentials in Aqueous Solution* (Monographs in Electroanalytical Chemistry and Electrochemistry Series, Vol. 6), Marcel Dekker, New York. (Commissioned by IUPAC to replace the earlier values in Latimer's book.)  
 Burgess, J. (1988) *Ions in Solution*, Ellis Horwood, Chichester.  
 Fromhold, A.T., Jr (1980) *Theory of Metal Oxidation*, North Holland Publishing Co., Amsterdam and Oxford.

- Jolly, W.L. (1976) *Inorganic Chemistry*. McGraw Hill, New York. (Redox reactions, and aqueous solutions.)
- Johnson, D.A. (1968) *Some Thermodynamic Aspects of Inorganic Chemistry*. Cambridge University Press, Cambridge. (Lattice energies etc.)
- Latimer, W.M. (1952) *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2nd ed., Prentice Hall, New York. (Old, but until very recently the standard source of oxidation potential data.)
- Rosotti, H. (1978) *The Study of Ionic Equilibria in Aqueous Solution*, Longmans, London. (Redox reactions, solubility.)
- Sanderson, R.T. (1966) The significance of electrode potentials, *J. Chem. Ed.*, 43, 584–586.
- Sharpe, A.G. (1969) *Principles of Oxidation and Reduction* (Royal Institute of Chemistry Monographs for Teachers No. 2), London.
- Sharpe, A.G. (1981) *Inorganic Chemistry*, (Chapter 7: Inorganic chemistry in aqueous media), Longmans, London.
- Vincent, A. (1985) *Oxidation and Reduction in Inorganic and Analytical Chemistry: A Programmed Introduction*, John Wiley, Chichester.

### Abundance and extraction of the elements

- Cox, P.A. (1989) *The Elements: Their origins, Abundance and Distribution*, Oxford University Press, Oxford.
- Ellingham, H.J.T. (1944, 1948) *J. Soc. Chem. Ind. Lond.*, 63, 125; *Disc. Faraday Soc.*, 4, 126, 161. (Original paper on Ellingham diagrams.)
- Fergusson, J.E. (1982) *Inorganic Chemistry and the Earth: Chemical Resources, Their Extraction, Use and Environmental Impact* (Pergamon Series on Environmental Science, Vol. 6), Pergamon Press, Oxford.
- Ives, D.J.G. (1969) *Principles of the Extraction of Metals* (Royal Institute of Chemistry Monographs for Teachers No. 3), London.
- Jeffes, J.H.E. (1969) Extraction Metallurgy, *Chemistry in Britain*, 5, 189–192.

### PROBLEMS

1. (a) How does the size of atoms vary from left to right in a period, and on descending a group in the periodic table? What are the reasons for these changes?  
 (b) Can you explain the large atomic radii of the noble gases?  
 (c) Why is the decrease in size between Li and Be much greater than that between Na and Mg or K and Ca?
2. Explain what is meant by the ionization energy of an element. How does this vary between hydrogen and neon in the periodic table? Discuss how the variation can be related to the electronic structure of the atoms.
3. (a) What is the correlation between atomic size and ionization energy?  
 (b) Account for the fact that there is a decrease in first ionization energy from Be to B, and Mg to Al.  
 (c) Suggest the reason for the decrease in first ionization energy from N to O, and P to S.  
 (d) Explain why the substantial decrease in first ionization energy

- observed between Na and K, and Mg and Ca, is not observed between Al and Ga.
- (e) What is the significance of the large increase in the third ionization energy of Ca and the fifth ionization energy of Si?
  - (f) Why is the first ionization energy of the transition elements reasonably constant?
  4. (a) What is electronegativity, and how is it related to the type of bond formed?  
 (b) What are Fajans' rules?  
 (c) Predict the type of bonds formed in HCl, CsCl, NH<sub>3</sub>, CS<sub>2</sub> and GeBr<sub>4</sub>.
  5. (a) List the different scales of electronegativity and briefly describe the theoretical basis behind each.  
 (b) Give four examples to show how electronegativity values may be used to predict the type of bond formed in a compound.
  6. Use a modified Born–Haber cycle suitable for the estimation of electrode potentials to explain:  
 (a) Why Li is as strong a reducing agent as Cs  
 (b) Why Ag is a noble metal and K a highly reactive metal.
  7. (a) What are the standard electrode potentials, and how are they related to the electrochemical series?  
 (b) Explain the recovery of copper from solution using scrap iron.  
 (c) How is it possible to preferentially deposit metals electrolytically, e.g. Cu, Ni, and Zn from a solution containing all three?  
 (d) Why is it possible to obtain zinc by electrolysis of an aqueous solution even though the electrode potentials would suggest that the water should decompose first?
  8. (a) Explain why Cu<sup>+</sup> disproportionates in solution.  
 (b) Explain why the standard reduction potentials for Cu<sup>2+</sup> → Cu<sup>+</sup> and Cu<sup>+</sup> → Cu are +0.15 and +0.50 volt, respectively, yet that for Cu<sup>2+</sup> → Cu is + 0.34 volt.
  9. Name the eight most abundant elements in the earth's crust and place them in the correct order.
  10. Describe the following named metallurgical processes: (a) Bessemer, (b) BOP, (c) Kroll, (d) Van Arkel, (e) Hall-Héroult, (f) Parkes.
  11. Which elements occur in the native state?
  12. List five ores which are smelted, and give equations to show what occurs during smelting.
  13. Describe the extraction of three different elements using carbon as the reducing agent.
  14. Draw an Ellingham diagram for metal oxides and explain what information can be obtained from it. In addition explain why most of

the lines slope upwards from left to right, why the lines change in slope, and what happens when a line crosses the  $\Delta G = 0$  axis..

15. Use the Ellingham diagram for oxides to find:
  - (a) if Al will reduce chromium oxide
  - (b) at what temperature C will reduce magnesium oxide, and
  - (c) at what temperature mercuric oxide will decompose into its elements.
16. Explain in detail the processes involved in the production of pig iron and steel.
17. Describe the extraction of two metals and two non-metals by electrolysis.
18. Describe the extraction of magnesium and bromine from sea water.