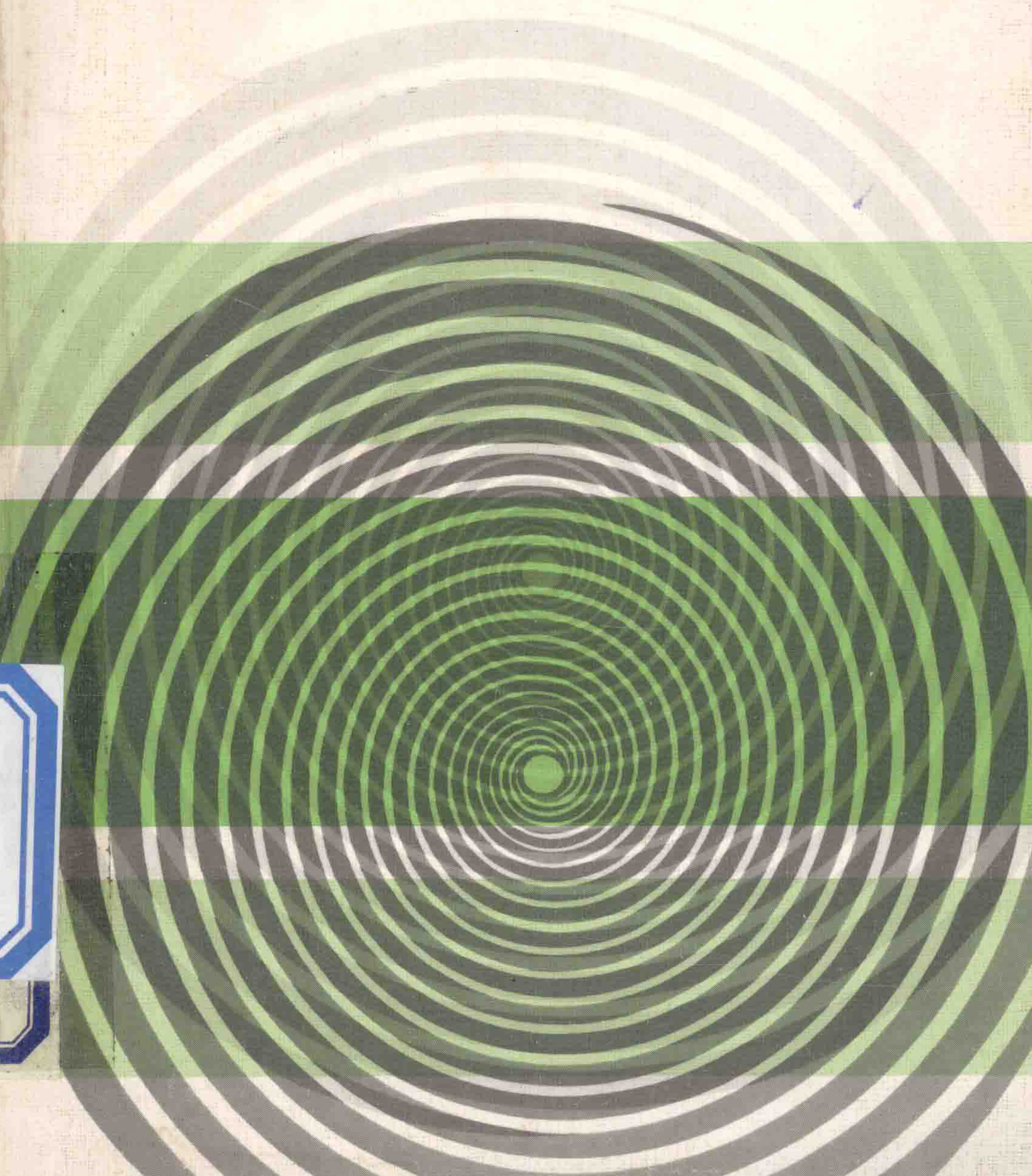
ESSENTIAL IDEAS IN INORGANIC CHEMISTRY

D.E.Wilson



ESSENTIAL IDEAS IN INORGANIC CHEMISTRY

D. E. WILSON, M.A., Ph.D.
Deputy Head, Maidstone Grammar School
Formerly Head of Chemistry, Manchester Grammar School

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ESSENTIAL IDEAS IN INORGANIC CHEMISTRY

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ESSENTIAL IDEAS IN ORGANIC CHEMISTRY
ESSENTIAL IDEAS IN PHYSICAL CHEMISTRY

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Contents

Preface v
1 Introduction 1
2 The periodic table 7
3 The s-block elements 21
4 Aluminium and related elements 35
5 Group IV: carbon, silicon, germanium, tin, lead 46
6 Group V: nitrogen, phosphorus, arsenic, antimony, bismuth 62
7 Oxygen and sulphur 80
8 The halogens 94
9 The noble gases 107
10 Hydrogen 111
11 The transition metals 126
12 Aqueous ionic equilibria 151
Index 165
Electronic configurations of the elements 168
Periodic table 170

1

Introduction

1.1 THE SCOPE AND ARRANGEMENT OF THIS BOOK

This book is concerned with inorganic chemistry, that is, the study of the individual properties of elements and compounds, other than those containing both carbon and hydrogen. Because of the multiplicity of carbon–hydrogen compounds, their properties are best considered as a separate division of chemistry, called organic chemistry. The other major division, physical chemistry, is concerned with the more general properties common to all elements and compounds.

> Inorganic chemistry would be concerned with the properties of such compounds as NaOH, $CaCl_2$, SO_2 and CO_2.
> Organic chemistry would be concerned with the properties of such compounds as CH_3Cl, H_2CO, C_3H_8 and C_2H_6O.
> Physical chemistry would be concerned with the boiling points, solubilities or bonding of any of the above compounds.

These divisions should not be regarded as watertight boundaries.

The aim of this book is to present inorganic chemistry in terms of the physical principles by which the properties of inorganic compounds are classified and predicted. Each chapter is concerned with trends, classification, and reasons for them; these might be likened to the bone and sinew of a body. The flesh and outward appearance, in this analogy, are the facts and individual peculiarities of each reaction. Although less emphasis is placed on these, detailed summary tables appear at the end of each appropriate chapter. In most cases, one chapter covers the elements of one group of the periodic table.

As a result of this approach, a number of topics regarded as part of physical chemistry are referred to continually in the text and are used as unifying themes. For a full treatment of these you should consult a physical chemistry textbook. The following summary outlines the topics and the depth to which each is referred.

(1) *Electronic structure and bonding:* the nature of electrons, the structure of the atom including s, p and d as terms to describe energy levels, ionic, covalent and co-ordinate bonding, dipole and hydrogen-bond interaction.

(2) *Thermodynamic cycles:* the use of Hess' Law, the use of the Born–Haber cycle including the meaning of the terms in it, the meaning and use of bond enthalpies, the significance and limitation of enthalpy change as a guide to reaction.

(3) *Redox potentials:* the signficance and limitation of redox potential as a guide to reactions.

(4) *Acid–base theory:* interpretation of acid–base reactions in terms of proton transfer, the nature of $H^+(aq)$ water, as a source of H^+ or OH^- ion, pK_a as a method of comparing acid strength. A fifth unifying principle, the periodic classification, is dealt with at length in chapter 2.

Where industrial chemistry is described, some comment is made about the economic factors involved. Remember that the chemical industry operates in order to make profits, and not to illustrate the finer points of chemistry on the tonnage scale. The reactions and purifications needed to make a particular product are often chosen differently in industry and in the laboratory. The differences are best studied by means of some of the excellent case studies now available.

The case study approach is also recommended for a study of pollution. Problems of pollution are often simply solved by the application of technology (e.g. the removal of sulphur dioxide from flue gases by an alkali wash) but invariably add to the cost of the product or activity. The really difficult problem is economic: what are you prepared to pay or do to have the nuisance removed?

1.2 THE NAMES OF INORGANIC COMPOUNDS

In most cases, the oxidation state of the central element is used to name a compound. The oxidation state is a measure of the degree of oxidation of an element, since it shows how many electrons have been added to or removed from it. To find the oxidation state of an atom in a molecule or ion, it is assumed (quite fictitiously!) that the molecule is ionic. The most electropositive elements (H, alkali metals) or most electronegative elements (O, F, Cl, etc.) are given the charge that they would normally carry. The atom under examination is then given the charge necessary to account for the actual charge on the molecule (zero) or ion. Roman numerals are used to indicate oxidation states, to prevent confusion with real charge.

The following examples show how this works in practice:

(i) CrO_3	Take O as O^{2-}; $3O^{2-}$ make a total of 6−. Net charge on molecule is zero. Therefore the oxidation state of chromium must be 6+, written Cr^{VI}.
(ii) HIO_4	Take H as H^+ and O as O^{2-}. One H^+ and $4O^{2-}$ make a total of 7−. Net charge on molecule is zero. Therefore the oxidation state of iodine must be 7+, written I^{VII}.

(iii) $CuCl_4^{2-}$ Take Cl as Cl^-; $4Cl^-$ make a total of 4−.
Net charge on ion is 2−.
Therefore the oxidation state of copper must be 2+, written Cu^{II}.

(iv) VO_2^+ Take O as O^{2-}; $2O^{2-}$ make a total of 4−.
Net charge on ion is 1+.
Therefore the oxidation state of vanadium is 5+, written V^V.

(v) NH_2OH Take H as H^+ and O as O^{2-}.
$3H^+$ and one O^{2-} make 1+.
Net charge on molecule is zero.
Therefore the oxidation state of nitrogen is 1−, written N^{-I}.

The oxidation state may be positive, negative, or zero as is the case for any uncombined element.

Since oxidation corresponds to losing electrons, i.e. gaining positive charge, an increase in oxidation state corresponds to oxidation. Conversely, a decrease in oxidation state corresponds to reduction.

The rules for naming compounds are as follows:

(a) *Substances which exist as individual covalent molecules.* Oxidation states are not used. 'Di', 'tri', 'tetra', 'penta' and 'hexa' are used to show 2, 3, 4, 5 and 6 substituents on an atom.

$SiCl_4$	silicon tetrachloride
SF_6	sulphur hexafluoride
NO	nitrogen oxide
NO_2	nitrogen dioxide

(b) *Substances which exist as giant lattices, whether covalent or ionic.* The oxidation state is written in brackets after the appropriate element

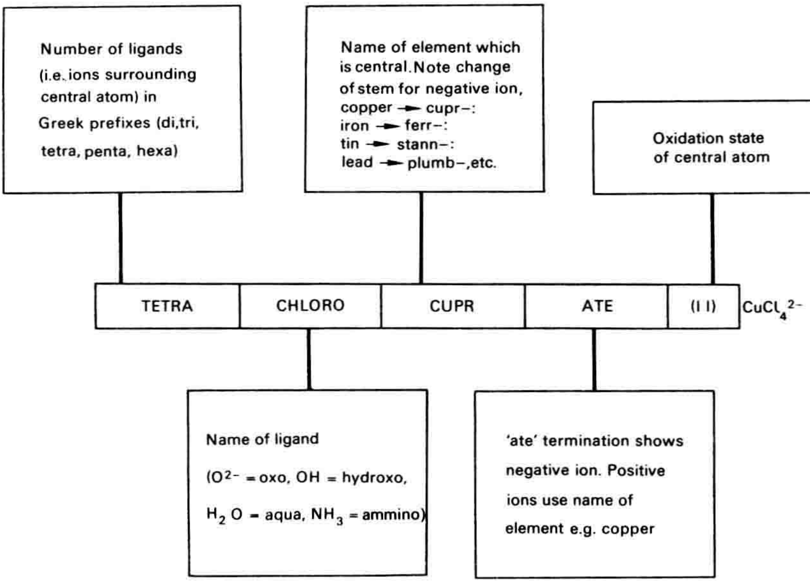
CrO_3	chromium(VI) oxide
SiO_2	silicon(IV) oxide

(c) *Substances which contain ions.* The name of the ion is built up sequentially. The name of the other ion present is then added, e.g. K_2CuCl_4, potassium tetrachlorocuprate(II). Here are some other examples

$Cu(H_2O)_6^{2+}\ SO_4^{2-}$	hexaquacopper(II) sulphate(VI)
HIO_4	iodic(VII) acid
$K_4Fe(CN)_6$	potassium hexacyanoferrate(II) (note II for oxidation state, not IV for 4−)

The definition of oxidation as loss of electrons can be applied easily if the oxidation state is known. For example:

$Zn(0) \longrightarrow Zn(II)Cl_2$: zinc goes from 'Zn^0' to 'Zn^{2+}' losing 2 electrons: oxidised
$H_2S(-II) \longrightarrow S(0)$: sulphur goes from 'S^{2-}' to 'S^0' losing 2 electrons: oxidised


Number of ligands (i.e. ions surrounding central atom) in Greek prefixes (di,tri, tetra, penta, hexa)
Name of element which is central. Note change of stem for negative ion, copper → cupr–: iron → ferr–: tin → stann–: lead → plumb–,etc.
Oxidation state of central atom
TETRA
CHLORO
CUPR
ATE
(I I)
CuCl4 2−
Name of ligand (O2− = oxo, OH = hydroxo, H2O = aqua, NH3 = ammino)
'ate' termination shows negative ion. Positive ions use name of element e.g. copper

More complex examples:

$MnO_4^- \longrightarrow MnO_2$: manganese goes from '$Mn^{7+}$' to '$Mn^{4+}$' gaining 3 electrons: reduced

$NO_3^- \longrightarrow NH_3$: nitrogen goes from 'N^{5+}' to 'N^{3-}' gaining 8 electrons: reduced

1.3 BALANCING EQUATIONS

Since electrons are never freed in chemical reactions, but transferred entirely from reductant to oxidant, the stoichiometry of redox reactions can be calculated instantly. Taking an example from above, manganate(VII) can be used to oxidise hydrogen sulphide.

If MnO_4^- gains 3 electrons in becoming MnO_2
and H_2S loses 2 electrons in becoming S

then, without further ado, $2MnO_4^-$ reacts with $3H_2S$ (written $2MnO_4^- \equiv 3H_2S$). This corresponds to a transfer of a total of six electrons. To take another example, nitrate(V) can be reduced to ammonia by aluminium powder:

$NO_3^- \longrightarrow NH_3$; oxidation state change $+V \longrightarrow -III = -8$
$Al \longrightarrow Al(OH)_6^{3-}$; oxidation state change $0 \longrightarrow +III = +3$

therefore 8 Al reacts with $3NO_3^-$ (written $8\,Al \equiv 3NO_3^-$). This corresponds to a transfer of twenty-four electrons.

This technique only balances reactions: it does not tell you the conditions for a particular reaction (e.g. nitrate(V) and aluminium need to be in sodium hydroxide solution). Nor does the technique tell you what product is formed (e.g. manganate(VII) is only reduced to manganese(IV) oxide in neutral solution but in acid solution $Mn(H_2O)_6^{2+}$ is formed).

For many purposes the above equivalence is sufficient. In other cases a full balanced equation is necessary. Sometimes this may be achieved by inspection:

$$H_2S^{-II} \longrightarrow S^0 \text{ and } S^{IV}O_2 \longrightarrow S^0$$
$$\therefore 2H_2S \equiv SO_2 \text{ or } 2\,H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

More often, and especially for reactions in aqueous solution, 'half-equations' have to be built up. The following example shows how this can be done. Manganate(VII) ions can be reduced to hydrated manganese(II) ions in acid solution by iron(II) ions.

(1) Establish the change in oxidation state.	$MnO_4^-(VII) \longrightarrow Mn^{2+}(II)$
(2) Enter in the number of electrons.	$MnO_4^- + 5e^- \longrightarrow Mn^{2+}$
(3) If in acid, add enough protons to balance change (in alkali, hydroxide ions must be used).	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$
(4) The half equation will now balance if the appropriate number of molecules of water are entered.	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$
The other half equation is simpler:	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
(5) Add 5 times the second half equation to the first, so that the number of electrons transferred in each equation is the same.	$MnO_4^- + 8H^+ + 5e^- + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+} + 5e^-$
(6) Cancelling the electrons gives a balanced equation.	$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

If potassium manganate(VII), sulphuric(VI) acid, and iron(II) sulphate(VI) are used, the full equation can now be written following the pattern of the last equation

$$KMnO_4 + 4H_2SO_4 + 5FeSO_4 \longrightarrow MnSO_4 + 4H_2O + \tfrac{5}{2}Fe_2(SO_4)_3 + \tfrac{1}{2}K_2SO_4$$

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Here is another example. Potassium dichromate(VI) in dilute acid oxidises hydrogen sulphide to sulphur.

(i) $Cr_2O_7^{2-}(VI) \longrightarrow 2Cr^{3+}(III)$ $\quad$ $H_2S(-II) \longrightarrow S(0)$

(ii) $Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+}$ $\quad$ $H_2S \longrightarrow S + 2e^-$

(Note: $2 \times 3e^-$ required since 2 moles of Cr change by 3 oxidation states)

(iii) $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+}$ $\quad$ $H_2S \longrightarrow S + 2e^- + 2H^+$

(iv) $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$ $\quad$ $H_2S \longrightarrow S + 2e^- + 2H^+$

(v) $Cr_2O_7^{2-} + 14H^+ + 6e^- + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S + 6e^- + 6H^+$

(vi) $Cr_2O_7^{2-} + 14H^+ + 3H_2S \longrightarrow 7H_2O + 3S + 6H^+$

2

The Periodic Table

2.1 INTRODUCTION

The atomic number of an element is the number of protons in the nucleus. If elements are arranged in order of increasing atomic number, it is found that elements having similar properties recur at regular intervals, at first every eighth element, then every eighteenth, and finally every thirty-second. For example

${}_{3}\mathrm{Li}$ — ${}_{11}\mathrm{Na}$ — ${}_{19}\mathrm{K}$ — ${}_{37}\mathrm{Rb}$ — ${}_{55}\mathrm{Cr}$
or ${}_{4}\mathrm{Be}$ — ${}_{12}\mathrm{Mg}$ — ${}_{20}\mathrm{Ca}$ — ${}_{38}\mathrm{Sr}$ — ${}_{56}\mathrm{Ba}$
or ${}_{9}\mathrm{F}$ — ${}_{17}\mathrm{Cl}$ — ${}_{35}\mathrm{Br}$ — ${}_{53}\mathrm{I}$

This recurrence of properties is now built into the familiar periodic table (endpapers) and seems such an obvious way to classify the elements that it is perhaps worth recalling the difficulties of Mendeleyev, who first proposed the scheme.

The information that he had to work with was:

(1) a knowledge of the properties of a number of elements—but this was incomplete. Germanium and gallium were two elements of relatively low atomic mass still to be discovered.

(2) a knowledge of the atomic masses of these elements—but several of these were wrong. Some were wrong because a wrong valency had been assumed for the element, as in the case of beryllium. Beryllium was known to form an oxide containing 36 per cent beryllium and thought to be $\mathrm{Be_2O_3}$. This is consistent with a relative atomic mass of 13.5 $\left(\dfrac{(2 \times 13.5)}{(2 \times 13.5) + (3 \times 16)} \times 100 = 36\right)$; in fact the formula is BeO and the atomic mass is 9. If the former mass applied, beryllium would be placed between carbon and nitrogen; if the latter, then it would be placed between lithium and boron. Other atomic masses were wrong because of analytical difficulties, e.g. osmium was thought to have an atomic mass of 198.6; it was checked in 1912 and found to be 190.9.

(3) a knowledge of the periodic variation of molar volume, set out by Lothar Meyer a few years before—but this property shows less clear-cut trends than atomic radius, discussed below. Atomic radius is a function only of the electronic structure of the element: but the volume of one mole is complicated by the type of bonding in the element and/or the packing of atoms into a crystal.

Mendeleyev's bold proposals, involving the alteration of established atomic masses and the leaving of gaps for new elements, got a hostile reception. However, the accuracy of his predictions (table 2.1) eventually won support. One prediction not borne out concerned the pair of elements tellurium and iodine. In this case the atomic mass of the first element is greater than the second, although its position in the periodic table is confirmed by its properties. Mendeleyev thought that the atomic mass was wrong. Today it is recognised that isotopes of tellurium contain rather more neutrons than isotopes of iodine. This affects the atomic mass, but not the atomic number used for ordering elements today. Argon/potassium and cobalt/nickel are another two pairs of elements showing the same behaviour.

Property	*Atomic mass*	*Density*/ $\mathrm{g\,cm^{-3}}$	*Valency*	*Boiling point* XCl_4/°C	*Boiling point* $X(C_2H_5)_4$/°C
Eka-silicon, predicted	72	5.5	4	90	160
Germanium found	72.6	5.47	4	86	163.5

Table 2.1 Mendeleyev's predictions for germanium.

2.2 PROPERTIES SHOWING PERIODIC BEHAVIOUR

2.2.1 **Group behaviour**

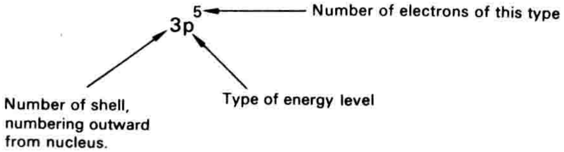
Elements falling in the same vertical column are known as a group and show considerable similarity of behaviour. Where there are differences, there is commonly a gradual trend from the element at the top of the column to the one at the bottom. It was on this basis that Mendeleyev made his predictions. The behaviour of groups is considered in the subsequent chapters of this book, and the remainder of this chapter is devoted to variations across the periodic table.

2.2.2 **Electronic structure**

Because the elements in the periodic table are placed in order of increasing atomic number (reading left to right and top to bottom) each atom has one more proton in its nucleus than the previous one. Hence the number of electrons must increase in the same way in order to maintain electrical neutrality. The electrons form the outer regions of the atom, and so are responsible for interactions with other atoms, namely, the chemical properties.

Each electron falls into a vacancy in one of the energy levels possessed by the atom. When one level is full, the next electron must go into a level further from the nucleus, where it is less firmly held. The energy levels may take up to two electrons (s-type levels), six electrons (p-type levels), or ten electrons (d-type levels), and so on. The s-, p- and d-type levels are characterised by the symmetry of the regions of space, or orbitals, in which that type of electron is to be found. s orbitals are spherically symmetrical, p orbitals are cylindrically symmetrical and so down to lower orders of symmetry. The first shell nearest the nucleus contains two electons, both in an s orbital written s^2; the second shell contains s and p electrons making a total of eight; the third shell contains s, p and d electrons to a total of eighteen, etc., so that the nth shell contains $2n^2$ electrons. With this information the shape of the periodic table can be explained.

The notation employed is


$3p^5$
Number of electrons of this type
Number of shell, numbering outward from nucleus.
Type of energy level

Period	*Comment*
1	The two elements H and He contain one and two s electrons respectively. This completes the first shell
2	The elements Li to Ne are built up by filling the second shell with electrons. The eight elements reflect eight electrons ($s^2 + p^6$)
3	Essentially the same as period 2
4	The third shell awaits completion while two s electrons of the fourth shell are added (K, Ca); then the third shell is completed with ten d electrons (ten elements Sc–Zn) before continuing the fourth shell with six p electrons (six elements Ga–Kr)
5	Essentially the same as period 4

Table 2.2 Periods and electronic structure.

Perhaps the key point to emerge from the above is that the noble gases (He–Rn) act as a reference stage. Their electronic structure in each case (except He) is the 'stable' octet of two s and six p electrons. (Helium cannot have p electrons, since only the first shell is in use, but it has nevertheless a stable full shell of two s electrons.)

The three major blocks which appear on inspecting the periodic table are related to the noble gas structure as follows:

(a) the first and second columns on the left (groups I and II). These elements contain one and two electrons, respectively, more than the noble gas 'core'. These extra electrons are in an s orbital and the elements are said to be s-block elements.

(b) the six columns on the left (groups III–VIII). Here the p orbitals are being filled, and the elements contain between one p electron (group III) and six p electrons (group VIII). These are the p-block elements.

(c) the elements in the centre. Although possessing an exterior similar to that of an s-block element, each element differs from the previous one in having one extra d electron. Thus Sc is made up of an Ar core, plus the two s electrons needed to create Ca, plus one d electron

$$\begin{aligned} \text{Sc} &\equiv [\text{Ar}] + 4s^2 + 3d^1 \\ \text{Ti} &\equiv [\text{Ar}] + 4s^2 + 3d^2 \quad \text{and so on.} \end{aligned}$$

A full list of electronic structures is given in appendix 2. A key point, which must be emphasised, is the strict similarity between elements in any one group. An electronic structure is common to a group, for example

$\text{Li} = [\text{He}] + 2s^1$, $\text{Na} = [\text{Ne}] + 3s^1$, $\text{K} = [\text{Ar}] + 4s^1$, $\text{Rb} = [\text{Kr}] + 5s^1$
or $\text{C} = [\text{He}] + 2s^2 2p^2$, $\text{Si} = [\text{Ne}] + 3s^2 3p^2$, $\text{Ge} = [\text{Ar}] + 4s^2 4p^2$, $\text{Sn} = [\text{Kr}] + 5s^2 5p^2$

2.2.3 **Bonding**

The types of bonds formed by an element depends closely on its electronic structure, and hence are related to the periodic table.

Electron arrangement	*Reasoning*	*Example*
s and p orbitals exactly full: eight electrons in outer shell (two electrons for He in first shell)	An extra electron has to go into a higher shell and would be weakly held: removal of electrons is also unlikely (see ionisation energy in next section). Therefore inert	Noble gases (see below in table) (Chapter 9)
One or two more electrons than the 'stable' noble gas core	The extra electron has gone into a shell further out than any previous, with only one unit increase in the nuclear charge. It is weakly held and readily lost to form cations X^+ or X^{2+}	Alkali and alkaline earth metals (Chapter 3)
One or two electrons less than the 'stable' noble gas core	There is a vacancy which available electrons can easily occupy. Hence reactive, forming anions X^- or X^{2-}	Oxygen, sulphur and halogens (Chapters 7 and 8)
About 4 electrons in outer shell, i.e. both half full and half empty	Removal of four electrons requires more energy than can be regained in a chemical reaction. No ions, only covalent bonds formed	Group 4 (Chapter 5)

Electron arrangement	*Reasoning*	*Example*
Electrons of highest energy in a 'd' orbital	The 3d orbital occupies a position in space closer to the nucleus than the 4s shell, which is already occupied. Electrons are removed easily because of crowding, but subject to the criterion that removing the fourth or later electrons from a highly charge positive ion is too expensive in energy terms. No definite number of electrons removed, therefore variable valency	Transition metals (Chapter 1)

Table 2.3 Possibilities of bonding.

These considerations also allow one to predict the principal valency of an element. For ionic compounds, the ion is usually formed by gaining or losing the number of electrons needed to establish the noble gas octet. By inspection, this creates a valency equal either to the number of the group, or to the difference between this number and eight. Covalent compounds may also display these two valencies, either by sharing all their electrons (in which case the valency is the number of the group) or by sharing just enough to make up a full shell (in which case the valency becomes the difference above). For instance, consider the oxides and hydrides in table 2.4.

Group	*Number of electrons in outer shell*	*Principal valencies*	*Oxide*	*Hydride*
I	1	1	Na_2O	NaH
II	2	2	MgO	MgH_2
III	3	3	Al_2O_3	not known
IV	4	4	SiO_2	SiH_4
V	5	3, 5	P_2O_5	PH_3
VI	6	2, 6	SO_3	SH_2
VII	7	1, 7	Cl_2O_7	ClH
VIII	8	0	not formed	not formed

Table 2.4 Principal valencies.

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