Table 1.4 The periodic table

Group / Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		*d*-block										*p*-block					
1	^{1}H																^{1}H	^{2}He
2	^{3}Li	^{4}Be											^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
3	^{11}Na	^{12}Mg											^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
4	^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
5	^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{50}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
6	^{55}Cs	^{56}Ba	^{57}La	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Tl	^{82}Pb	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
7	^{87}Fr	^{88}Ra	^{89}Ac															
								f-block										
Lanthanides				^{58}Ce	^{59}Pr	^{60}Nd	^{61}Pm	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu	
Actinides				^{90}Th	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es	^{100}Fm	^{101}Md	^{102}No	^{103}Lr	

1st period	1*s*				elements in this period 2
2nd period	2*s*			2*p*	elements in this period 8
3rd period	3*s*			3*p*	elements in this period 8
4th period	4*s*		3*d*	4*p*	elements in this period 18
5th period	5*s*		4*d*	5*p*	elements in this period 18
6th period	6*s*	4*f*	5*d*	6*p*	elements in this period 32

The alkali metals appear in a vertical column labelled Group 1, in which all elements have one *s* electron in their outer shell, and hence have similar properties. Thus when one element in a group reacts with a reagent, the other elements in the group will probably react similarly, forming compounds which have similar formulae. Thus reactions of new compounds and their formulae may be predicted by analogy with known compounds. Similarly the noble gases all appear in a vertical column labelled Group 18, and all have a complete outer shell of electrons. This is called the long form of the periodic table. It has many advantages, the most important being that it emphasizes the similarity of properties within a group and the relation between the group and the electron structure. The *d*-block elements are referred to as the transition elements as they are situated between the *s*- and *p*-blocks.

Hydrogen and helium differ from the rest of the elements because there are no *p* orbitals in the first shell. Helium obviously belongs to Group 18, the noble gases, which are chemically inactive because their outer shell of electrons is full. Hydrogen is more difficult to place in a group. It could be included in Group 1 because it has one *s* electron in its outer shell, is univalent and commonly forms univalent positive ions. However, hydrogen is not a metal and is a gas whilst Li, Na, K, Rb and Cs are metals and are solids. Similarly, hydrogen could be included in Group 17 because it is one electron short of a complete shell, or in Group 14 because its outer shell is half full. Hydrogen does not resemble the alkali metals, the halogens or Group 14 very closely. Hydrogen atoms are extremely small, and have many unique properties. Thus there is a case for placing hydrogen in a group on its own.

FURTHER READING

Karplus, M. and Porter, R.N. (1971) *Atoms and Molecules*, Benjamin, New York.

Greenwood, N.N. (1980) *Principles of Atomic Orbitals*, Royal Institute of Chemistry Monographs for Teachers No. 8, 3rd ed., London.

PROBLEMS

1. Name the first five series of lines that occur in the atomic spectrum of hydrogen. Indicate the region in the electromagnetic spectrum where these series occur, and give a general equation for the wavenumber applicable to all the series.

2. What are the assumptions on which the Bohr theory of the structure the hydrogen atom is based?
3. Give the equation which explains the different series of lines in th atomic spectrum of hydrogen. Who is the equation named after Explain the various terms involved.
4. (a) Calculate the radii of the first three Bohr orbits for hydrogen (Planck's constant $h = 6.6262 \times 10^{-34}$ J s; mass of electron $m = 9.1091 \times 10^{-31}$ kg; charge on electron $e = 1.60210 \times 10^{-19}$ C permittivity of vacuum $\varepsilon_0 = 8.854185 \times 10^{-12}\ \text{kg}^{-1}\ \text{m}^{-3}\ \text{A}^2$.) (Answers: 0.529×10^{-10} m; 2.12×10^{-10} m; 4.76×10^{-10} m; tha is 0.529 Å 2.12 Å and 4.76 Å.)
   (b) Use these radii to calculate the velocity of an electron in each o these three orbits.
   (Answers: $2.19 \times 10^6\ \text{m s}^{-1}$; $1.09 \times 10^6\ \text{m s}^{-1}$; $7.29 \times 10^5\ \text{m s}^{-1}$.)
5. The Balmer series of spectral lines for hydrogen appear in the visible region. What is the lower energy level that these electronic transitions start from, and what transitions correspond to the spectral lines at 379.0 nm and 430.0 nm respectively?
6. What is the wavenumber and wavelength of the first transition in the Lyman, Balmer and Paschen series in the atomic spectra of hydrogen?
7. Which of the following species does the Bohr theory apply to? (a) H, (b) H^+, (c) He, (d) He^+, (e) Li, (f) Li^+, (g) Li^{+2}, (h) Be, (g) Be^+, (h) Be^{2+}, (i) Be^{3+}
8. How does the Bohr theory of the hydrogen atom differ from that of Schrödinger?
9. (a) Write down the general form of the Schrödinger equation and define each of the terms in it.
   (b) Solutions to the wave equation that are physically possible must have four special properties. What are they?
10. What is a radial distribution function? Draw this function for the 1*s*, 2*s*, 3*s*, 2*p*, 3*p* and 4*p* orbitals in a hydrogen atom.
11. Explain (a) the Pauli exclusion principle, and (b) Hund's rule. Show how these are used to specify the electronic arrangements of the first 20 elements in the periodic table.
12. What is an orbital? Draw the shapes of the 1*s*, 2*s*, $2p_x$, $2p_y$, $2p_z$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals.
13. Give the names and symbols of the four quantum numbers required to define the energy of electrons in atoms. What do these quantum numbers relate to, and what numerical values are possible for each? Show how the shape of the periodic table is related to these quantum numbers.

14. The first shell may contain up to 2 electrons, the second shell up to 8, the third shell up to 18, and the fourth shell up to 32. Explain this arrangement in terms of quantum numbers.

15. Give the values of the four quantum numbers for each electron in the ground state for (a) the oxygen atom, and (b) the scandium atom. (Use positive values for m_l and m_s first.)

16. Give the sequence in which the energy levels in an atom are filled with electrons. Write the electronic configurations for the elements of atomic number 6, 11, 17 and 25, and from this decide to which group in the periodic table each element belongs.

17. Give the name and symbol for each of the atoms which have the ground state electronic configurations in their outer shells: (a) $2s^2$, (b) $3s^2 3p^5$, (c) $3s^2 3p^6 4s^2$, (d) $3s^2 3p^6 3d^6 4s^2$, (e) $5s^2 5p^2$, (f) $5s^2 5p^6$.

2 Introduction to bonding

ATTAINMENT OF A STABLE CONFIGURATION

How do atoms combine to form molecules and why do atoms form bonds
A molecule will only be formed if it is more stable, and has a lower energ
than the individual atoms.

To understand what is happening in terms of electronic structure, con
sider first the Group 18 elements. These comprise the noble gases, heliu
neon, argon, krypton, xenon and radon, which are noteworthy for thei
chemical inertness. Atoms of the noble gases do not normally react wit
any other atoms, and their molecules are monatomic, i.e. contain only on
atom. The lack of reactivity is because the atoms already have a lov
energy, and it cannot be lowered further by forming compounds. The lov
energy of the noble gases is associated with their having a complete oute
shell of electrons. This is often called a *noble gas structure*, and it is ar
exceptionally stable arrangement of electrons.

Normally only electrons in the outermost shell of an atom are involved in forming bonds, and by forming bonds each atom acquires a stable electron configuration. The most stable electronic arrangement is a noble gas structure, and many molecules have this arrangement. However, less stable arrangements than this are commonly attained by transition elements.

TYPES OF BONDS

Atoms may attain a stable electronic configuration in three different ways: by losing electrons, by gaining electrons, or by sharing electrons.

Elements may be divided into:

1. Electropositive elements, whose atoms give up one or more electrons fairly readily.
2. Electronegative elements, which will accept electrons.
3. Elements which have little tendency to lose or gain electrons.

Three different types of bond may be formed, depending on the electropositive or electronegative character of the atoms involved.

Electropositive element + Electronegative element } Ionic bond

Electronegative element + Electronegative element } Covalent bond

Electropositive element + Electropositive element } Metallic bond

Ionic bonding involves the complete transfer of one or more electrons from one atom to another. Covalent bonding involves the sharing of a pair of electrons between two atoms, and in metallic bonding the valency electrons are free to move throughout the whole crystal.

These types of bonds are idealized or extreme representations, and though one type generally predominates, in most substances the bond type is somewhere between these extreme forms. For example, lithium chloride is considered to be an ionic compound, but it is soluble in alcohol, which suggests that it also possesses a small amount of covalent character. If the three extreme bond types are placed at the corners of a triangle, then compounds with bonds predominantly of one type will be represented as points near the corners. Compounds with bonds intermediate between two types will occur along an edge of the triangle, whilst compounds with bonds showing some characteristics of all three types are shown as points inside the triangle.

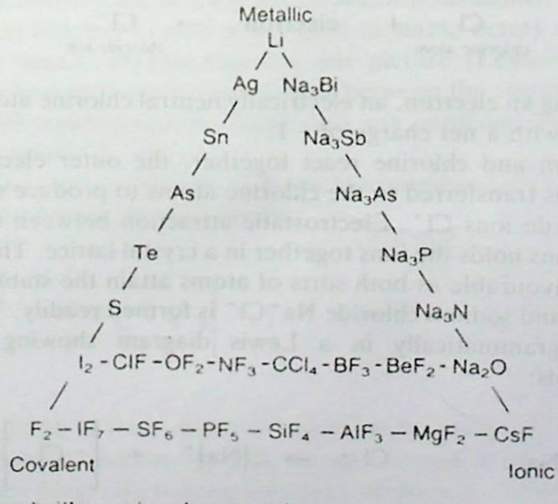


Figure 2.1 Triangle illustrating the transitions between ionic, covalent and metallic bonding. (Reproduced from *Chemical Constitution*, by J.A.A. Ketelaar, Elsevier.)

TRANSITIONS BETWEEN THE MAIN TYPES OF BONDING

Few bonds are purely ionic, covalent or metallic. Most are intermediate between the three main types, and show some properties of at least two and sometimes of all three types.

Ionic bonds

Ionic bonds are formed when electropositive elements react with electronegative elements.

Consider the ionic compound sodium chloride. A sodium atom has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^1$. The first and second shells of electrons are full, but the third shell contains only one electron. When this atom reacts it will do so in such a way that it attains a stable electron configuration. The noble gases have a stable electron arrangement and the nearest noble gas to sodium is neon, whose configuration is $1s^2\ 2s^2\ 2p^6$. If the sodium atom can lose one electron from its outer shell, it will attain this configuration and in doing so the sodium acquires a net charge of +1 and is called a sodium ion Na^+. The positive charge arises because the nucleus contains 11 protons, each with a positive charge, but there are now only 10 electrons. Sodium atoms tend to lose an electron in this way when they are supplied with energy, and so sodium is an electropositive element:

$$\underset{\text{sodium atom}}{Na} \rightarrow \underset{\text{sodium ion}}{Na^+} + \text{electron}$$

Chlorine atoms have the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. They are only one electron short of the stable noble gas configuration of argon $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, and when chlorine atoms react, they gain an electron. Thus chlorine is an electronegative element.

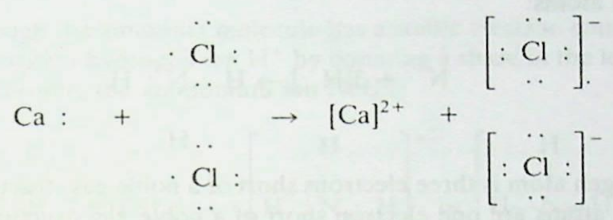
$$\underset{\text{chlorine atom}}{Cl} + \text{electron} \rightarrow \underset{\text{chloride ion}}{Cl^-}$$

Through gaining an electron, an electrically neutral chlorine atom becomes a chloride ion with a net charge of −1.

When sodium and chlorine react together, the outer electron of the sodium atoms is transferred to the chlorine atoms to produce sodium ions Na^+ and chloride ions Cl^- Electrostatic attraction between the positive and negative ions holds the ions together in a crystal lattice. The process is energetically favourable as both sorts of atoms attain the stable noble gas configuration, and sodium chloride Na^+Cl^- is formed readily. This may be illustrated diagrammatically in a Lewis diagram showing the outer electrons as dots:

$$\underset{\text{sodium atom}}{Na\,\cdot} + \underset{\text{chlorine atom}}{\cdot\,\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\,:} \rightarrow \underset{\text{sodium ion}}{[Na]^+} + \underset{\text{chloride ion}}{\left[\,:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\,\right]^-}$$

The formation of calcium chloride $CaCl_2$ may be considered in a similar way. Ca atoms have two electrons in their outer shell. Ca is an electropositive element, so each Ca atom loses two electrons to two Cl atoms, forming a calcium ion Ca^{2+} and two chloride ions Cl^-. Showing the outer electrons only, this may be represented as follows:

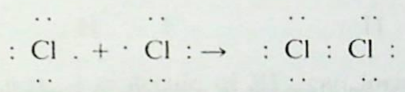


calcium atom chlorine atoms calcium ion chloride ions

Covalent bonds

When two electronegative atoms react together, both atoms have a tendency to gain electrons, but neither atom has any tendency to lose electrons. In such cases the atoms share electrons so as to attain a noble gas configuration.

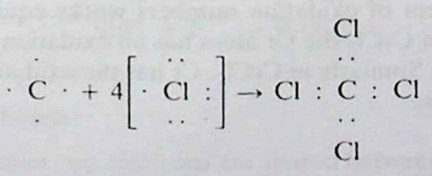
First consider diagrammatically how two chlorine atoms Cl react to form a chlorine molecule Cl_2 (only the outer electrons are shown in the following diagrams):



chlorine atoms chlorine molecule

Each chlorine atom gives a share of one of its electrons to the other atom. A pair of electrons is shared equally between both atoms, and each atom now has eight electrons in its outer shell (a stable octet) – the noble gas structure of argon. In this electron dot picture (Lewis structure), the shared electron pair is shown as two dots between the atoms Cl : Cl. In the valence bond representation, these dots are replaced by a line, which represents a bond Cl—Cl.

In a similar way a molecule of tetrachloromethane CCl_4 is made up of one carbon and four chlorine atoms:



The carbon atom is four electrons short of the noble gas structure, so it forms four bonds, and the chlorine atoms are one electron short, so they each form one bond. By sharing electrons in this way, both the carbon and all four chlorine atoms attain a noble gas structure. It must be emphasized