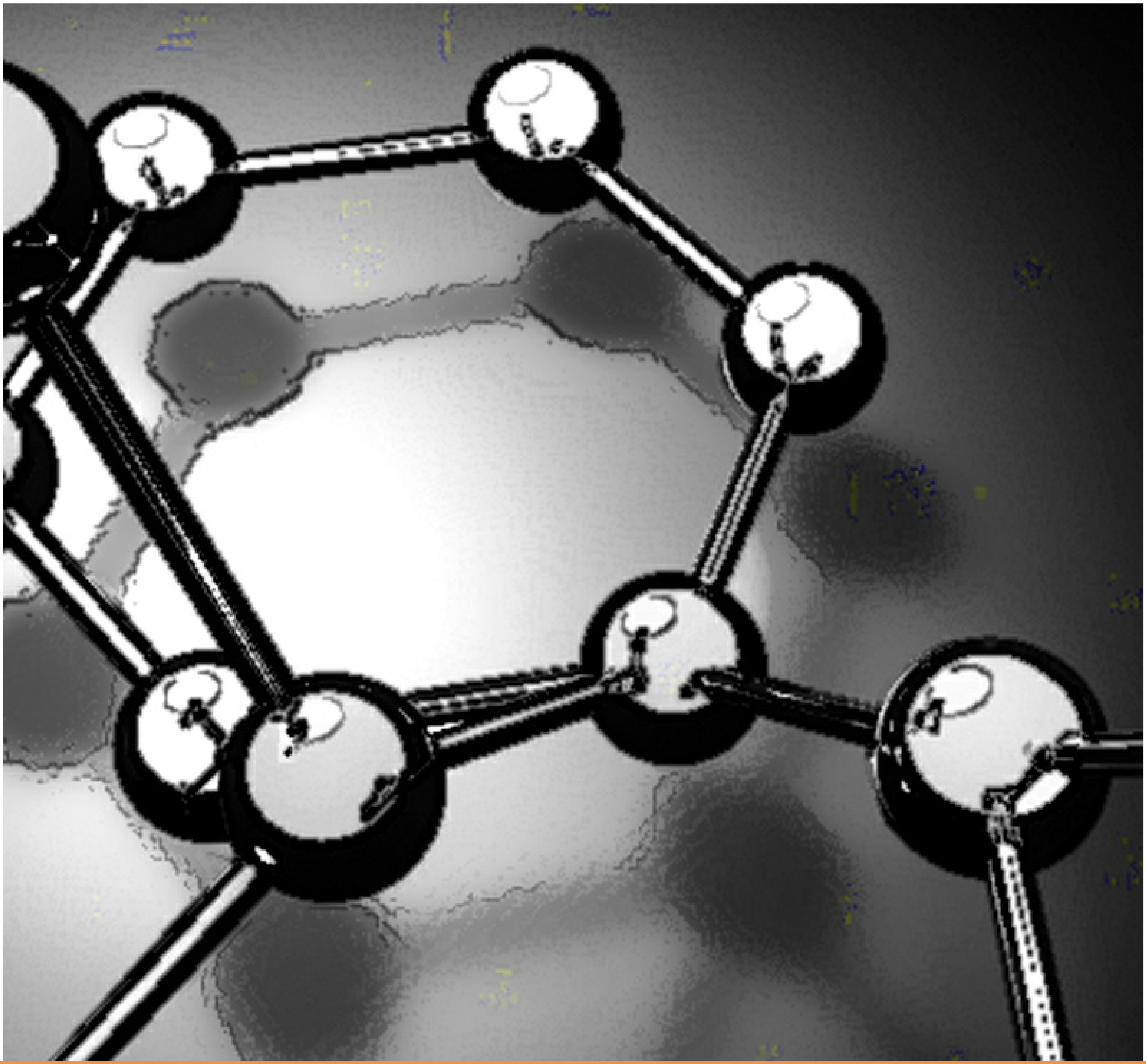

Introduction to Inorganic Chemistry

Key ideas and their experimental basis

Peter G. Nelson

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Contents

1 Introduction

Chemistry

Chemistry comprises two related but distinct activities:

(i) the quest for an understanding of matter and material change,
(ii) the utilization of material change for human ends.

Ideally, the first activity provides the necessary know-how for the pursuit of the second, but in practice, the help it can give is only partial, and the second activity has to fall back on trial and error techniques in order to achieve its ends. This means that a good chemist is one who not only has a mastery of chemical theory, but also a good knowledge of chemical facts. With such a knowledge, he can direct a trial and error approach to practical problems in the most promising directions.

Inorganic Chemistry

Organic chemistry is usually defined as the chemistry of compounds of carbon, inorganic chemistry being then the chemistry of all the other elements. This distinction is not a completely satisfactory one, however, since there are many compounds of carbon that are quite different from those studied by organic chemists (e.g. tungsten carbide, used for tipping cutting tools) and there are many compounds of other elements that are very similar to those studied under organic chemistry (e.g. the silicon analogues of the hydrocarbons). It is best, therefore, to think of inorganic chemistry as the chemistry of all the elements, with organic chemistry as being a more detailed study of certain important aspects of one of them - viz. the hydrocarbons and their derivatives.

Thinking of inorganic chemistry in this way brings together aspects of the chemistry of an element that would otherwise tend to become separated. For example, alcohols and ethers are usually dealt with under organic chemistry and are not thought of as being part of the chemistry of oxygen. Once they are, however, they can be set alongside the other compounds of oxygen, and a relationship immediately becomes apparent that might otherwise be lost, viz. that expressed by the formulae:

$$\mathrm{H{-}O{-}H} \qquad \mathrm{R{-}O{-}H} \qquad \mathrm{R{-}O{-}R'}$$

This course

My aim in this course is to derive the key ideas of inorganic chemistry from chemical observations. I do this by following the reasoning of chemists who have developed these ideas.

Many instructors take a different approach. They start with the quantum theory of atoms and molecules, and deduce the key ideas from this. The quantum theory enables the energy of an atom or molecule to be calculated, and the average motion of the electrons in it. With the help of modern computers, it gives remarkably accurate results.

The quantum theory, however, is essentially a *physical* theory, developed to explain observations like the atomic spectrum of hydrogen. Chemical ideas do not emerge from it easily. The theory is also very mathematical. Most chemists have to accept the results of quantum-mechanical calculations on trust. My approach avoids these problems. While I bring in the quantum theory where it is helpful, my treatment is essentially *chemical*. This makes for an easier introduction to the subject, and leads, I believe, to a better understanding of the key ideas, and the chemical thinking behind them.

Broader context

As defined above, chemistry is a very broad subject. It extends from the scientific study of substances (“pure” chemistry) to their manufacture and use (“applied” chemistry). It requires both mental effort and practical skill. It impacts on the world both intellectually and practically. When studying any particular part of chemistry, this broader context needs to be kept continually in mind.

Acknowledgment

I am very grateful to my colleagues with whom I have discussed the material in this course over many years, especially Dr. David A. Johnson, the late Dr. John R. Chipperfield, and the late Dr. B. Michael Chadwick. John encouraged me to put the course on the internet and prepared the text for this. I dedicate the web version to his memory.

Further reading

There are several textbooks of introductory inorganic chemistry. As these take a different approach from me, they are best read *after* this course, as a complement to it. However, I shall occasionally suggest that you look up something in a standard textbook, so it would be helpful if you had one to hand.

For a fuller discussion of the scope of chemistry, see my article:

“What is chemistry?”, *Education in Chemistry*, 1983, Vol. 20, pp. 122-125.

2 The relative importance of different elements

From an academic point of view, all elements might be said to be equally important. The chemistry of each has to be understood in detail if the chemistry of matter as a whole is to be understood in detail. From the point of view of the world at large, however, the relative importance of different elements varies widely, and some elements are little more that chemical curiosities. In a university course of inorganic chemistry, a balance has to be struck between a uniform treatment of all of the elements, and a greater concentration on the socially more important ones.

The question of which are the socially more important elements is to some extent a matter of opinion. A chemist working in the plastics industry would doubtless come up with a different list from one working in the metals industry, and someone working with agricultural chemicals would doubtless have different ideas from someone working on ceramics. Most people would agree, however, that among the most important elements are (i) the more abundant elements, (ii) elements that are consumed on a very large scale, and (iii) elements that are actively sought for despite very poor resources. Data on each of these categories are presented below.

2.1 The relative abundance of different elements

The figures below give the relative abundance of different elements in the atmosphere, the hydrosphere, the lithosphere, and the biosphere. The figures are necessarily approximate, and slightly different values may be found in other places. The percentages are percentages by mass - the percentage numbers of atoms would of course be different. All abundances over 0.1% have been included. The figures reveal that some 99% of the matter in the world around us is made up of as few as 14 elements. Note, however, that many of the remaining elements in the biosphere, despite their low concentration, are essential to its healthy continuance.

Atmosphere	
Nitrogen	75.5%
Oxygen	23.0%
Argon	1.4%
Total	99.9%

Hydrosphere

Oxygen	85.8%
Hydrogen	10.7%
Chlorine	2.1%
Sodium	1.1%
Total	99.7%

Lithosphere

Oxygen	46.6%
Silicon	27.7%
Aluminum	8.1%
Iron	5.0%
Calcium	3.6%
Sodium	2.8%
Potassium	2.6%
Magnesium	2.1%
Titanium	0.4%
Total	98.9%

Biosphere

Oxygen	52.4%
Carbon	39.4%
Hydrogen	6.6%
Nitrogen	0.5%
Calcium	0.4%
Potassium	0.2%
Total	99.5%

2.2 The relative consumption of different elements

The figures below give the annual world consumption of different elements, as elements and compounds, in millions of tons. The figures vary from year to year and are necessarily approximate. Siliceous materials and limestone used for building purposes have been excluded, and a lower limit has been set at 0.1 million tons.

	Millions of tons per year
Carbon	1000-10000
Iron, sodium	100-1000
Calcium, nitrogen, oxygen, potassium, sulfur	10-100
Aluminium, barium, chlorine, chromium, copper, fluorine, hydrogen, lead, magnesium, manganese, phosphorus, zinc	1-10
Boron, nickel, tin, titanium, zirconium	0.1-1

Of the 25 elements in the table, 10 are very plentiful, and appear in the first three tables of the previous section (2.1). Of the remainder, the majority occur in relatively concentrated deposits, from which they or their compounds can be extracted fairly easily (e.g. hydrocarbons from petroleum). For copper, lead, zinc, nickel, and tin, demand is such that less concentrated deposits have to be worked, down to 0.5% in the case of copper and 0.2% in the case of tin (see below).

2.3 Elements sought after from very low-grade ores

The following table gives the minimum metal content that an ore must have before it can be mined and smelted economically with present-day technology. Values are given up to a limit of 0.5%, and may be compared with the value for iron of 25%.

Platinum	0.0003%
Gold	0.001%
Silver	0.01%
Uranium	0.2%
Mercury	0.2%
Tin	0.2%
Molybdenum	0.3%
Copper	0.5%

Exercise

Make sure you know what all the elements in the above list look like. If possible, look at samples yourself. (If you see a sample of uranium, this will be of the “depleted” element, with its most radioactive isotopes removed.)

Questions

(1) Why are the metals listed in the last section so much sought after?
(2) Are there any elements that you would reckon to be important that have not been included in the above discussion?

(Click here for answers http://bit.ly/fQhJgG or see Appendix 1)

Further reading

For a fuller discussion of the relative importance of different elements, including other measures, see:

“Important elements”, *Journal of Chemical Education*, 1991, Vol. 68, pp. 732-737.

3 Classification of elements into metals and nonmetals

3.1 Types of element

The classification of elements into metals and nonmetals, with the intermediate category of semimetal, is a fundamental one in inorganic chemistry.

Metallic elements are characterized by the following properties under ordinary conditions:

(i) high lustre, high opacity over the visible spectrum;
(ii) high electrical and thermal conductivity.

Nonmetals are characterized by:

(i) no lustre, high transparency over the visible spectrum;
(ii) low electrical and thermal conductivity.

Semimetals are characterized by:

(i) high opacity over the visible spectrum, little or no lustre;
(ii) intermediate electrical conductivity.

Notes

(1) “High opacity over the visible spectrum” is a way of saying that the substance absorbs light strongly over the whole range of the visible spectrum, or at least over the whole range beyond the red. If it is not lustrous, therefore, the substance appears black to the eye, or very dark brown.

“High transparency over the visible spectrum” is a way of saying that the substance absorbs light weakly over the greater part of the visible spectrum, if not over all of it. If no light is absorbed, the substance appears colourless or white. (Colourless substances look white when finely divided because light is scattered from the many crystal faces. Similarly, coloured substances become paler on grinding.) If some light is absorbed, the substance appears coloured, the colour being the complementary one to the colour of the light that is absorbed.

The complementary colours to the main spectral colours (red, orange, yellow, green, blue, and violet) are obtained by writing the colours in order round a circle. Those appearing opposite each other are complementary.

Question

What is the colour of a substance that absorbs (a) in the violet, (b) in the violet and green?

(Click here for answers http://bit.ly/ieL47J or see Appendix 1)

(2) It is possible to be more quantitative about the distinction in electrical conductivity. Electrical conductivity (κ) is defined as the reciprocal of the resistivity, ρ:

$$\kappa = 1/\rho$$

The resistivity is defined by the equation

$$R = \rho(l/A)$$

where R is the resistance of a uniform conductor, l is its length, and A is its cross sectional area. The SI unit of ρ is ohm meter (Ω m) and its value is equal to the resistance that a meter cube of the substance offers to the passage of electricity from one parallel face to another. The SI unit of κ is thus Ω^{-1} m^{-1}.

On the basis of their ability to transmit an electric current, materials can be divided into four main classes:

Ordinary conductors, characterized by having conductivities greater than about 10^5 $\Omega^{-1}\mathrm{m}^{-1}$ at room temperature, which fall with increase of temperature.

Semiconductors, characterized by having conductivities between about 10^{-7} and 10^5 $\Omega^{-1}\mathrm{m}^{-1}$ at room temperature, which rise with increase of temperature, and are highly sensitive to traces of impurity.

Electrolytic conductors, characterized by the chemical decomposition that takes place at the points at which a direct current enters and leaves the material. (The words "electrolysis", "electrolyte", "electrolytic", come from the Greek *lyō*, loosen.)

Insulators, characterized by conductivities of less than about 10^{-7} $\Omega^{-1}\mathrm{m}^{-1}$ at room temperature, rising with increase in temperature.

In these terms, metals are conductors, semimetals are semiconductors, and nonmetals are insulators.

(3) It is necessary to specify "under ordinary conditions" because, under extreme conditions, the character of a substance can change profoundly. Thus:

- (i) gases at very low pressures become good conductors of electricity, as in a discharge tube at low pressure;
- (ii) metals at high temperatures vaporize, and lose their metallic properties completely (e.g. mercury boils at 357 ºC to give a colourless vapour, which is a poor conductor of electricity at ordinary pressures);
- (iii) semimetals and nonmetals at very high pressures become metallic in character (e.g. at 150 atmospheres iodine becomes a very good conductor of electricity).

(4) A further characteristic of metals that is usually given is that, in the solid state, they are malleable (easily hammered into sheets) and ductile (easily drawn into wires). By contrast, nonmetals in the solid state are brittle and easily powdered. In practice, however, while the majority of elements that are metallic according to the above criteria are indeed malleable and ductile, there are a few that do not have this property, even when ultra-pure. (Slight traces of impurity can produce brittleness in metals. Thus, ordinary commercial tungsten is so brittle that it can only be worked with difficulty, whereas the ultra-pure metal can be cut with a hacksaw, turned, drawn, or extruded.) Since the exceptional elements include some whose metallicity has never been questioned - e.g. manganese, cobalt, and zinc - it seems better *not* to make malleability and ductility a characteristic of metals, but rather a property possessed by most of them.

Zinc is a particularly interesting case, because it is malleable at some temperatures and brittle at others. Thus, it is brittle at room temperature, but softens above 100 ºC. At 205 ºC, however, it becomes brittle again, and can then be powdered in a mortar.

3.2 Assignment of elements to classes

In most cases, this is straightforward.

The clear-cut nonmetals are: hydrogen, nitrogen, oxygen, fluorine, sulfur, chlorine, bromine, and the inert or noble gases (helium, neon, argon, krypton, xenon).

The clear-cut semimetals are boron, silicon, germanium, and tellurium.

The clear-cut metals constitute all of the remaining elements, with the exception of the problem cases discussed below.

Problem cases

Carbon. Under ordinary conditions, carbon exists in two common forms, graphite and diamond, of which graphite is the more stable. Diamond is definitely nonmetallic, but graphite has properties on the borderline between a semimetal and a metal. Thus, it is a shiny, black solid, readily separated into flakes, with a metallic conductivity in the plane of the flakes, and a semimetallic conductivity perpendicular to the plane. Other forms include black, petrol-soluble “fullerenes”. When pure, these are insulators.

Phosphorus. This exists in a number of different forms: one white, several red, and several black. The white form can be made by condensing the vapour. It melts at 44 °C and boils at 280 °C. A red form is obtained when the white form is heated to just below its boiling point. A black form can be obtained by heating the white form under a very high pressure, or in the presence of a mercury catalyst. The yellow and red forms are insulators; the black forms are semiconductors. The most stable form under ordinary conditions is black; all forms, however, melt to a colourless liquid.

Arsenic. This can be obtained in several forms, ranging from a yellow one, which is similar to white phosphorus, to a grey one, which is a metal. The metallic form is the most stable under ordinary conditions; the yellow one is very unstable.

Antimony. This can also be obtained in several forms, ranging from yellow to metallic. The metallic form is again the most stable, with the yellow very unstable.

Selenium. This exists in three red forms, one black form, and one grey. The red and black forms are insulators; the grey is a semiconductor. The latter is the most stable.

Iodine. Iodine crystallizes in blackish-grey opaque scales, with an almost metallic lustre. In the plane of the scales, it has the conductivity of a semiconductor; perpendicular to the plane it is an insulator.

Exercise

If you were asked to place each of the problematic elements into one of three categories, metal, semimetal, and nonmetal, where would you place them? (In doing this exercise do not be surprised if you have difficulty in some cases, or if you come to different conclusions from other people. Many of the fundamental ideas of chemistry are not as exact as is often made out. We have to get used to rules that have exceptions, and classifications that produce border-line cases. This is of the character of chemistry, which in terms of exactitude of its theories, stands very much between physics on the one hand and biology on the other.)

(Click here for answers http://bit.ly/g7Vnat or see Appendix 1)

3.3 Volatilities of metals and nonmetals

The volatility of a substance is the ease with which the substance is vaporized. It is conveniently measured by the temperature at which the substance boils or sublimes at atmospheric pressure.

A broad generalization concerning the relative volatilities of metals and nonmetals is the following:

Metals are generally involatile, i.e. they have boiling points in excess of 500 ºC. Only mercury has a boiling point below 500 ºC, this being at 357 ºC. Most metals have their boiling point somewhere between 1000 ºC and 4000 ºC. The highest value is for tungsten, at 5660 ºC.

Nonmetals vary from being very volatile to very involatile. All the definite nonmetals listed above have boiling points below 500 ºC, and most are gases at room temperature. The least volatile is sulfur, boiling at 445 ºC. If, however, we include carbon among the nonmetals, as surely we should, this lies at the opposite extreme of volatility, boiling at 4830 ºC.

3.4 Chemical properties of metals and nonmetals

There are many chemical differences between metals and nonmetals. These will become apparent in the following chapters.

Some elements have very similar properties and are grouped into families. These include:

Alkali metals: Li, Na, K, Rb, Cs
Alkaline earth metals: (Mg,) Ca, Sr, Ba
Halogens: F, Cl, Br, I
Inert or noble gases: He, Ne, Ar, Kr, Xe

“Alkali” is an Arabic word meaning “the ash” (ash from plants contains sodium and potassium carbonates). “Halogen” means “producer-of (-gen) salt (Greek *hals*)”. Some chemists class magnesium as an alkaline earth metal as it is quite similar to calcium, often occurring with it in nature.

The gases He, Ne, Ar, Kr, and Xe were called “inert” when they were thought to be completely inactive. Their name was changed to “noble” after the xenon fluorides were discovered in 1962. This was because metals having a low activity (but nevertheless some activity) like gold and platinum are sometimes called “noble” as they are used for noble purposes. The change was inept. “Inert” need not imply complete inactivity, and “noble” is hardly apt (commoners breathe in these gases no less than nobles do!).

Other families will be discussed in a later chapter.

4 Binary compounds

4.1 General classification of compounds

Compounds can be classified according to the number of different elements that they contain: binary (two), ternary (three), etc.

4.2 Limiting types of binary compound

Corresponding to the two limiting types of element, metal and nonmetal, there are three limiting types of binary compound:

(i) *Metallic*	These are formed principally by the combination of a metal with a metal, and have the characteristics of a metal.
(ii) *Nonmetallic*	These are formed principally by the combination of a nonmetal with a nonmetal, and have the characteristics of a nonmetal.
(iii) *Salt-like*	These are formed principally by the combination of a metal with a nonmetal, and constitute a new class of material.

4.3 Metallic compounds

These have the same characteristic properties as metallic elements.

An example is the compound Mg_2Sn. This is made by fusing together a mixture of magnesium and tin of the appropriate composition, and cooling the resulting melt. The product is homogeneous, as can be seen by cutting and polishing it, and examining the polished surface under a microscope. If more magnesium or tin is used than required by the formula Mg_2Sn, the product ceases to be homogeneous - crystals of Mg_2Sn can be seen embedded in a matrix of smaller crystals containing the excess of magnesium or tin. The compound Mg_2Sn is a bluish-white lustrous solid, having all the properties of a metal.

Metal-metal systems vary in character between the following extremes:

(i) Those in which the two metals are able to form solid solutions with each other over the whole composition range from 100% of one to 100% of the other. An example of such a system is that between silver and gold.

(ii) Those in which the two metals are completely immiscible with each other, even in the liquid state. An example of such a pair of metals is iron and lead.

(iii) Those in which a number of compounds are formed. In the copper-zinc system, for example, there are three (see below).

Metallic compounds fall into one of two categories of compound:

(i) *Stoicheiometric compounds.* These are compounds that obey the law of constant composition to very high accuracy, e.g. CH_4, NaCl, and Mg_2Sn. They are also called "definite" compounds or "Daltonides". [The word "stoicheiometric" comes from "stoicheiometry", the name given to the measurement of the proportions of elements in compounds (Greek *stoicheion,* element, *metron*, measure).]

(ii) *Non-stoicheiometric compounds.* These have a variable composition within certain limits. They are also called "indefinite" compounds or "Berthollides" (after the French chemist Claude Berthollet, 1748-1822, who disputed the law of constant composition).

Examples of non-stoicheiometric compounds are provided by the copper-zinc system. The three compounds referred to above have the following compositions at 300 ºC:

$$CuZn_{0.85–0.95}, CuZn_{1.4–2.0}, \text{ and } CuZn_{2.5–6.2}.$$

The same compositions are obtained at room temperature if the solids are cooled fairly quickly. The first compound, however, is metastable at room temperature, and when cooled very slowly, decomposes at about 250 ºC into a mixture of the second compound and $CuZn_{0–0.5}$, a solid solution of zinc in copper (brass).

The formulae of compounds of this type are normally written either in the way I have done, or in terms of some kind of idealized formula, using a *circa* ("round about") sign ~. The choice of idealized formula is based upon structural or theoretical considerations, and is not without arbitrariness. In the case of copper-zinc compounds, the idealized formulae are

$$CuZn, Cu_5Zn_8, \text{ and } CuZn_3,$$

and the compounds are written

$$\sim CuZn, \sim Cu_5Zn_8, \text{ and } \sim CuZn_3.$$

Notice that the first of these (CuZn) lies outside the composition range of the actual compound.

While metallic compounds are generally formed by the combination of a metal with a metal, they can sometimes be formed in the combination of a metal with a nonmetal. This occurs in circumstances where the influence of the metal can predominate over the influence of the nonmetal, namely (i) when the ratio of metal atoms to nonmetal atoms is relatively high, (ii) when the nonmetallic character of the nonmetal is relatively weak, or (iii) when both circumstances pertain.

An example of a compound of this type is silver subfluoride, Ag_2F, made by leaving metallic silver in contact with the normal fluoride, AgF, in the dark. It forms small crystals with a bronze reflex, and is a good conductor of electricity.

Other examples of compounds of this type are the suboxides of rubidium and caesium, made by fusing the normal oxides, Rb_2O and Cs_2O, with the parent metals. These are lustrous and have good electrical conductivities, diminishing with increase of temperature. There are several for each metal, examples being Rb_9O_2, which is copper coloured, and Cs_7O, which is bronze.

Another set of examples is provided by the lower oxides of titanium, made by heating titanium dioxide with the metal. These are lustrous and good conductors of electricity. They are non-stoicheiometric, their formulae being

$$\sim Ti_6O, \sim Ti_3O, \sim Ti_2O, Ti_{1.3-1.5}O, \text{ and } \sim TiO.$$

To these may be added the nitrides of titanium,

$$\sim Ti_2N \text{ and } \sim TiN,$$

which are also metallic in character.

4.4 Nonmetallic compounds

These have the characteristic properties of nonmetals. Like the latter, they vary from being very volatile to very involatile. They are almost always stoicheiometric; only in the case of certain polymers does variable composition arise.

Examples of volatile nonmetallic compounds are very familiar: methane, ammonia, water. Examples of involatile compounds are silicon carbide (SiC) and silica (SiO_2). The former is manufactured by heating silica with graphite and is sold under the name carborundum. The commercial product is black, but when pure it is colourless. It melts at about 2700 ºC. Pure silica also forms colourless crystals, melting to a colourless liquid at about 1600 ºC and boiling at about 2400 ºC. Both compounds are insulators. Conductivity measurements have also been made on liquid silica, in which state it remains a poor conductor (cf. salt-like compounds).

Exercise

Make a list of the principal binary compounds formed between each of the following pairs of elements, and alongside each compound write down its appearance and volatility:

(i) oxygen and hydrogen
(ii) carbon and oxygen
(iii) nitrogen and hydrogen
(iv) phosphorus and oxygen
(v) sulfur and hydrogen
(vi) sulfur and oxygen
(vii) sulfur and chlorine
(viii) sulfur and fluorine

(Use a suitable textbook.)

(Click here for answers http://bit.ly/e92Qed or see Appendix 1)

Nonmetallic compounds are generally formed by the combination of a nonmetal with a nonmetal, but combinations of a metal and a nonmetal can also be nonmetallic if the influence of the nonmetal predominates. This occurs (i) when the ratio of metal atoms to nonmetal atoms is relatively low, (ii) when the metallic character of the metal is relatively weak, or (iii) when both circumstances pertain.

Good examples of nonmetallic compounds of metals are provided by the highest oxides of chromium and manganese. These have the formulae CrO_3 and Mn_2O_7, and are similar to the highest oxides of sulfur and chlorine, SO_3 and Cl_2O_7. Thus, CrO_3 is a red solid melting at 196 ºC, and Mn_2O_7 is a dark red oil. Further, electrical measurements on CrO_3 show this to be an insulator in both the solid and liquid state (cf. next section). Both compounds decompose below their boiling point, Mn_2O_7 explosively.

4.5 Salt-like compounds

These represent a new class, characterized by the following properties:

(i) no lustre, high transparency over the visible spectrum,

(ii) either (a) low electrical conductivity in the solid state, but high conductivity in the molten state and in aqueous solution, conduction being of the electrolytic type, or (b) high electrolytic conductivity in both the solid and the liquid state.

They are brittle in the solid state, and generally have low volatilities.

Examples

An example of a compound of this type is of course salt itself (i.e. “common salt”, sodium chloride). This forms colourless, brittle crystals, which melt to a colourless liquid at 801 ºC, and boil to a colourless vapour at 1413 ºC. In the solid, it has the electrical conductivity of an insulator, but the liquid has a conductivity of about $10^2\ \Omega^{-1}m^{-1}$. When a direct current is passed through the melt, chlorine gas is evolved at the positive electrode (the anode) and metallic sodium is formed at the negative electrode (the cathode). This process is used industrially for the preparation of sodium, except that the temperature is lowered by the addition of another salt, e.g. calcium chloride, which depresses the freezing point of the sodium chloride.

Sodium chloride also conducts electricity when dissolved in water. Strong solutions have a similar conductivity to the melt. A direct current again leads to chemical change at the electrodes, only this time hydrogen is produced at the cathode. This is to be expected, since sodium reacts with water to give hydrogen.

Compounds that are good electrolytic conductors in the solid state are relatively rare. One example is silver iodide above about 150 ºC.

Notes

(1) The amounts of substance produced during electrolysis are given by Faraday's laws. These may be stated as follows:

First law. The amount of chemical change produced by a current is proportional to the quantity of electricity passed.

Second law. The quantity of electricity required to split up 1 mole of NaCl is the same as that required to split up 1 mole of KCl, or 1 mole of NaF, or ½ mole of $MgCl_2$, or 1/3 mole of AlF_3, etc. This quantity is called the Faraday constant, F, and has the value 96500 coulombs per mole (C mol^{-1}).

(2) Substances that give conducting solutions in water, but are themselves poor conductors in the liquid state, are not to be reckoned salt-like, but nonmetallic. For example, hydrogen chloride or hydrochloric acid gas, made by treating sodium chloride with concentrated sulfuric acid, dissolves in water to give a conducting solution. The gas itself, however, condenses at –85 ºC to a colourless liquid that is a very poor conductor of electricity. Hydrogen chloride is thus classed as a nonmetallic compound, and the electrical behaviour of its solution in water attributed to some change that takes place on dissolution. Evidence for such a change can be found in the high heat of solution of hydrogen chloride, as compared with that for sodium chloride:

	ΔH
HCl(g)	-74 kJ mol^{-1}
NaCl(c)	$+4$kJ mol^{-1}

(These values are for the dissolution of one mole in one hundred moles of water.)

(3) It is not easy to distinguish between a non-conducting salt-like compound and a nonmetallic compound. The only characteristic difference between them is in the conductivity of the melt, which can only be obtained at a high temperature. The following short cuts, however, can be used fairly safely:

- (i) If the compound is soluble in water with a small heat of solution, and the solution conducts electricity, it is almost certainly salt-like.
- (ii) If the compound is composed of similar elements to those of another compound whose character is known, and it has the elements in the same proportions, it probably belongs to the same class.

As an example of (ii), consider sodium oxide, Na_2O, and potassium oxide, K_2O. Since lithium oxide, Li_2O, is known to be a good electrolytic conductor in the liquid state, analogy suggests that Na_2O and K_2O should also be good electrolytic conductors in the liquid state, and therefore also salt-like.

(4) Some metal-nonmetal pairs form a single compound (e.g. sodium and chlorine); others form more than one compound. For example:

- Sodium combines with a limited amount of oxygen to form sodium oxide (Na_2O) and with excess to form sodium peroxide (Na_2O_2). The latter reacts with water to give hydrogen peroxide (H_2O_2).

- Iron combines with chlorine to form iron dichloride ($FeCl_2$) and iron trichloride ($FeCl_3$), and with oxygen to form the oxides ~FeO, Fe_3O_4, and Fe_2O_3.

- Chromium and manganese form several compounds with oxygen, the main ones being Cr_2O_3, CrO_2, and CrO_3, and MnO, Mn_3O_4, Mn_2O_3, MnO_2, and Mn_2O_7. The highest of these were discussed above.

Exercise

List the compounds formed between the following pairs of elements:

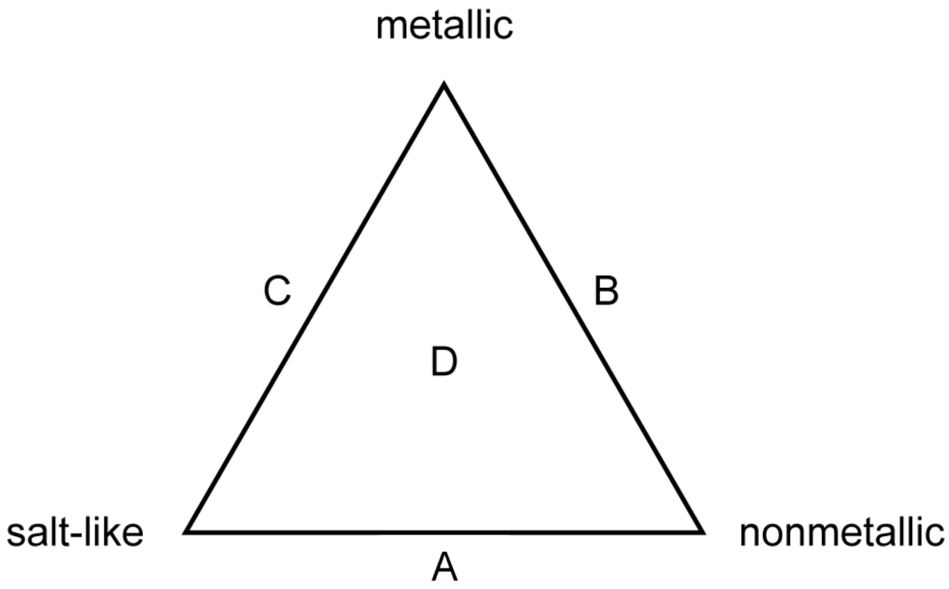
(i) calcium and chlorine
(ii) aluminium and chlorine
(iii) copper and chlorine
(iv) calcium and oxygen
(v) aluminium and oxygen
(vi) iron and oxygen
(vii) copper and oxygen

(Click here for answers http://bit.ly/eJaNIL or see Appendix 1)

4.6 Intermediate types of binary compound

The three types of binary compound that we have been considering are what we have called "limiting types". In other words they represent extremes, and most binary compounds fall somewhere in between these extremes.

As can be seen from the following diagram, there are four intermediate types, corresponding to the one intermediate type between metallic and nonmetallic elements:



The properties of the intermediate types can be inferred from the properties of the limiting types.

Thus:

Type A: High transparency, no lustre, weak electrolytic conductivity in fused state.

Type B: High opacity, possibly some lustre, semiconducting in solid and liquid.

Type C: High opacity, possibly some lustre, both electrolytically conducting and semiconducting (i.e. with a direct current, chemical decomposition takes place, but less than the amount required by Faraday's laws).

Type D: Like C, but conductances weaker.

In practice, determining the degree of salt-like character is difficult, since it requires accurate electrochemical measurements at high temperatures on melts.

Names

Type	**Chemical name**	**Electrical name**
Metallic	Metal	Conductor
Nonmetallic	Nonmetal	Insulator
Salt-like	*	Electrolyte
Type A	*	Semi-electrolyte
Type B	Semimetal†	Semiconductor
Type C	*	Mixed conductor
Type D	*	Mixed conductor

* No general name.
† Restricted to good semiconductors.

Examples

Type A: Beryllium chloride, $BeCl_2$, and zinc chloride, $ZnCl_2$. These are colourless, and in the fused state, they conduct electricity electrolytically. Their conductivities are only a fraction, however, of those of fused $MgCl_2$ and $CaCl_2$ (about 0·5 Ω^{-1} m^{-1}, as compared with about 100 Ω^{-1} m^{-1}).

Type B: Iron monoxide, ~FeO. This is black, and has a conductivity at room temperature of 2×10^3 Ω^{-1} m^{-1}. Electrolytic conduction in the melt is negligible.

Type C/D: Dicopper sulfide, ~Cu_2S. This is also black. At room temperature, it is a semiconductor, with a conductivity of 3 Ω^{-1} m^{-1}. At higher temperatures, the conductivity rises, and electrolytic conduction makes a contribution, reaching about 85% at 400 °C.

Further reading

"Classifying substances by electrical character", *Journal of Chemical Education*, 1994, Vol. 71, pp. 24-26.

"Quantifying electrical character", *Journal of Chemical Education*, 1997, Vol. 74, pp. 1084-1086.

"Quantifying molecular character", *Journal of Chemical Education*, 2000, Vol. 77, pp. 245-248.

5 On the nature of the limiting types of binary compound

In this chapter, I shall discuss the limiting types of binary compound. I shall do this on the assumption that matter is composed of atoms, but without any reference to the structure of the atom as we now understand it. This something that I shall bring in later.

5.1 Nonmetallic compounds

5.1.1 Volatile

The nature of compounds of this type can be arrived at by the following kind of argument:

(i) Gases are readily compressed, whereas liquids and solids are not. This suggests that, in gases, atoms are joined together in relatively small clusters, which are dispersed throughout the volume occupied by the gas.

(ii) Gases exert a pressure on the surface of a container. This suggests that the clusters of atoms are in continual, random motion, their bombardment of the walls creating the pressure we observe.

(iii) If the temperature of a gas is lowered at constant volume, its pressure drops (according approximately to the gas law, $P_1V_1/T_1 = P_2V_2/T_2$). This suggests that the lowering of the temperature has the effect of slowing down the motion of the clusters.

(iv) If the temperature of a gas is lowered far enough, the gas liquefies. If is cooled further, it solidifies. This suggests that there are forces between the clusters that are capable of holding the clusters together once their motion has been slowed down.

(v) The distinction between volatile and involatile substances must therefore lie in the relative strengths of the forces between the clusters. In the case of volatile substances, the forces must be relatively weak.

(vi) This conclusion is supported by the following observations:

(a) The latent heats of vaporization of volatile substances are relatively low. For example:

	ΔH
Methane	10 kJ per mole of CH_4
Chlorine	20 kJ per mole of Cl_2
Salt	170 kJ per mole of NaCl
Iron	350 kJ per mole of Fe

(The values of ΔH are for the vaporization of the liquid at the boiling point.)

(b) Coloured volatile substances generally have the same colour in the liquid and the solid as they have in the gas, suggesting that the interactions between the clusters in the condensed state is relatively slight. For example, chlorine retains its yellow colour in the liquid and the solid: by contrast, sodium is purple in the vapour and becomes metallic in the condensed state.

(c) Structure determinations show that, for volatile substances, the clusters that are present in the gaseous state are still present in the solid state, with relatively long distances between them. For example, electron diffraction of gaseous chlorine reveals the presence of diatomic clusters with an interatomic distance of 2.0 Å, while X-ray diffraction of solid chlorine reveals the presence of the same clusters, packed together in an orderly way, with the chlorine-chlorine distances *between* the clusters of 3.3 Å at their shortest.

(vii) The presence of clusters in a volatile liquid, held together but moving about, is supported by the phenomenon of Brownian motion. When pollen grains are suspended in water and viewed with a microscope, they are seen to be undergoing a continual jerky motion, as if they are continually being bombarded by the clusters that make up the water.

In the above discussion “cluster” has been used to keep the argument fresh, and to avoid anticipating the conclusion. We can now substitute the technical word “molecule”, from the Latin *molecula*, meaning “a little mass”. The weak forces between molecules are called van der Waals’ forces, after the Dutch physicist who invoked them to explain the deviation of real gases from the behaviour predicted by the gas laws.

On the constitution of molecules

The formulae of the following molecules

$$H_2, Cl_2, HCl$$

can be accounted for by supposing that hydrogen and chlorine atoms are capable of uniting with one other atom, almost as if each atom had a single hook on it, and could engage the hook of another atom to form a single connection (“bond”) between them:

$$H–H, Cl–Cl, H–Cl$$

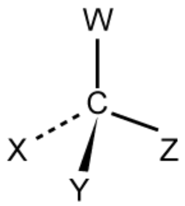
Similarly, the formulae of the following molecules

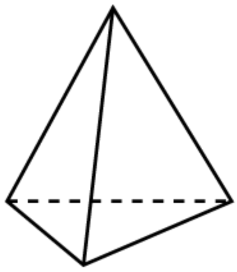
$$CH_4, CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4$$

suggest that the carbon atom is capable of forming four such bonds:

The formulae of a great many compounds can be rationalized in this kind of way, as is done routinely in organic chemistry. The number of bonds formed by an atom is called its valency. This is discussed further in Chapter 8.

There is a good deal of evidence that the bonds around an atom are in definite directions in space. Thus, for example, compounds made up of molecules of the type Cwxyz, where w, x, y, and z are different atoms or groups of atoms, can be resolved into optically active isomers, familiar from organic chemistry. These are isomers whose crystals are the mirror image of each other, and which rotate plane polarized light in opposite directions. Formation of such isomers would not be possible if the molecules were planar (there would be only one isomer), but is consistent with their being tetrahedral in shape:





The molecule shown now differs from its mirror image [draw this and show that it is different]. This arrangement of four atoms around a carbon atom has been confirmed by numerous electron diffraction studies of carbon compounds in the gas phase and X-ray diffraction of carbon compounds in the solid state.

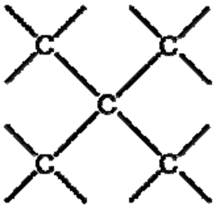
5.1.2 Involatile nonmetallic compounds

Some nonmetallic compounds are involatile because their molecules are very large (e.g. higher paraffins). Although the van der Waals interactions between atoms in different molecules are small (they are the same as the interactions between atoms of small molecules), there are so many atoms that the total interaction between molecules is large. Compounds of this type nevertheless dissolve in volatile solvents (e.g. higher paraffins in lower ones), because each molecule can interact with as many solvent molecules as it can get round it. These interactions add up to overcome the large interaction between molecules of the compound. Very large molecules are called “macromolecules”.

Other involatile nonmetallic compounds are different in being insoluble in volatile solvents (e.g. diamond, silicon carbide, and silica). The nature of these compounds can be inferred as follows:

(i) From the above discussion of volatile compounds, the molecules of these compounds in the vapour phase must interact very strongly in the liquid and solid phases.

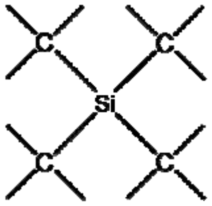
(ii) In many volatile compounds, carbon atoms are known to bond to four other atoms in directions defined by a tetrahedron (see above). Now if carbon atoms were to bond to each other in this kind of way, instead of a small molecule being produced, a continuous three-dimensional network would be formed, each atom being held in the network by very strong bonds - the same kind of bonds that hold the atoms of each molecule together in volatile compounds. In two dimensions this may be drawn:



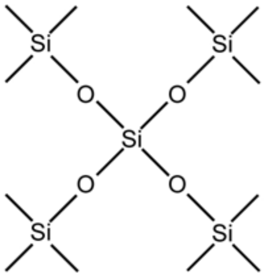
Such a structure would satisfy (i) and suggests itself for diamond.

(iii) A determination of the structure of diamond by X-ray crystallography shows that it indeed has this structure, with carbon-carbon bond lengths of 1.54 Å, as compared with 1.53 Å in C_2H_6. (For a picture, click here http://bit.ly/hhA4OJ or see Appendix 2.)

(iv) In a similar way, we can "guess" the structures of silicon carbide and silica. Silicon also forms volatile compounds in which the silicon atom is surrounded by a tetrahedron of other atoms (e.g. simple molecules like SiH_4 and $SiCl_4$, and resolvable ones of the type Siwxyz). Silicon carbide could thus have a similar structure to that of diamond:



Further, since oxygen forms compounds in which its atom has two neighbours, silica could have a structure of the diamond type, only with an oxygen atom between every pair of silicon atoms:



That silicon carbide and silica indeed have structures of this kind has been shown by X-ray crystallography. (Both compounds are polymorphic, but in each case, the different forms have the same arrangement of nearest neighbours, and differ only in the relative orientation of more distant neighbours.)

Compounds of this type thus consist of giant assemblies of atoms tightly held together. Such assemblies of atoms are called “frameworks” and such compounds “nonmolecular”.

Liquefaction of compounds of this type involves the breaking of some of the bonds, for only in this way can atoms move positions. Clearly, however, the system will resist whole-scale breaking of bonds, and fluidity will rely on a process whereby the breaking of one bond is compensated for by the remaking of another bond somewhere else. Consequently, the fluidity of such compounds in the liquid state is low: that is, their viscosity is high.

Vaporization of compounds of this type does require a break-up of the network of bonds, and the vapour effectively consists of fragments of the solid. In the case of diamond, these are C_2 molecules; for silica, they are SiO_2 molecules. Silicon carbide decomposes.

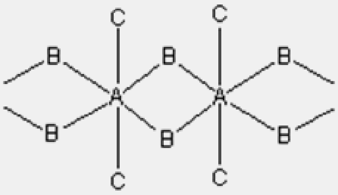
Note

It is important to be able to work out the overall composition of a compound from diagrams of the kind given in the discussion above. This can be done by picking out the central atom in the diagram, counting the number of nearest neighbours to it (x), and then working out the share that the central atom has of these neighbours. This is done by counting the number of other atoms of the same type that the central atom has to share each neighbour with (y), from which the share the central atom has of each neighbour is $1/y$. The composition is then AB_z, where A represents the central atom, B its neighbour, and $z = x/y$. The method can readily be extended to cases where there is more than one kind of neighbour.

Exercise

(i) Verify the compositions of silicon carbide and silica from the above diagrams.

(ii) Work out the composition of a compound having the following structure:



(Click here for answers http://bit.ly/h2WMuP or see Appendix 1)

5.2 Salt-like compounds

These are composed of ions. The evidence for this is relatively simple:

(i) A solution of salt in water conducts electricity: a solution of sugar does not. Something must be carrying the charge.

(ii) In dilute solution, the elevation of the boiling point of water or the depression of the freezing point is approximately twice as great for a certain number of moles of salt as it is for the same number of moles of sugar. Thus, instead of behaving like a solution containing NaCl molecules, it behaves as if twice as many particles are present. Between them these particles must be the carriers of the charge, and since salt itself is neutral, they must be either

$$\mathrm{Na}^{x+} \text{ and } \mathrm{Cl}^{x-} \text{ or } \mathrm{Na}^{x-} \text{ and } \mathrm{Cl}^{x+}.$$

(iii) When an electric current is passed through molten salt, chlorine is formed where a conventional current enters the melt (the positive electrode or anode) and sodium where it leaves (the negative electrode or cathode). The sodium particles must therefore be Na^{x+} because they release conventional (positive) electricity to the wire leading from the cathode. The chloride particles must accordingly be Cl^{x-}. Faraday called Na^{x+} and Cl^{x-} “ions” from the Greek *ion* meaning “goer”, “cations” being goers to the cathode and “anions” to the anode.

(iv) The value of x can be found by dividing the quantity of electricity required to deposit one mole of sodium, or produce the equivalent amount of hydrogen (½ mol of H_2), F, by the Avogadro constant, L:

$$x = F/L$$

This value was called the “electron” before the particle that bears this name was discovered. If we give it the symbol e, the sodium and chloride ions can be written

$$\mathrm{Na}^{e+} \text{ and } \mathrm{Cl}^{e-}$$

However, the e is always dropped, the charge (q) being replaced by the “charge number”, $z = q/e$. The electron itself is written e^-, and its positive counterpart, the positron, e^+.

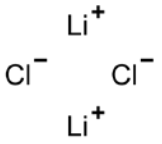
(v) The idea that salt contains ions is further supported by the structure of the solid, as determined by X-ray diffraction. Instead of there being discrete molecules in the solid as there are in the case of chlorine, each sodium atom is surrounded by chlorine atoms, and each chlorine atom by sodium atoms, just as one would expect if they were oppositely charged ions. (For a picture, click here http://bit.ly/fDtj3g or see Appendix 2.)

(vi) Further support is provided by calculations of the energy of the solid based upon the idea that it is made up of fairly hard charged spheres. Good agreement with experiment is obtained. (Details are given in some textbooks.)

(vii) Mass spectrometric analysis of sodium chloride vapour shows that, at temperatures a little above the boiling point, the vapour contains NaCl, Na_2Cl_2, and Na_3Cl_3 molecules, the proportion of Na_2Cl_2 and Na_3Cl_3 decreasing with increase of temperature. For NaCl, spectroscopic measurements give the sodium-chlorine distance (r) as 2.36 Å and the dipole moment (μ) as 3.00×10^{-29} coulomb meter. If μ is conceived of as arising from a positive and negative charge of magnitude xe a distance r apart, we can write

$$\mu = xer$$

From this and $e = 1.60 \times 10^{-19}$ coulomb, we obtain $x = 0.8$. This corresponds to a charge distribution of $Na^{0.8+}Cl^{0.8-}$, which is reasonably close to that expected for an ion pair, Na^+Cl^-. Further, electron diffraction studies of Li_2Cl_2, which is formed in higher concentrations than Na_2Cl_2, indicate that it has the rhombus-shaped structure that we would expect it were made up of ions:



The picture of sodium chloride that we arrive at is as follows:

(i) In the solid, the compound is made up of ions, held together in a giant assembly by the attraction of opposite charges, each cation being immediately surrounded by anions, and each anion by cations.

(ii) In the liquid, the ions have enough kinetic energy to move about. Even so, the arrangement of the ions at any instant differs little from that in the solid, each cation being surrounded by a majority of anions and vice versa.

(iii) In the vapour, there are molecules, the molecules being small aggregates of ions. These readily condense into the liquid and solid since the electrostatic energy of the system is significantly higher when each ion has several neighbours of opposite charge than when it has a few.

(iv) At very high temperatures, the molecules dissociate into atoms, as when sodium chloride is introduced into a flame.

Exercise

(i) Obtain an expression for the electrostatic energy of a Na^+Cl^- molecule in terms of the cation-anion distance, *r*.
(Hint: click here http://bit.ly/flCfG7 or see Appendix 1)

(ii) From this obtain an expression for the electrostatic energy that one mole of Na^+ and Cl^- ions would have if they were all in the form of widely separated Na^+Cl^- molecules.
(Hint: click here http://bit.ly/dSyEo0 or see Appendix 1)

(iii) Repeat (i) and (ii) for $(Na^+Cl^-)_2$ molecules, assuming that they are square.
(Hint: click here http://bit.ly/dIEVnL or see Appendix 1)

(iv) Compare your results with the corresponding expression for the solid,

$$E = -1.748Le^2/4\pi\varepsilon_0 r$$

(This is derived in some textbooks.)

(v) Evaluate the electrostatic energy in the three cases using $Le^2/4\pi\varepsilon_0$ = 1389 kJ Å mol^{-1} and the observed values of *r*:

NaCl(g)	2.36 Å
Na_2Cl_2(g)	2.5 Å (estimated)
NaCl(c)	2.81 Å

(Click here for answers http://bit.ly/eGnrYa or see Appendix 1)

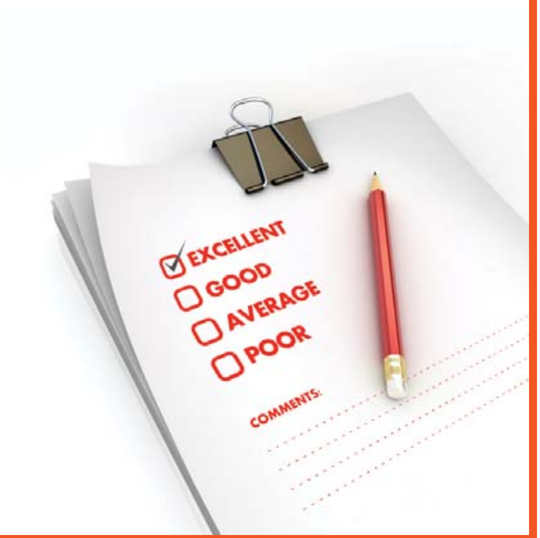
5.3 Metallic compounds

The nature of these is more difficult to determine. However, we can get so far along the following line:

(i) Metals conduct electricity without electrolysis taking place. The carriers of electricity cannot therefore be ions. They must either be some kind of charged entity that can travel through a conductor without affecting it or else a component of the atoms making up the conductor, which, by a process of successive displacement from one atom to another, can effectively be transferred from one end of the conductor to the other.

(ii) When an electric current is passed through a tube of gas at low pressure, rays can be seen to emerge from the negative electrode (the cathode). These rays are drawn towards a plate carrying a positive charge, and must therefore be carrying negative charge. They are likewise deflected by a magnet. From measurements of these deflections, the ratio of the charge to the mass can be determined for the particles making up the rays, and this is found to be the same, irrespective of the particular gas in the tube or the particular metal forming the cathode. This suggests that the particles are a common constituent of matter, and that they not only carry electricity through the gas, but also through the metal that supplies the electricity to the gas, the particles streaming without change from one into the other.

(iii) Measurement of the charge on these particles gives a value identical in magnitude with the charge on the sodium ion worked out above, viz. F/L. This gives us our terminology for the particle ("electron") and mode of conduction ("electronic"): it also gives us something else. It suggests that metal atoms may be thought of as being composed of metal ions and electrons, sodium atoms being Na^+ with one electron, magnesium atoms Mg^{2+} with two, and so on.



(iv) A simple model of a metal, therefore, is that of a collection of metal ions, held together by the appropriate number of electrons situated between them, the electrons being readily made to move by supplying further electrons at one point of the metal and taking electrons away at another. In the solid, the electrons hold the ions together in a rigid assembly: in the liquid, the ions are free to move.

(v) The constitutional formulae of metals can thus be written in the same way as the constitutional formulae of salts. The latter are properly written as exemplified by $(Na^+Cl^-)_n$, with n a very large number ($\sim 10^{22}$ for a 1 g crystal), but this is usually abbreviated to Na^+Cl^-, that is, to one unit of the complete assembly (cf. Chap. 6). In an analogous way, metallic sodium can be written Na^+e^-, metallic magnesium $Mg^{2+}(e^-)_2$, etc. A metallic compound like Cs_7O may similarly be written $(Cs^+)_7(e^-)_5O^{2-}$.

(vi) Support for these formulations is provided by the latent heats of vaporization of metals:

	ΔH
Sodium, $Na^+ e^-$	90 kJ mole^{-1}
Magnesium, $Mg^{2+}(e^-)_2$	130 kJ mole^{-1}
Aluminium, $Al^{3+}(e^-)_3$	290 kJ mole^{-1}

These values are for the vaporization of the liquid at the boiling point into gaseous atoms. It can be seen that the strength of binding increases as the number of opposite charges increases.

The vapours of metals are, as we have seen, quite different from the solids and liquids. In general, metals vaporize into a mixture of atoms and diatomic molecules, the proportion of the latter diminishing with increase of temperature. Thus, sodium metal just above the boiling point contains about 99% of sodium atoms and 1% of Na_2 molecules. On vaporization of a metal, therefore, the individual ions or pairs of ions become separated from each other, carrying their electrons with them. The mechanism for the conduction of electricity accordingly breaks down, and metallic properties disappear.

Exercise

Write down a constitutional formula for the compound Na_2K. How do you think the strength of binding in this will compare with that in metallic sodium or potassium?

(Click here for answers http://bit.ly/g7ORnR or see Appendix 1)

5.4 Limiting types of chemical bond

Corresponding to the three limiting types of binary compound there are three limiting types of chemical bond. These are named as follows:

Type of binary compound	**Type of chemical bonding**	
	Original name	*Modern name*
Metallic	Metallic	Metallic
Nonmetallic	Nonpolar	Covalent
Salt-like	Polar	Ionic

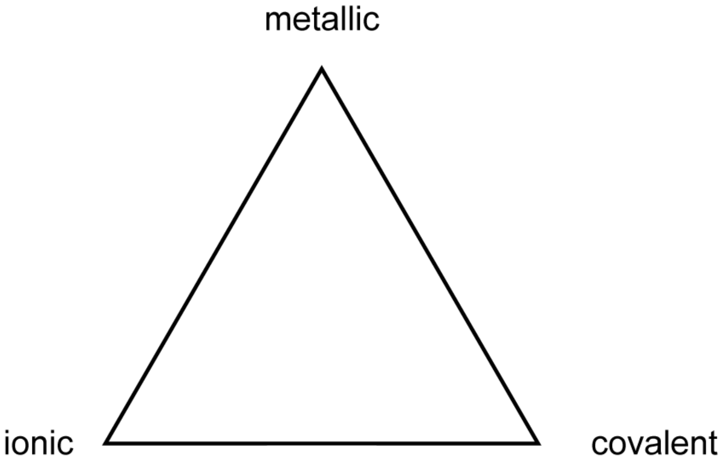
The character of these may be inferred from the nature of metallic, nonmetallic, and salt-like compounds.

Ionic bonding involves the transfer of electrons from metal atoms to nonmetal atoms and the binding together of the ions produced by the attraction of opposite charges.

Metallic bonding involves the binding together of metal ions by electrons instead of anions.

Covalent bonding involves some other kind of interaction between atoms, with neither the electrical polarization that is involved in ionic bonding nor the mobility of electrons that is possible with metallic bonding.

Between these limiting types are bonds of intermediate character, corresponding to the intermediate types of binary compound:



Positions of bonds on this diagram may be expected to correlate approximately with the positions of compounds on the diagram given in Chapter 4. More precise assignments require further discussion.

Degree of ionic character (“ionicity”)

To determine the degree of ionic character (i) of a bond, we need to measure the charges on the atoms. This is in general difficult. Indeed, according to the quantum theory, this is something that cannot be done precisely even in principle.

However, we saw earlier that the charges on the atoms in a diatomic molecule (AB) can be approximately determined from its dipole moment (μ). If there is transfer of charge from atom A to atom B to give $A^{x+}B^{x-}$, the value of x is approximately given by

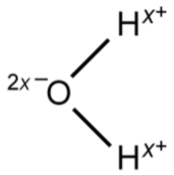
$$\mu = xer$$

where r is the internuclear distance. The value is approximate because there may be displacement of charge *within* the atoms contributing to μ.

In the table below, values of x are given for hydrogen halide molecules, as calculated from μ and r. These give the values of i shown in the last column.

	r/Å	$\mu/10^{-30}$ C m	x	i
HF	0.917	6.07	0.41	41%
HCl	1.275	3.60	0.18	18%
HBr	1.410	2.74	0.12	12%
HI	1.600	1.47	0.06	6%

This method can be extended to other molecules. For example, to the same approximation, the charge distribution in the water molecule can be pictured as follows:



The dipole moment associated with each bond is then xer, where r is the O–H distance, and the dipole moment associated with the whole molecule is given by

$$\mu = 2xer \cos \tfrac{1}{2}\theta$$

where θ is the H–O–H angle. From the observed values of r (0.957 Å), θ (104.5°), and μ (6.17×10^{-30} C m), x is calculated to be 0.33. The charge distribution is thus $O^{0.66-}(H^{0.33+})_2$, and the ionic character of each bond 33%. The considerable polarity explains many of the unusual properties of water.

This method rests on the assumption that there is little displacement of charge within the atoms concerned. Quantum-mechanical calculations support this assumption for the above molecules, giving similar values of x:

HF ~0.5 HCl ~0.2 HBr ~0.1 HI ~0.05 H_2O ~0.4

However, the assumption does not hold for all molecules.

For bonds in solids, assessing the degree of ionic character is more difficult. That this can vary, however, is clear enough. For example, cadmium chloride ($CdCl_2$) has a less ionic kind of structure than sodium chloride. In the latter, as we have seen, cations are surrounded by anions and anions by cations. In $CdCl_2$, however, while the cations are surrounded by anions (I will still call them ions), the anions only have cations on one side, to give a layer structure (for a picture, click here http://bit.ly/hJuhK9 or see Appendix 2). Mercury dichloride ($HgCl_2$) has an even more covalent type of structure, in which there are discrete, linear $HgCl_2$ units, similar to the molecules in the vapour.

An approximate method of gauging the ionic character of bonds will be given in Chapter 7.

Degree of metallic character (“metallicity”)

The degree of metallic character of a bond in a binary compound is best measured by the electrical conductivity of the compound. Strictly speaking, the property is not of an isolated bond (as in Na_2) but of bonds in concert.

Further reading

“To be a molecule, or not to be?” *Education in Chemistry*, 1996, Vol. 33, pp. 129-130.

6 Types of formula

6.1 Empirical formulae

The empirical formula of a compound is the simplest possible formula indicating the relative numbers of different atoms in it. The formula is determined from the composition of the compound.

Examples: ethane, CH_3 salt, NaCl

6.2 Molecular formulae

The molecular formula of a compound indicates the total numbers of different atoms in a molecule of it. For molecular compounds, the molecular formula is determined from the empirical formula and the molecular mass of the compound. For nonmolecular compounds, it is set at the empirical formula multiplied by infinity, representing a very large number (Chap. 5).

Examples: C_2H_6 $(NaCl)_\infty$

In practice, a mixture of empirical and molecular formulae are used - NaCl alongside C_2H_6. Even hybrid formulae are used, e.g. Na_2O_2 (as this compound contains O_2^{2-} ions). Ideally, the different formulae should be distinguished, e.g. with brackets:

$$(NaCl) \quad [C_2H_6] \quad (Na_2[O_2])$$

In practice, we have to be able to tell one from the other.

6.3 Structural formulae

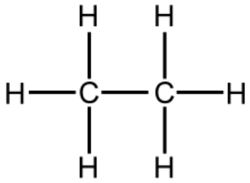
The structural formula of a compound indicates the way in which the atoms are united in the molecule. There are two main types: (i) constitutional formulae, (ii) descriptive formulae.

(i) Constitutional formulae

(a) *Covalent compounds: bond formulae*

These are determined from the valencies of the atoms (Chap. 8) and such structural information as is required.

Example:



(b) *Ionic compounds: ion formulae*

These are determined from the charges on the ions.

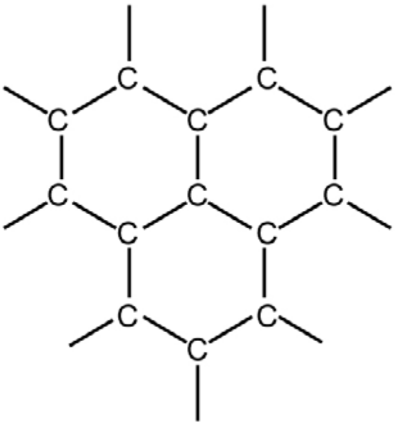
Example: Na^+Cl^-

(ii) Descriptive formulae

These do not attempt to give any indication of the bonding.

(a) *Single stroke formulae*

These are formulae in which bonded atoms are connected up with a single stroke, with no indication of bond number or polarity. They are usually used for compounds in which the bonds have an intermediate bond number or polarity (Chaps. 7 and 8). An example is the following representation of one layer of graphite:



This kind of representation is also used in referring to bond distances in a compound, as in the statement "the C–C bond length in graphite is 1.42 Å". Care needs to be taken not to confuse formulae of this kind with bond formulae [(i)(a) above].

(b) *Descriptive formulae of crystals*

If the crystal structure of a nonmolecular compound is known, the arrangement of atoms can be represented in the form $[AB_{x/y}]_\infty$, or more generally $[AB_{x/y}B'_{x'/y'}\ldots]_\infty$, where x is the number of nearest neighbours B to A, and y is the number of nearest neighbours A to B - $1/y$ being the share atom A has of each neighbouring atom B (Chap. 5).

Example: $[NaCl_{6/6}]_\infty$

This indicates that, in crystalline sodium chloride (for structure, click here http://bit.ly/gXzbqk or see Appendix 2), each sodium atom (ion) is surrounded by six chlorine atoms (ions), each of which is shared between six sodium atoms (ions), giving an empirical formula NaCl. Crystallographers call the number of nearest neighbours the "coordination number".

Exercise

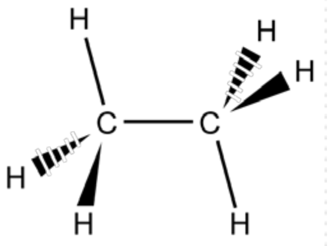
Write a structural formula of the kind just described for (i) silicon carbide, (ii) silica (see Chap. 5).

(Click here for answers http://bit.ly/h2hRGE or see Appendix 1)

6.4 Geometrical formulae

The geometrical formula of a compound represents the geometrical arrangement of the atoms in the molecule. It is determined from the structure of the compound. To represent the geometry properly really requires a three-dimensional model, but we have to try to do this in two dimensions.

Example:



7 Classification of elements according to the electrochemical series

7.1 Electrical and chemical series

The elements can be arranged in series on the basis of (i) certain electrical properties, (ii) certain chemical properties.

Contact series

When two different metals are placed in contact with each other, one metal assumes a slight positive charge and the other a slight negative charge. For example, zinc in contact with copper becomes positive and the copper negative. Similarly, tin in contact with copper becomes positive, while tin in contact with zinc becomes negative. From experiments of this sort, the metallic elements can be placed in a series, such that those on the left of an element in the series become positive in contact with it, and those on the right become negative:

..., Zn, ..., Sn, ..., Cu, ...

The development of positive and negative charges evidently arises from a transfer of electrons between the two metals, from the one that is more willing to part with them to the one that is more willing to accept them.

The contact series can be made quantitative by measuring the electrical force required to resist the transfer of electrons from one metal to another. This is called the “contact potential” or “contact potential difference”. Alternatively, the so-called “work function” (ϕ) of each metal can be measured. This is the work that has to be done to remove an electron from it, and is found to be equal to the energy that is released when an electron is added to it. The contact potential between two metals (1, 2) is thus given by $(\phi_1 - \phi_2)/e$.

Electromotive series

When two different metals are placed in contact with an electrolytic conductor, and are connected with a wire, a current flows from one metal to the other. For example, when zinc and copper are placed in contact with dilute hydrochloric acid, a conventional current flows from the copper to the zinc, the copper becoming the positive pole and the zinc the negative. (These signs are the opposite of those in the previous section because when we say that the zinc is the negative pole we mean that *the wire attached to it* is negative. As we shall see below, the zinc gives up electrons to the wire connecting it to the copper, just as it gives up electrons to the copper when it is in direct contact with this.) Similarly, when copper and tin are placed in contact with dilute hydrochloric acid, the tin becomes the negative pole, while with zinc and tin, the zinc becomes the negative pole. From experiments of this sort, the metallic elements can again be placed in a series, with those on the left becoming the negative pole in association with those on the right:

..., Zn, ..., Sn, ..., Cu, ...

What is happening when zinc and copper are placed in contact with dilute hydrochloric acid and connected with a wire is that the zinc dissolves in the solution in the form of Zn^{2+} ions, releasing two electrons per atom into the wire. At the copper, an equivalent number of electrons are taken from the wire by the process

$$2H^+ + 2e^- \rightarrow H_2$$

the solution remaining neutral since Zn^{2+} has replaced $2H^+$. The zinc goes into the solution instead of the copper because of its greater willingness to give up electrons.

The series obtained in the above way for metals can be extended to nonmetals by using an inert conductor in contact with the nonmetal and the solution. For hydrogen, a copper plate dipping into the solution and bathed with the gas will serve as an electrode, and this is effectively what we have been using above. For quantitative work, a platinum plate is better. A similar arrangement can be used for chlorine.

The series can be put on to a quantitative basis by measuring the electrical force that is required to stop the flow of electricity in the wire connecting the two electrodes (the “electromotive force” or e.m.f.). For satisfactory results, it is necessary to ensure that the chemical processes taking place at the electrodes are rapid - which is why platinum is preferred for the hydrogen electrode. Also, it is necessary to fix the concentrations of the ions that are involved in the electrode reactions, since the ease of formation or discharge of ions depends on concentration. The higher the concentration, the harder it is to form more ions and the easier it is to discharge them - a principle akin to the law of mass action. In practice, the concentrations are set at the equivalent of 1 mole per 1000 g of water for a solution in which all the ions are moving independently (so-called “unit activity”), and all electrodes are referred to the hydrogen electrode. The results are called “standard electrode potentials” (or “standard reduction potentials”), E^o. Unfortunately, however, a quantitative comparison between metals and nonmetals is not, in general, possible, because the concentration effect acts in opposite directions for cations and anions, and the relationship between the cation series and the anion series depends on the concentration chosen as standard.

Exercise

Draw up a cation series and an anion series from the values of E^o given in a textbook. Include in your series the following elements: sodium, potassium, magnesium, calcium, aluminium, iron, copper, zinc, tin, hydrogen, fluorine, chlorine, bromine, and iodine. For metals that form more than one ion in solution, use the most negative value of E^o. This has the effect of presenting the metal at its most metal-like. The alternative is to enter the metal in the series more than once, with an appropriate label to indicate the ion concerned.

Note that not all the values given in textbooks have been obtained from measurements of e.m.f. Quite a number have been determined indirectly.

(Click here for answers http://bit.ly/fBroUW or see Appendix 1)

The electromotive series that we have been discussing is for aqueous solutions. Similar series can be established for other solutions including solutions in molten salts. These series are all similar, but are not identical. Differences of order are quite numerous. For the most part, however, these arise where the potentials are close together, where differences in order are less significant. Sometimes, however, more serious differences occur.

Displacement series

When metallic zinc is introduced into a solution of copper dichloride, the green colour of the solution slowly fades, and a red layer of copper is deposited on the zinc. The zinc has evidently displaced the copper from the solution of its chloride:

$$CuCl_2(aq) + Zn \rightarrow ZnCl_2(aq) + Cu$$

Similarly, tin displaces copper from copper dichloride solution, while zinc displaces tin from tin dichloride solution. From such experiments, the metals can again be placed in a series, with those on the left displacing those on the right from their compounds in solution:

..., Zn, ..., Sn, ..., Cu, ...

As with the electromotive series, there are really many displacement series, according to the kind of system (aqueous solution, molten chloride, etc.) in which the displacement is occurring.

Affinity series

The figures below give the heat change when copper, zinc, and tin each combine with ½ mole of O_2. Values are given for the formation of both the lower and the higher oxide in the case of copper and tin:

Oxide formed	ΔH
Cu_2O	-169 kJ per mole of Cu_2O
CuO	-157 kJ per mole of CuO
ZnO	-348 kJ per mole of ZnO
SnO	-286 kJ per mole of SnO
SnO_2	-290 kJ per ½mole of SnO_2

If the more negative of these figures are taken as a measure of the relative affinities of copper, zinc, and tin towards oxygen, they may be used to form the beginnings of an affinity series, elements on the left having a greater affinity towards oxygen than elements on the right:

..., Zn, ..., Sn, ..., Cu, ...

Strictly speaking, the affinity of two elements is measured by the "standard free energy" of combination, not the heat. This refinement makes little difference to the order of values, however.

Similar series can be drawn up for the affinity of the elements towards chlorine, fluorine, sulfur, etc. As with the electromotive series, these are all similar to each other, but not identical. Differences of order occur. Again, they generally arise where the values are close together; sometimes, however they are more serious.

Note that the electromotive series is an affinity series for the formation of compounds in solution. Likewise the displacement series.

7.2 The electrochemical series

The contact series, the various electromotive series, the displacement series, and the various affinity series turn out to be remarkably similar to each other. Though by no means all identical, their similarities sufficiently outweigh their differences to encourage the formation of a single series as an approximate expression of all of them. This series is called the electrochemical series.

Inevitably, there has been much discussion and argument about the exact order in which the elements should be put in the conflated series. Inorganic chemistry is not an exact science, as I have commented before. Nevertheless, all chemists are agreed about the *general* position that each element should have in the series - far left, mid right, etc. - and carry this assignment in their heads as a rough measure of the character of the element concerned.

A partial electrochemical series is as follows:

Strongly electropositive: K, Na, Ca

Fairly strongly electropositive: Mg, Al, Zn

Moderately electropositive: Fe, Sn, Pb

Weakly electropositive: Cu, Hg, Ag, Si

Approximately electro-neutral: B, H, P, Pt

Weakly electronegative: Au, C, N, S, I

Moderately electronegative: Br, Cl

Strongly electronegative: O, F

Elements in the earlier categories are called “electropositive” because of their tendency to form positive ions, and elements in the later categories are similarly called “electronegative”. The order within each category is approximately in the direction of decreasing electropositive, or increasing electronegative, character, but this is suggestive only.

As can be seen, the series broadly divides the metals from the nonmetals, though there is some intermixing of these in the middle categories. There are a few differences from the electromotive series for aqueous ions, but these are not significant. The biggest surprise is the location of gold in the weakly electronegative category. This is forced upon us by the relatively low affinity of gold towards fluorine, oxygen, and chlorine, but has been confirmed by a study of the compound CsAu. This is not metallic, but a semiconductor in the solid state and an electrolytic conductor in the liquid state, the concentration of caesium in the melt surrounding the cathode increasing in accordance with Faraday's laws for the discharge of Cs^+ ions. It has the same structure as CsCl, and evidently has the basic constitution Cs^+Au^-.

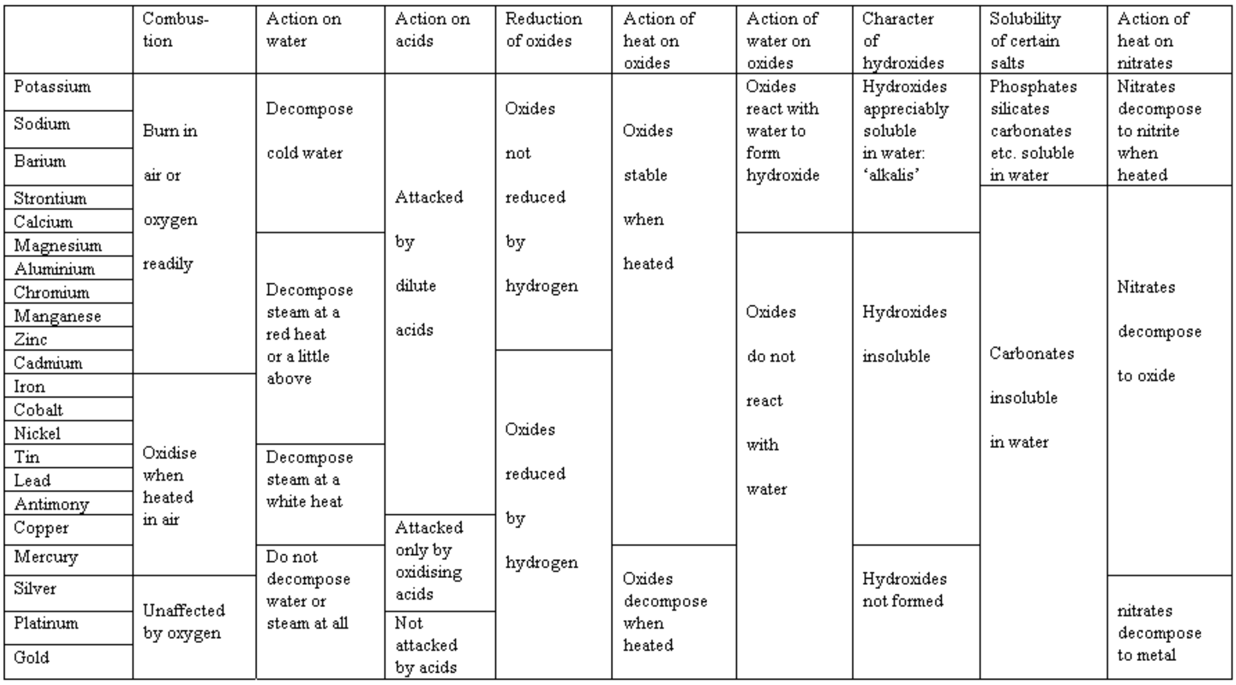
Uses of the electrochemical series

The main use of the electrochemical series is as a summary of the data on which it is based, in particular:

(i) the relative willingness of different elements to form cations or anions;

(ii) the affinity of different elements for each other.

It is possible, however, to correlate other properties of the elements and their compounds with position in the series, as is shown for metals in the table below.



	Combus-tion	Action on water	Action on acids	Reduction of oxides	Action of heat on oxides	Action of water on oxides	Character of hydroxides	Solubility of certain salts	Action of heat on nitrates
Potassium	Burn in air or oxygen readily	Decompose cold water	Attacked by dilute acids	Oxides not reduced by hydrogen	Oxides stable when heated	Oxides react with water to form hydroxide	Hydroxides appreciably soluble in water: 'alkalis'	Phosphates silicates carbonates etc. soluble in water	Nitrates decompose to nitrite when heated
Sodium									
Barium									
Strontium								Carbonates insoluble in water	Nitrates decompose to oxide
Calcium									
Magnesium		Decompose steam at a red heat or a little above				Oxides do not react with water	Hydroxides insoluble		
Aluminium									
Chromium									
Manganese									
Zinc									
Cadmium				Oxides reduced by hydrogen					
Iron	Oxidise when heated in air								
Cobalt									
Nickel									
Tin		Decompose steam at a white heat							
Lead									
Antimony									
Copper			Attacked only by oxidising acids						
Mercury		Do not decompose water or steam at all			Oxides decompose when heated		Hydroxides not formed		
Silver	Unaffected by oxygen								nitrates decompose to metal
Platinum			Not attacked by acids						
Gold									

[Platinum and gold dissolve in hot *aqua regia*, a mixture of concentrated nitric and hydrochloric acids. This chlorinates the metals and complexes the resulting chlorides (see later chapters).]

The electrochemical series is also used in determining the nomenclature of compounds (Section 7.5).

In using the series, care needs to be taken to remember that it is only an approximation, and can only be used as a rough guide to the properties of the elements. Provided that this is done, however, it constitutes a very useful classification, and although purists often despise it because of its approximate nature, the fact is that practising chemists make a great deal of use of it, if only subconsciously, in thinking of the chemistry of different elements. The same applies to the closely related concept of electronegativity, to be discussed in the next section (7.3).

7.3 Electronegativity

In so far that the electrochemical series expresses the relative willingness of different elements to form cations or anions, it is not unreasonable to suppose that the same series will express the relative willingness of different elements to adopt an ionic structure in their compounds as against a covalent one. Thus,

(i) the most electropositive metals might be expected to form fully ionic compounds with the most electronegative nonmetals;

(ii) other combinations of a metal with a nonmetal are likely to fall somewhere between the ionic and covalent extremes;

(iii) combinations of a nonmetal with a nonmetal will deviate from being fully covalent the further apart the two nonmetals are in the series.

These expectations are not easy to test because, as we saw in Chapter 5, the determination of the extent to which a compound is ionic or covalent is generally very difficult. Nevertheless, we saw in Chapter 5 that there are good grounds for believing that sodium chloride is predominantly ionic. This supports expectation (i). We also saw that cadmium chloride is less ionic than sodium chloride and mercury dichloride even less. This accords with the positions of these metals in the electrochemical series, thereby supporting (ii). We also saw that the polarity of the hydrogen halide molecules increases in the series

$$HI < HBr < HCl < HF$$

This accords precisely with expectation (iii) - the polarity increases as the difference in electrochemical character between hydrogen and the halogen increases. Moreover, the polarity of each bond in the H_2O molecule ($H^{0.4+}O^{0.4-}$) lies between the polarities of HCl ($H^{0.2+}Cl^{0.2-}$) and HF ($H^{0.5+}F^{0.5-}$) as required by the positions of Cl, O, and F in the electrochemical series. [Note, however, that the total charge on the oxygen atom in H_2O (–0.8) is greater than the charge on the fluorine atom in HF. This is because the former has two hydrogen atoms to draw electrons from whereas the latter has only one.]

In the context of the ionic character of bonds, the degree of negative electrochemical character is called “electronegativity” (χ). This is formally defined as “the power of an atom in a molecule to attract electrons to itself”. Various attempts have been made to quantify electronegativity in this sense. The results again differ in detail but agree in general terms. They also broadly agree with the electrochemical series derived above.

A simple method is that of Mulliken. This is based on the model of a covalent bond that will be discussed in Chapter 11. On this model, a single bond is formed by the sharing of an electron on each atom, $A\cdot$ and $B\times$ giving $A\overset{\cdot}{\times}B$. Mulliken argued that the tendency of A in $A\overset{\cdot}{\times}B$ to hold on to the pair $\overset{\cdot}{\times}$ is given by the energy required to remove $\overset{\cdot}{\times}$ from $A\overset{\cdot}{\times}$ on its own, that is, from the ion $[A\overset{\cdot}{\times}]^-$. This is given by $A + I$, where A is the energy required to remove the first electron (the electron affinity of atom A) and I is the energy required to remove the second (the ionization potential of A). His index of electronegativity is thus

$$\chi = k(A + I)$$

where k is a constant chosen to bring his scale into line with the first scale that was suggested, that of Pauling. (For details of Pauling's method, click here http://bit.ly/eEbRWz or see Appendix 3.)

A table of electronegativities is given in most textbooks.

Exercise

Using electronegativities from a textbook, verify that these give a similar series to the electrochemical series.

(Click here for answers http://bit.ly/guIRMp or see Appendix 1)

Use of electronegativities

Electronegativities are used to predict bond type. The greater the difference in electronegativity between two atoms ($\Delta\chi$) the greater the ionic character (i) of a bond between them is expected to be. Several different relations between i and $\Delta\chi$ have been proposed. A simple one is

$$i \sim \Delta\chi/2 \text{ (for } \Delta\chi \leq 2\text{) or 1 (for } \Delta\chi > 2\text{)}$$

Any relation can only give approximate values since bond type is an imprecise quantity.

Some chemists also use average electronegativity (χ_{av}) to divide metallic bonds from ionic and covalent ones. Metallic bonds are indicated by a low value of χ_{av} (less than about 2) with a low value of $\Delta\chi$ (less than about 1). However, there is only a partial correlation between electronegativity and metallic character. For example, the value of χ for silicon is lower than the value for some metals, and the values of χ_{av} and $\Delta\chi$ for ~TiO (which is metallic) are similar to the values for MgO and CaO. Metallic character is best gauged from electrical conductivity.

Exercise

Use electronegativity values to locate the bonds in the following compounds in the triangle of bonding given earlier (Chap. 5).

(i) Calcium fluoride, CaF_2

(ii) Sulfur bromide, S_2Br_2.

(iii) Zinc chloride, $ZnCl_2$.

(iv) Magnesium silicide, Mg_2Si.

(Click here for answers http://bit.ly/fFz6sy or see Appendix 1)

An interesting case is caesium oxide, Cs_2O. Electronegativities would suggest that this is the most ionic oxide. However, there are indications that it may not be. First, Cs_2O is orange whereas caesium halides are white. Second, it has a layer structure like that of $CdCl_2$ (with O in place of Cd and Cs in place of Cl). The lesson is not to treat electronegativity as too precise a quantity.

7.4 Polar numbers

For certain purposes (e.g. nomenclature), chemists like to work out the charges that the atoms in a compound would have if all the bonds were completely polarized and the bonding was ionic. This can be done as follows:

> Use electronegativities to decide which atoms will be positive and which negative, and see whether either element is one that is known to form ions of the appropriate sign, in melts or in solution, of only a single type. Consider, for example, carbon tetrachloride, CCl_4. Chlorine is more electronegative than carbon. The only stable anion formed by chlorine is Cl^-. The completely polarized form of CCl_4 must therefore be $C^{4+}(Cl^-)_4$.

Some elements having only one stable cation or anion are as follows:

Element	**Cation**	**Anion**
Hydrogen	H^+	H^-
Sodium	Na^+	
Potassium	K^+	
Magnesium	Mg^{2+}	
Calcium	Ca^{2+}	
Aluminium	Al^{3+}	
Fluorine		F^-
Chlorine		Cl^-
Bromine		Br^-

Elements forming more than one stable cation or anion can be used if the correct ion can be identified. For example, *oxygen* forms several anions. These are O^{2-} (if oxides like Na_2O are completely ionic) and anions containing O–O bonds (e.g. O_2^{2-}). Compounds containing the latter give H_2O_2 with acid. If no H_2O_2 is formed, the appropriate ion is O^{2-}. Similarly, *sulfur* forms S^{2-} and anions containing S–S bonds (e.g. S_2^{2-}). Compounds containing the latter give sulfur with acid. *Iodine* forms I^- and I_3^-. Compounds containing I_3^- give brown solutions in water.

The charges on the ions when a compound is written in its hypothetical ionic form are called the "polar numbers" or "oxidation numbers" of the elements concerned. Thus the polar number of carbon in CCl_4 is +4 and of chlorine –1. "Polar number" is the original term and somewhat more expressive than "oxidation number": but the latter is now used almost universally.

Exercise

What are the oxidation numbers of the elements in each of the following compounds?

(i) Methane, CH_4.

(ii) Iron dichloride, $FeCl_2$.

(iii) Sodium hydride, NaH.

(iv) Silicon dioxide, SiO_2.

(v) Carbonyl chloride, $COCl_2$.

(vi) Hydroxylamine, NH_2OH.

(vii) Hydrogen peroxide, H_2O_2.

(viii) Silicon carbide, SiC.

(Click here for answers http://bit.ly/hIoKBI or see Appendix 1)

7.5 Nomenclature of binary compounds

Binary compounds are named by citing the name of the electropositive constituent first, unmodified, followed by the name of the electronegative constituent, modified to end in -ide. For this purpose, an agreed series is used, based on the electrochemical series given above.

Examples: sodium chloride
hydrogen sulfide

In a small number of cases, when the name of the element has to be modified, the Latin name is used.

Copper	Cuprum
Gold	Aurum
Iron	Ferrum
Lead	Plumbum
Silver	Argentum
Tin	Stannum

Example: sodium plumbide

The proportions of the constituents may be indicated in one of the following ways:

(i) By means of Greek numerical prefixes (mono, di, tri, tetra, penta, hexa, etc.). The prefix mono is omitted except where confusion would arise.

Example: iron dichloride

(ii) By means of the oxidation numbers of the elements where these are not obvious, indicated by a Roman numeral placed immediately following the name of the element (without a space).

Example: iron(II) chloride

(Note that when an oxidation number is used with the symbol for an atom of an element, it is placed as a superscript without brackets, e.g. Fe^{II}.)

(iii) In the case of genuinely ionic compounds, the proportions may be indicated by means of the charges on the ions where these are not obvious, indicated by an Arabic numeral followed by the sign of the charge placed in parentheses immediately following the name of the ion (without a space).

Example: iron(2+) chloride

An older method that was used to indicate the proportions when a metal forms two series of compounds, based on two different cations (e.g. Fe^{2+} and Fe^{3+}), was to alter the name of the metal to end in -ous for the lower series and -ic for the higher, e.g.

$FeCl_2$	ferrous chloride
$FeCl_3$	ferric chloride

This method has the merit of elegance, but is now disfavoured.

Exercise

Name the following compounds:

(i) $SnCl_4$;

(ii) OF_2;

(iii) Mg_2Sn.

(Click here for answers http://bit.ly/hBK3gd or see Appendix 1)

Further reading

The nomenclature given above is that recommended by the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC). This is set out in:

G.J. Leigh (editor), *Nomenclature of Inorganic Chemistry: Recommendations 1990*, Blackwell, Oxford, 1990.

8 Valency

The valency of an element is a number, or set of numbers, from which the formulae of many of its compounds can be derived. Metallic compounds are excluded, since the formulae of these cannot generally be rationalized in this kind of way.

8.1 Ordinary valency

The valency (V) of an atom may be defined as the number of hydrogen or fluorine atoms with which the atom will combine. The assumption is made that hydrogen and fluorine are always univalent.

To obtain the number of hydrogen or fluorine atoms (X) with which an atom (A) will combine, one looks at compounds formed between A and X, and picks out the one in which there are no A–A bonds. If this is molecular it will have the formula AX_n, if non-molecular $(AX_n)_\infty$. The valency of A is then given by n.

When neither hydrogen nor fluorine is suitable for the determination of valency, other atoms can be used, provided that their valencies have first been established relative to hydrogen or fluorine. The most useful is the oxygen atom, though this must be employed with care, for the following reasons:

(i) since oxygen is bivalent, the simplest molecules formed between A and O may be of the type A_2O_n, and one has to be certain that these do not contain A–A bonds;

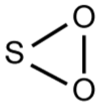
(ii) one also has to be certain that any molecules considered do not contain peroxo groups, -O–O-;

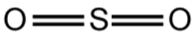
(iii) oxygen is sometimes capable of forming molecules of types that are not paralleled by any formed by univalent elements (e.g. CO).

The valencies of some of the more important elements are given in the Table at the end of this chapter. For some elements there is only one valency; for others there are several. These valencies enable bond formulae to be drawn for many molecules of the elements concerned, as is done routinely in organic chemistry.

Notes

(i) When an element has more than one valency, there may be some ambiguity in drawing the bond formulae of some of its compounds unless further details are known. For example, since sulfur has valencies of 2, 4, and 6, the sulfur dioxide molecule could be formulated as (I) or (II):

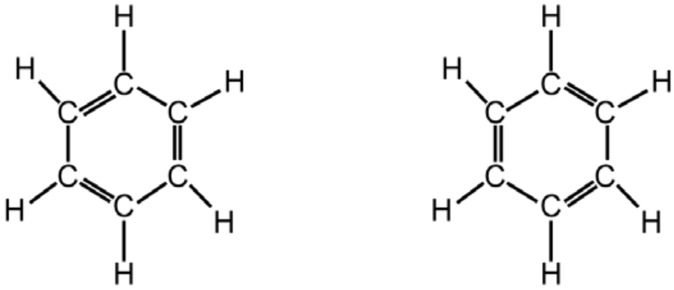

(I)


(II)

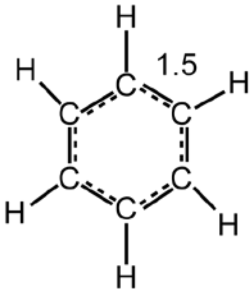
Formula (II) is accepted because sulfur dioxide does not behave like a peroxide, and microwave spectroscopy gives the O–S–O angle as 119.5º and the S–O distance as 1.43 Å. The latter is similar to the distance in molecules that have to be written with a double SO bond, e.g. 1.45 Å in $SOCl_2$. Three-membered rings, with angles of 60°, are unusual in molecules.

(ii) Even for atoms having a single valency, there can be a choice of structure. For example, the oxide of a quadrivalent element (A) can have a molecular structure with double bonds (e.g. CO_2), a framework structure with single bonds (e.g. SiO_2), a chain structure with both single and double bonds (e.g. SeO_2), or a framework structure with fractional bonds (see below). Note, however, that valency gives the right atomic composition (in this case AO_2) whatever the structure.

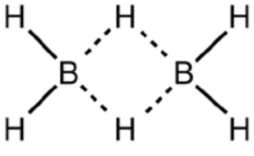
(iii) Some molecules have to be drawn with fractional bonds. For example, if benzene is drawn with integral bonds, two formulae are obtained:



These contain alternating single and double bonds, but in the actual molecule, all the C–C bond distances are the same (1.40 Å), and have a value intermediate between that for a typical single bond (1.54 Å) and typical double bond (1.34 Å). This problem can be resolved by drawing benzene with 1½ bonds:



A second example is the simplest hydride of boron, diborane (B_2H_6). This has the structure



If the bridge bonds in this are assigned a bond number of ½, the boron atoms have their usual valency of 3.

A third example is crystalline sodium chloride, regarded as made up of atoms. This has a structure in which each sodium atom is surrounded by six chlorine atoms, and each chlorine atom by six sodium atoms (for a picture, click here http://bit.ly/h2NPNi or see Appendix 2). Since sodium and chlorine atoms have a valency of one, the bonds between neighbouring atoms have a value of 1/6.

(iv) Since the word "valency" comes from the Latin *valencia* (meaning "power"), its numerical value is properly indicated by Latin numerical prefixes: uni, bi, tri (or ter), quadri, quinque, etc. - e.g., bivalent, quadrivalent. In practice, however, Greek prefixes (mono, di, tri, tetra, penta, etc.) are often used (or worse still, a mixture).

Exercises

(i) Write a bond formula for each of the following molecules:

- (a) hydrazine, N_2H_4
- (b) dinitrogen trioxide, N_2O_3
- (c) nitrous acid, HNO_2 [= HONO]
- (d) sulfuric acid, H_2SO_4 [= $(HO)_2SO_2$]

(ii) Rutile (TiO_2) has a framework structure in which each Ti atom is surrounded by six O atoms and each O atom by three Ti atoms. What is the value of the bonds?

(Click here for answers http://bit.ly/iaJGIs or see Appendix 1)

8.2 Electrovalency

The electrovalency (E) of an atom is the charge on the ion that it forms in units of e. This is determined by measuring the quantity of electricity that is required to discharge the ion in electrolysis, or from the formula of binary compounds knowing the charge on the other ion present. Care is needed to establish the molecular formula of the ion. For example, mercury forms two series of compounds, exemplified by the nitrates (containing NO_3^- ions):

	Empirical formula
(I)	$HgNO_3$
(II)	$Hg(NO_3)_2$

Most members of the series are weak electrolytes, but the nitrates are good conductors in aqueous solution, and from their composition, might be supposed to contain Hg^+ and Hg^{2+} ions respectively. However, a study of the formation of (I) by shaking a solution of (II) with mercury shows that the equilibrium is less well represented by the equation

$$\mathrm{Hg(l) + Hg^{2+}(aq) = 2Hg^{+}(aq)} \qquad (1)$$

than by the equation

$$\mathrm{Hg(l) + Hg^{2+}(aq) = Hg_2^{2+}(aq)} \qquad (2)$$

The formulation of (I) as $\mathrm{Hg_2^{2+}(NO_3^-)_2}$ has been confirmed by X-ray diffraction of the hydrate.

Exercise

Show that the following results conform better to equation (2) than to equation (1).

Initial concentration of Hg^{2+}	**Equilibrium concentration of Hg^{2+}**
1.50 M	0.013 M
1.00 M	0.009 M
0.50 M	0.004 M

(Click here for answers http://bit.ly/hiUTYx or see Appendix 1)

Electrovalencies can take positive or negative values, whereas ordinary valencies can only be positive. Some elements have just one electrovalency: others have more than one. As with ordinary valencies, electrovalencies enable the formulae of compounds to be worked out, and thus constitute both an aid to the memory and a tool for prediction.

The electrovalencies of some of the more important elements are given in the Table at the end of the chapter.

There is an evident relationship between electrovalency and valency. This is

$$|E| = V$$

where $|E|$ is the modulus of E (the value without the sign). For the fluorine atom, for example, for which $V = 1$ and $E = -1$, $|E| = 1 = V$.

8.3 Covalency

The covalency (C) of an atom may be defined as the number of covalent bonds (bonds with no polar character) an atom will form. For an atom in a non-polar molecule this is given by

$$C = V$$

For example, for the hydrogen atoms in the H_2 molecule, $C = V = 1$. The bond in this molecule is thus a single covalent bond:

$$H—H$$

Here a blue line is used to indicate a specifically *covalent* bond.

The covalencies of some important elements are given in the Table at the end of the chapter. These can be used in the same way as ordinary valencies to predict the formulae of low-polarity compounds, as discussed in the next section.

8.4 Applicability of the three kinds of valency (V, E, and C)

Electrovalency is applicable to high-polarity compounds, covalency to low-polarity. Ordinary valency is applicable to all kinds.

However, ordinary valency hides an important difference between covalency and electrovalency. Electrovalency determines the composition of compounds uniquely, covalency does not. This is because ions are forced to combine together in proportions determined by their charge, whereas atoms can be covalently bonded together in all sorts of arrangements. Thus, magnesium and chlorine form only one compound, $MgCl_2$, according to their respective electrovalencies of +2 and –1. Hydrogen and sulfur, on the other hand, with their covalencies of 1 and 2, can form a whole series of compounds, H_2S, HS, H_2S_3, HS_2, etc.:

H–S–H H–S–S–H H–S–S–S–H etc.

This difference must be remembered, otherwise the statement that an element has a particular valency might lead one to imagine the formation of compounds that are quite unrealistic, e.g.

Cl–Mg–Cl Cl–Mg–Mg–Cl Cl–Mg–Mg–Mg–Cl etc.

Compounds of intermediate character

Since covalency applies to predominantly covalent compounds and electrovalency to predominantly ionic ones, the question arises: what about compounds that are intermediate between ionic and covalent? Is there any way of rationalizing the formulae of these?

The answer is that compounds on the nonpolar side of the intermediate category can be successfully dealt with by treating them as if they were covalent, and compounds on the polar side by treating them as if they were ionic. Thus, even though water and hydrogen peroxide are markedly polar substances, their compositions are correctly given by the covalencies of hydrogen (1) and oxygen (2):

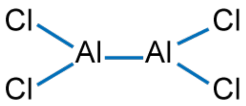
H–O–H H–O–O–H

Similarly, the composition of aluminium chloride is correctly given by the electrovalencies of aluminium (+3) and chlorine (–1),

$$Al^{3+}(Cl^-)_3,$$

even though molten aluminium chloride is a poor conductor.

Note, however, that either method fails when applied to compounds in the opposite category. Thus, the electrovalencies of hydrogen (+1) and oxygen (–2) would lead us to expect only one oxide of hydrogen, namely H_2O, while the covalencies of aluminium (3) and chlorine (1) would lead us to envisage the formation of aluminium chlorides besides $AlCl_3$, e.g.



[Compounds of this type are formed with less electronegative groups, e.g. $–CH_2CH(CH_3)_2$.]

Inevitably, there are occasions when it is difficult to decide which of the two methods to use. For example, for the zinc-chloride system, the electrovalencies of the two elements (+2 and –1 respectively) would suggest the formation of one compound ($ZnCl_2$), whereas the covalencies (2, 1) would suggest the formation of more than one ($ZnCl_2$, Zn_2Cl_2, etc.). Until fairly recently, chemists have settled for the former. It is now known, however, that zinc will dissolve in molten zinc chloride to give a yellow glass containing Zn_2^{2+} ions, analogous to Hg_2^{2+}.

Exercise

Suggest formulae for the chlorides of a quadrivalent element having an electronegativity of (i) 2.0, (ii) 1.0.

(Click here for answers http://bit.ly/fVN5Kw or see Appendix 1)

8.5 Extension

The concept of electrovalency can be extended to atoms in semi-polar molecules. We saw in Chapter 5 that the charge distribution in the HF molecule is approximately $H^{0.5+}F^{0.5-}$. Thus if, as for an ion, we set the electrovalency of an atom in a molecule equal to its charge, the electrovalency of the H atom in HF is about +0.5, and of the F atom, –0.5. I shall call electrovalency in this sense “semi-polar electrovalency”, and give it the symbol E^s.

The covalency of an atom in a semi-polar molecule may likewise be defined by:

$$C^s = V - |E^s|$$

where $|E^s|$ is the modulus of E^s. For example, for the H atom in the HF molecule, for which $E^s \sim +0.5$, $C^s \sim 1 - |+0.5| = 0.5$. Likewise, for the F atom, $C^s \sim 1 - |-0.5| = 0.5$. Thus, the single bond in the HF molecule (H—F) is made up of 0.5 of a covalent bond and 0.5 of an ionic bond:

$$^{0.5+}\mathrm{H}\underset{0.5}{\text{----}}\mathrm{F}^{0.5-}$$

I shall call formulae of this kind “semi-polar bond formulae”.

The above equation may also be written

$$V = C^s + |E^s|$$

The equation in this form divides ordinary valency into covalency and electrovalency.

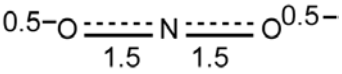
The main value of dividing valency in this way is that it enables constitutional formulae to be written for many polyatomic ions. The peroxide ion, $[O_2]^{2-}$, for example, can be written as follows:

$$^{-}\mathrm{O}\text{—}\mathrm{O}^{-}$$

Here the oxygen atoms have their usual valency of 2, made up of $C^s = 1$ and $E^s = -1$. Similarly, the nitrite ion, $[NO_2]^-$, can be written as:

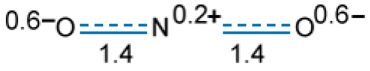
$$\mathrm{O{=}{=}N\text{—}O^{-}}$$

Here black lines are drawn because no account has been taken of the polarity of the bonds. A better formulation, which takes account of the fact that the two N–O bonds are of equal length, is:



$$^{0.5-}\mathrm{O}\underset{1.5}{\text{------}}\mathrm{N}\underset{1.5}{\text{------}}\mathrm{O}^{0.5-}$$

To draw a semi-polar bond formula, one needs to know the polarity of the ion. Calculations using the quantum theory give about $O^{0.6-}N^{0.2+}O^{0.6-}$, from which



$${}^{0.6-}O \underset{1.4}{-\,-\,-\,-\,-} N^{0.2+} \underset{1.4}{-\,-\,-\,-\,-} O^{0.6-}$$

Note, however, that the correct atomic composition (NO_2) and overall charge (−1) are obtained whichever formula is used.

Polyatomic ions will be considered further in the next chapter.

Exercise

Verify that the nitrogen atom in the above formulae for the nitrite ion has a valency of 3, and each of the oxygen atoms, 2.

(Click here for answers http://bit.ly/hcVsvs or see Appendix 1)

Table: Principal valencies of some important elements

Column 2 gives the principal valencies of some important elements and the formulae of the compounds on which they are based. Molecules are in bold type. Column 3 gives the electrovalencies of ions. Column 4 gives covalencies for atoms forming low-polarity bonds.

Element	*V*	*E*	*C*
Hydrogen	1 ($\mathbf{H_2}$, $\mathbf{HF}$)	+1 [note (i)] −1 [note (ii)]	**1**
Sodium	1 (NaH, NaF)	+1	
Potassium	1 (KH, KF)	+1	
Magnesium	2 (MgH_2, MgF_2)	+2	
Calcium	2 (CaH_2, CaF_2)	+2	
Iron	2 (FeF_2) 3 (FeF_3)	+2 +3	
Copper	1 ($CuCl$, Cu_2O) [note(iii)] 2 (CuF_2)	+1 +2	
Zinc	2 (ZnH_2, ZnF_2)	+2	
Boron	3 ($\mathbf{BF_3}$)		**3**
Aluminium	3 (AlH_3, AlF_3) [note (iv)]	+3	**3**
Carbon	4 ($\mathbf{CH_4}$, $\mathbf{CF_4}$)		**4**
Silicon	4 ($\mathbf{SiH_4}$, $\mathbf{SiF_4}$)		**4**
Tin	2 (SnF_2) 4 ($\mathbf{SnH_4}$, SnF_4)	+2	 **4**
Lead	2 (PbF_2) 4 (PbF_4)	+2	 **4**
Nitrogen	3 ($\mathbf{NH_3}$, $\mathbf{NF_3}$) 5 [note (v)]		**3** (5) [note (vi)]
Phosphorus	3 ($\mathbf{PH_3}$, $\mathbf{PF_3}$) 5 ($\mathbf{PF_5}$)		**3** (5) [note (vi)]
Oxygen	2 ($\mathbf{H_2O}$, $\mathbf{OF_2}$)	−2	**2**
Sulfur	2 ($\mathbf{H_2S}$) 4 ($\mathbf{SF_4}$) 6 ($\mathbf{SF_6}$)	−2	**2** (4) [note (vi)] (6) [note (vi)]
Fluorine	1 ($\mathbf{HF}$, $\mathbf{F_2}$)	−1	**1**
Chlorine	1 ($\mathbf{HCl}$, $\mathbf{ClF}$) 3 ($\mathbf{ClF_3}$) 5 ($\mathbf{ClF_5}$) 7 [note (vii)]	−1	**1** (3) [note (vi)] (5) [note (vi)] (7) [note (vi)]
Argon	0	0	**0**

Notes

(i) H^+ only exists in solvated form.

(ii) H^- exists in Na^+H^- etc.

(iii) I have assumed here that, in CuCl, chlorine has its usual valency of 1. Cu_2O is an ordinary oxide.

(iv) Aluminium forms molecular $Al[CH(CH_3)_2]_3$. The lower alkyls tend to dimerize: they are partly dimeric in the vapour, and also completely so in benzene solution. The dimers have a similar structure to B_2H_6 with Al– –C– –Al bonds.

(v) There are many compounds of nitrogen that seem to require a valency of 5, even though NF_5 does not exist. Foremost among these are compounds containing the nitro group, $-NO_2$, e.g. nitromethane, CH_3NO_2; nitrobenzene, $C_6H_5NO_2$; nitric acid, $(HO)NO_2$; dinitrogen pentoxide vapour, $O(NO_2)_2$. These cannot be formulated with trivalent nitrogen, X–O–N=O, because in many cases isomers corresponding to the latter formulation exist, e.g. methyl nitrite, CH_3ONO. In addition, there are molecules of the type X_3NO, e.g. trimethylamine oxide, $(CH_3)_3NO$, made by oxidizing trimethylamine with hydrogen peroxide, and trifluoramine oxide, F_3NO, made by the action of an electric discharge on a mixture of NF_3 and O_2. These species show no signs of being $X_2N–O–X$, with trivalent nitrogen.

(vi) In practice, there is always considerable polarity in the bonds, and this value is never achieved (see Chapter 11).

(vii) Though ClF_7 does not exist, there are a few compounds of chlorine that require a valency of 7. These include Cl_2O_7, $FClO_3$, and F_3ClO_2, which do not contain –O–O–. The oxide reacts with water to give perchloric acid, $HClO_4$ $[(HO)ClO_3]$.

Further reading

"Valency", *Journal of Chemical Education*, 1997, Vol. 74, pp. 465–470. (Correction: p. 468, col. 1, para. 3 up, add "used in coordination".)

"Introducing valency", *Education in Chemistry*, 1997, Vol. 34, pp. 75–76, 80.

"Making the most of valency", *Education in Chemistry*, 2010, Vol. 47, pp. 83–85, 89. (Corrections: p. 138. Corrected version on-line.)

9 Pseudo-binary compounds

9.1 Introduction

A great many compounds of ternary or higher order behave as if they were compounds of binary order, with a group of atoms acting as if it was a single atom. Such a group is called a “radical”.

A classical example is provided by the cyanides, some of which are described below:

Hydrogen cyanide, HCN. This is manufactured by passing a mixture of methane and ammonia over a platinum catalyst at 1200 ºC:

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$

It is a colourless liquid, boiling at 26 ºC to a colourless gas. It is a poor conductor of electricity. Like most cyanides, it is extremely poisonous.

Sodium cyanide, NaCN. This is manufactured by absorbing gaseous hydrogen cyanide in aqueous sodium hydroxide or sodium carbonate. The compound is a colourless solid, melting at 564 ºC to a colourless liquid. The liquid conducts electricity with the formation of sodium at the cathode and a colourless gas at the anode. This gas is cyanogen, C_2N_2.

Potassium cyanide, KCN. This is similar to sodium cyanide.

Cyanogen, C_2N_2. This is a colourless gas, condensing at –21 ºC to a colourless liquid.

Cyanogen chloride, ClCN. This is made by passing chlorine into aqueous hydrogen cyanide:

$$HCN + Cl_2 \rightarrow HCl + ClCN$$

It is a colourless gas, condensing at 13 ºC to a colourless, mobile liquid.

From the above descriptions, it is clear that there is a close resemblance between cyanides and halides, both in composition and in character:

Composition		**Character**
Cyanide	Chloride	
HCN	HC1	Nonmetallic
NaCN	NaCl	Salt-like
KCN	KCl	Salt-like
ClCN	ClCN	Nonmetallic

This resemblance extends to the parent substances:

$(CN)_2$	Cl_2	Nonmetallic

So close is this resemblance that cyanogen is called a pseudo-halogen.

A second example is provided by ammonium compounds, e.g. ammonium chloride, NH_4Cl. These are very similar to alkali metal compounds. Indeed, ammonium compounds and potassium compounds often form mixed crystals with each other. Furthermore, electrolysis of ammonium chloride solution with a mercury cathode at 0 ºC gives a grey mass that is similar in character to sodium or potassium amalgam. Thus, it reduces copper dichloride solution to copper, zinc chloride to zinc, etc. On warming, it decomposes into ammonia and hydrogen in the proportions required by the equation

$$2NH_4(\text{amalgam}) \rightarrow 2NH_3 + H_2$$

The NH_4 radical is thus very much like an alkali metal atom in its behaviour.

9.2 On the nature of pseudo-binary compounds

The nature of pseudo-binary compounds follows from our discussion of binary compounds. The bonding between radicals and radicals or radicals and atoms is the same as the bonding between atoms and atoms. For example:

(i) The molecules HCN, ClCN, and $(CN)_2$ are held together with essentially covalent bonds:

$$\text{H–CN}, \quad \text{Cl–CN}, \quad \text{NC–CN}$$

(ii) The compounds NaCN and KCN are ionic:

$$Na^+[CN]^-, \quad K^+[CN]^-$$

(iii) Ammonium chloride is ionic:

$$[NH_4]^+Cl^-$$

(iv) Ammonium amalgam presumably contains:

$$[NH_4]^+e^-$$

Bonding *within* radicals is of a covalent character. Thus the full bond formula of the HCN molecule is

$$\text{H–C}\equiv\text{N}$$

while that of the $[CN]^-$ ion is

$$^-\text{C}\equiv\text{N}$$

The formula of the $[NH_4]^+$ ion will be discussed later.

Ions like $[CN]^-$ and $[NH_4]^+$ are called “molecular” ions. The square brackets indicate that the charge is somewhere on the radical as a whole, but they are often omitted: CN^- and NH_4^+. This should not be misinterpreted as implying, for example, that the charge on the cyanide ion is located on the nitrogen atom.

9.3 Some important radicals

Formula of radical	**Name as electropositive constituent of compounds**	**Name as electronegative constituent of compounds**
Non-metal-like (a) Forming one covalent bond or a singly charged anion		
OH		hydroxide
NO_2	nitryl	nitrite
NO_3		nitrate
CN	cyanogen	cyanide
SCN	thiocyanogen	thiocyanate
CH_3CO_2		acetate
CH_3 (Me)	methyl	methyl
C_6H_5 (Ph)	phenyl	phenyl
(b) Forming two covalent bonds or a doubly charged anion		
CO_3		carbonate
SO_3		sulfite
SO_4		sulfate
(c) Forming three covalent bonds or a triply charged anion		
PO_4		phosphate
Metal-like Forming a singly charged cation		
NH_4	ammonium	
NMe_4	tetramethylammonium	

Notes

(i) All the nonmetal-like radicals form covalent bonds with sufficiently electronegative atoms or radicals. This includes nitrate and sulfate, e.g. in $MeNO_3$ and Me_2SO_4.

(ii) All the nonmetal-like radicals form anions with sufficiently electropositive elements. This includes methyl and phenyl, e.g. in Na^+Me^- and Na^+Ph^-.

(iii) The NMe_4 radical forms a similar amalgam to NH_4.

Exercise

Draw a simple bond formula for each of the following ions:

(i) hydroxide, OH^-
(ii) thiocyanate, SCN^-
(iii) acetate, $CH_3CO_2^-$
(iv) carbonate, CO_3^{2-}
(v) sulfate, SO_4^{2-}

(Click here for answers http://bit.ly/eBBFaH or see Appendix 1)

9.4 Nomenclature

Nomenclature of radicals

The names given above are based on those recommended by IUPAC - the International Union of Pure and Applied Chemistry (see Chap. 7). Though not very systematic, they reflect long established usage. The use of the endings –ite and –ate to indicate a lower and higher oxo-anion (e.g. nitrite, nitrate) parallels the use of –ous and –ic to indicate a lower and higher cation (Chap. 7).

British schools teach different names as advised by the Association for Science Education (ASE):

IUPAC	**ASE**
nitrite	nitrate(III)
nitrate	nitrate(V)
sulfite	sulfate(IV)
sulfate	sulfate(VI)
acetate	ethanoate

The ASE names are derived from IUPAC rules for naming less common ions. These names, however, are only used in British schools. Everywhere else in the world (in the chemical literature, chemical industry, other sciences, and other countries), IUPAC names are used.

Nomenclature of pseudo-binary compounds

Pseudo-binary compounds are named in a similar way to binary compounds. In general, the name of the electropositive constituent is cited first, and that of the electronegative constituent second. Strictly speaking, this requires the incorporation of radicals in the electrochemical series, but in practice, this is only done very roughly. Thus NO_3 and SO_4 are always regarded as being the electronegative constituent of a compound, even though in a few cases this is disputable, e.g. in FNO_3.

Examples of nomenclature:

CH_3Cl	methyl chloride
$NaCH_3$	sodium methyl
$(CH_3)_2SO_4$	dimethyl sulfate
FNO_3	fluorine nitrate

(Note: some of these have alternative names, e.g. chloromethane.)

10 The Periodic Table

This was put forward by Mendeleev in 1869, predating the elucidation of the structure of the atom.

10.1 The Periodic Law

This was summed up by Mendeleev in the statement: "The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties."

Here, "atomic weight" is equivalent to relative atomic mass (RAM). We would now put atomic number. It was fortunate for Mendeleev that RAM largely parallels atomic number.

"Periodicity of properties" means that, after a certain number of elements, an element of similar properties to an earlier one occurs.

The property that Mendeleev most had in mind was valency.

Thus:

Element	**Valency**	
H	1	
He	0	
Li	1	
Be	2	
B	3	
C	4	8
N	3, (5)	
O	2	
F	1	
Ne	0	
Na	1	
Mg	2	
Al	3	
Si	4	8
P	3, 5	
S	2, 4, 6	
Cl	1, 3, 5, 7	
Ar	0	
K	1	
Ca	2	

Note that the repetition is not complete. Sulfur and chlorine have valencies additional to those of oxygen and fluorine. The Periodic Law is not an exact law. Like the Electrochemical Series, however, it is a useful approximation.

Moving on to heavier elements there is a complication. This can be seen in the following chart, where elements after argon are compared with the preceding eight elements.

Element	**Valency**		
Ar	0	(like Ne)	
K	1	like Na (valency = 1)	
Ca	2	like Mg (valency = 2)	
Sc	2, 3	like Al in main valency (3)	
Ti	2, 3, 4	like Si in main valency (4)	
V	2, 3, 4, 5	like P in highest valency (5)	
Cr	2, 3, 4, 5, 6	like S in highest valency (6)	
Mn	2, 3, 4, 5, 6, 7	like Cl in highest valency (7)	
Fe	2, 3, 4, 6		
Co	2, 3, 4		18
Ni	2, 3, 4		
Cu	1, 2, 3	like Na in lowest valency (1)	
Zn	2	like Mg (valency = 2)	
Ga	1, 3	like Al in main valency (3)	
Ge	2, 4	like Si in main valency (4)	
As	3, 5	like P (valencies = 3, 5)	
Se	2, 4, 6	like S (valencies = 2, 4, 6)	
Br	1, 3, 5, 7	like Cl (valencies = 1, 3, 5, 7)	
Kr	0, 2	like Ar in main valency (0)	

For the first few elements, there is a repetition of properties. Similarities then diminish and are confined to the highest valency. After a gap, they then start up again in the lowest valency, and continue in the main valencies until the next inert gas is reached, not 8 elements after argon, but 18.

This pattern repeats itself for the next 18 elements, ending in xenon. Then a similar complication occurs, there being 32 elements before the next inert gas is reached (the radioactive gas which used to be called "emanation", and is now named after its most stable isotope, radon). This pattern then repeats itself. Note that the lengths of the periods (2, 8, 8, 18, 18, 32, 32, …) are equal to $2a^2$ ($a = 1, 2, 3, …$).

Chemists have dealt with these complications in various ways, and suggested many different forms of Periodic Table. Before the advent of the quantum theory, the preferred form had eight groups. The periods of 18 elements were divided into two series of eight, with three elements in the same group. The periods of 32 elements were likewise divided into two, with 15 elements in one group and again three in another. The result looked like this:

I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K Cu	Ca Zn	Sc Ga	Ti Ge	V As	Cr Se	Mn Br	Fe Co Ni Kr
Rb Ag	Sr Cd	Y In	Zr Sn	Nb Sb	Mo Te	Tc I	Ru Rh Pd Xe
Cs Au	Ba Hg	La-Lu Tl	Hf Pb	Ta Bi	W Po	Re At	Os Ir Pt Em
Fr	Ra	Ac-					

Elements in each group are divided into two subgroups according to the degree of similarity between them. This form of table contorts the longer periods, but captures the relationships shown on the previous chart. Even the elements of the last group are related in their highest valency (Ru, Os, and Xe form volatile tetroxides, RuO_4, OsO_4, and XeO_4, valency = 8). This type of table is called the "short" form.

Some early chemists preferred a different form of table. They regarded the periods of 18 elements as containing additional series of 10 elements, and the periods of 32 elements, additional series of 10 and 14. They based this on (i) differences between the elements in these series and those in the periods of 8, and (ii) similarities between elements in these series. For example, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu are all metals exhibiting variable valency and forming coloured compounds. Most modern chemists treat the periods of 18 and 32 similarly, but base this largely on the quantum theory of atomic structure, according to which the series of 10 elements arise from the filling of a d shell, and of 14 from the filling of an f (for details, click here http://bit.ly/eekMTf or see Appendix 4). When the members of the additional series are put in separate groups, the result is the "long" form of table (where the numbers on the left signify the period number):

1	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	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	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 Em
7	87 Fr	88 Ra	89 Ac	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	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118

<–2–> <——————————14——————————> <————————10————————> <————6————>

Notes

(i) The positions of a few elements are open to debate, most importantly that of hydrogen.

(ii) Many modern chemists seem to prefer a mongrel table, with the 10-element series forming separate groups and the 14-element series in the Sc group.

(iii) Most of the more important elements are in the upper part of the table, so that we do not have to remember the whole of it in detail.

Exercise

Circle the more important elements in the above table, and verify point (iii) above.

(Click here for answers http://bit.ly/hLsuaO or see Appendix 1)

10.2 Nomenclature

(i) The periods are differentiated into either "short" periods (periods 1 - 3) and "long" periods (4 - 7) or "very short" (1), "short" (2 - 3), "long" (4 - 5), and "very long" (6 - 7). Care must be taken not to mix these two schemes up. On the former, the "first short period" is period 1: on the latter it is period 2.

(ii) In the long periods, the series of 10 elements are called "transition series" and the series of 14 "inner transition series". The elements themselves are called "transition elements" and "inner transition elements" respectively.

(iii) The transition series are differentiated into “first-row”, “second-row”, etc. The inner transition series are differentiated into “lanthanides” and “actinides” after the names of their first members.

(iv) The remaining groups are called “main groups” and the elements “main-group elements”. The rows are sometimes referred to as “first”, “second”, “third”, etc., but some chemists call H - He the first row, others Li - Ne. To be absolutely safe, it is best to refer to the “lithium row”, “sodium row”, etc.

(v) Various schemes have been used to label the groups. The main ones are set out in columns 2–4 below. The A/B numbering is based on the short form of table, IUPAC’s on the semi-long form.

Group (specified by first member)	European A/B	American A/B	IUPAC	**This text**
Lithium	IA	IA	1	1M
Beryllium	IIA	IIA	2	2M
Lanthanum	IIIA	IIIB	3	3IT
Cerium	IIIA	IIIB	3	4IT
…	…	…		…
Ytterbium	IIIA	IIIB	3	16IT
Scandium	IIIA	IIIB	3	3T
Titanium	IVA	IVB	4	4T
Vanadium	VA	VB	5	5T
Chromium	VIA	VIB	6	6T
Manganese	VIIA	VIIB	7	7T
Iron	VIIIA	VIIIB	8	8T
Cobalt	VIIIA	VIIIB	9	9T
Nickel	VIIIA	VIIIB	10	10T
Copper	IB	IB	11	11T
Zinc	IIB	IIB	12	See §10.5
Boron	IIIB	IIIA	13	3M
Carbon	IVB	IVA	14	4M
Nitrogen	VB	VA	15	5M
Oxygen	VIB	VIA	16	6M
Fluorine	VIIB	VIIA	17	7M
Helium	VIIIB	VIIIA	18	8M

The scheme most commonly used today is the one promoted by IUPAC. This was designed to resolve the confusion between the two A/B schemes. However, the IUPAC system has a serious deficiency. On the A/B schemes, the main groups are numbered 1–8, corresponding to the maximum valency exerted by elements in each group, and (except for He) the number of valence electrons possessed by their atoms (see Chapter 11). To recover this correspondence, I shall use the labels in the last column of the table above, where M stands for “main”, T for “transition”, and IT for “inner-transition”.

As the different schemes can easily be confused, when you use a label yourself, you should explain which system you are using. To be absolutely safe it is best to refer to the “carbon group”, “iron group”, etc.

(vi) The following groups of elements are referred to by the names indicated:

Group 1M	Alkali metals
(Mg,) Ca – Ra	Alkaline earth metals
Sc, Y, La – Lu	Rare earth metals
Ru – Pd, Os – Pt	Platinum metals
Group 11T	Coinage metals
Group 6M	Chalcogens
Group 7M	Halogens
Group 8M	Inert or noble gases

Note

"Chalcogen" is formed by analogy with "halogen", which means "producer of salt" (Chap. 3). Chalcogen means producer of calx, the substance left after a metal or mineral has been burned (Latin *calx*, lime, probably from Greek *khalix*, pebble, limestone; the word "chalk" comes from the same root).

10.3 Use of the table

The table brings together similar elements into groups. Thus, if we know the properties of some members of a group, we can work out approximately the properties of other members, thus easing the burden on the memory and helping us to make predictions. Note, however, that we need to know a certain amount of chemistry before we can use the Periodic Table. Properties can vary markedly within a group (think of Group 4M) and we need to know enough chemistry to establish the trends within a group before our predictions will be reliable. This operation is assisted by the relationship between trends in one group and trends in another, but even so, we should not underestimate how much chemistry we need to know before the Periodic Table will prove helpful to us.

10.4 General features

(i) Distribution of electronegativities

Electronegativities generally increase from left to right and from bottom to top.

(ii) Distribution of valencies

Main groups

Up to Group 4M, the principal valency is given by the group number, *N*. A valency two less, however, becomes increasingly important in going down Groups 3M and 4M.

Beyond Group 4M, the principal valency is given by 8 – *N*, but higher valencies occur for the heavier elements. These rise in units of two up to a maximum of *N*. They are brought out only with the most electronegative elements.

Transition groups

Up to Group 8T, the maximum valency is given by *N*, though this is not achieved by iron. The maximum valency collapses after Group 8T, falling to 2 by the zinc group.

Most elements have one or more valencies below the maximum, differing characteristically by ones.

Inner transition elements

The principal valency of the lanthanides is 3 throughout. The pattern of valencies for the actinides is similar to that for the transition series. For some of these elements, group relationships are weak.

Exercises

(i) Test the above statement about the distribution of electronegativities in the Periodic Table using a table of values from a textbook.

(ii) Test the above statement about the distribution of valencies of main-group elements in the Periodic Table using the list of valencies given in Chapter 8.

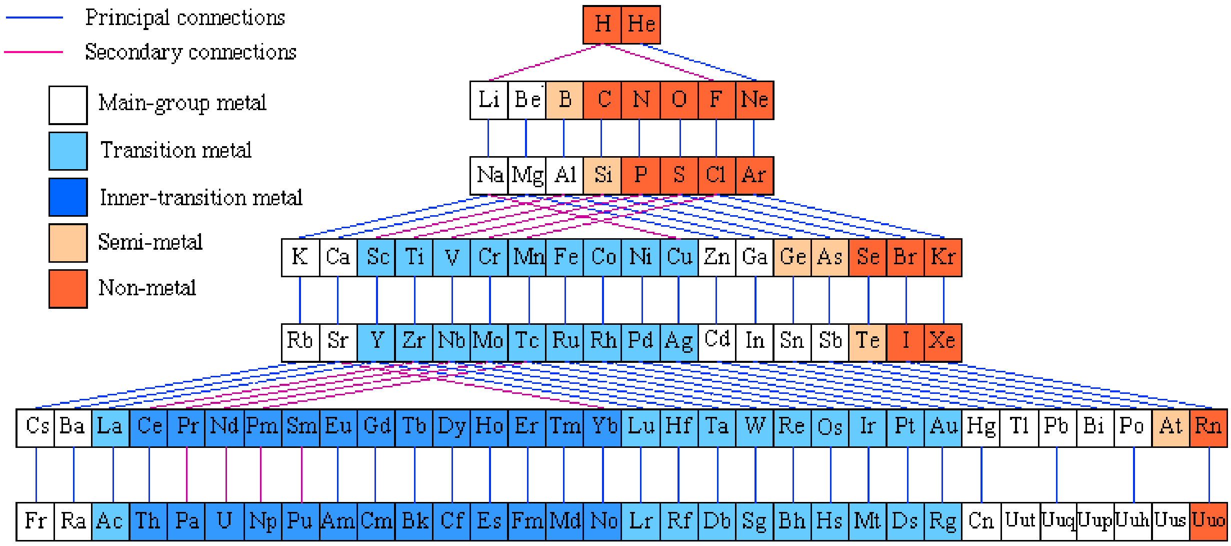
(iii) Use the Periodic Table to predict the general properties of element 114.

(Click here for answers http://bit.ly/fzTGJe or see Appendix 1)

10.5 A better form of table

A disadvantage of the form of table currently used is that it loses completely the secondary relationships shown in the chart in Section 10.1 (i.e. between 3-valent Sc and Al, 4-valent Ti and Si, 5-valent V and P, etc.). These relationships can be shown in a pyramidal form of table as pictured below. Principal connections are indicated by blue lines and secondary connections by red ones.

Hull Periodic Table, as at www.hull.ac.uk/chemistry/hullptable



You will notice that Mg is connected to Zn by a blue line as well as to Ca. This is because Zn, Cd, and Hg are like Mg in being bivalent metals. One trivalent compound of Hg has been reported, but this is very unstable (it decomposes within a few seconds at –78 °C). The effect of this connection is to make Zn, Cd, and Hg part of main group 2M, and to shorten the transition series. This means that the zinc group should not be labelled 12T, but as a subgroup of 2M (2M′).

Recent quantum-mechanical calculations, however, suggest that HgF_4 molecules might be stable enough for them to be formed from HgF_2 molecules and fluorine at low temperatures. HgF_2 molecules polymerize, but can be kept apart in an inert matrix. Workers have obtained possible evidence for the formation of HgF_4 by irradiating a matrix of mercury atoms and fluorine in solid neon. [X. Wang, L. Andrews, S. Riedel, and M. Kaupp, *Angew. Chem. Int. Ed.*, 2007, Vol. 46, pp. 8371-8375.] These studies, if confirmed, point to the zinc group being weakly transitional. Taking it as transitional simplifies the table and designation of groups.

Further reading

"Presenting the Periodic Table", *Education in Chemistry*, 1988, Vol. 25, pp.185-187.

"The best form of Periodic Table", *Education in Chemistry*, 1987, Vol. 24, pp.171-173.

"Labelling of the Periodic Table", *Chemistry International*, 1989, Vol. 11, pp. 171-173.

"Table for all seasons", *Chemistry World*, April 2009, pp. 37-38.

11 Interpretation of main-group valencies in terms of a simple model of main-group atoms

11.1 Basic theory

The valencies of main-group elements can be interpreted on the basis of a very simple model of atoms and bonding, as was done originally by Lewis (1916). Such a model is as follows:

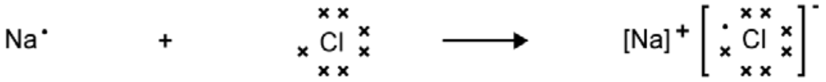
1. Atoms consist of a nucleus, shells of inner or "core" electrons, and a shell of outer or "valence" electrons. Except for hydrogen and helium, the number of valence electrons is given by the group number, *N*.

2. Except for hydrogen and helium, the number of electrons in a complete shell is eight. This is the number possessed by inert gas atoms (except He), and constitutes a stable arrangement. This arrangement is called an "octet".

3. For hydrogen and helium, the number of valence electrons is one (H) or two (He), and the number in a complete shell, two.

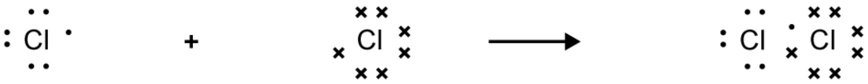
4. Atoms combine in ways that enable them to achieve an even number of electrons, especially a complete shell. (Very few main-group molecules have an odd number of electrons; exceptions are NO, NO_2, and ClO_2.)

5. One way atoms achieve complete shells is by the transfer of electrons from those with a smaller number of outer electrons to those with a larger number to form ions, e.g.



   This explains why the positive electrovalencies of main-group elements are given by +*N* and the negative electrovalencies by –(8 – *N*). (Here dots and crosses are used to indicate electrons from different atoms. Electrons are indistinguishable, however, and Lewis formulae are often drawn just with dots. I will use dots and crosses to start with, to help you to see where electrons have come from.)

6. Another mode of combination is by the sharing of electrons between atoms, e.g.

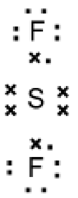


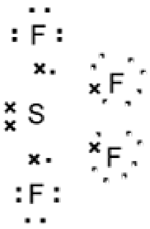
Each shared pair of electrons corresponds to a covalent bond - one pair to a single bond, two to a double bond, three to a triple bond. (Shared pairs are called “bond” pairs, unshared pairs “lone” pairs.) This mechanism explains why the principal covalencies of main-group elements are given by N up to Group 4M and $8 - N$ thereafter.

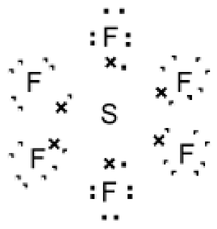
7. Combinations between the ionic and covalent extremes correspond to unequal sharing of the bonding electron pairs, e.g.:

Note that the bonding electrons are closer to the more electronegative atom.

8. In combination with atoms of more electronegative elements, some atoms can increase the number of electrons around them above the number for a closed shell, e.g.:


octet


10 electrons


12 electrons

This explains why, for elements beyond Group 4M, valencies can rise above $8 - N$, in twos, up to a maximum of N. When an element has such a valency, it is said to be “hypervalent”.

9. Hydrogen is a special case, having one electron in a shell of total capacity two. Stable arrangements can be achieved by the loss of an electron (to give H^+), gain of an electron (to give H^-), or sharing an electron pair as in H–H. The formation of H^- was predicted by Lewis and verified by examining the electrical properties of fused lithium hydride. The latter is obtained as a white powder, m.p. 680 ºC, by heating lithium in hydrogen. In the molten state, it conducts electricity, and lithium is deposited at the cathode and hydrogen at the anode, in quantities in accordance with Faraday’s Laws. (In the electrolysis of aqueous acids, of course, hydrogen appears at the cathode.)

Lewis’s theory explains the relations between ordinary valency, electrovalency, and covalency found in Chapter 8 (e.g. $V = |E| = C = 1$ for hydrogen).

Exercise

Write a Lewis structure for each of the following species:

(i) H_2O; (ii) NH_3; (iii) BF_3; (iv) N_2; (v) ClF_3; (vi) H_2SO_4.

(Click here for answers http://bit.ly/fK1fpQ or see Appendix 1)

11.2 Refinement of model in the light of the quantum theory of atoms

(i) The valence shell of 8 actually comprises two shells: an s shell of 2 and a p shell of 6 (for details, click here http://bit.ly/eekMTf or see Appendix 4). The valency of $N - 2$ for heavier members of Groups 3M and 4M corresponds to the non-participation of the s electrons in the bonding, as if they formed part of the core. This is called the “inert-pair” effect.

(ii) Calculations show that, in molecules formed by main-group elements, only s and p orbitals of the valence shell are used (not d). This sets an upper limit of 8 to the number of electrons in the valence shell. The reason why molecules like SF_6 can form is that the polarity of the bonds reduces the number of electrons in the valence shell of the central atom to ≤ 8. The 12 electrons in the Lewis structure reside in a somewhat larger shell than the valence shell, located partly on the fluorine atoms. This is called the “Lewis shell”.

For there to be ≤8 electrons in the valence shell of the sulfur atom in SF_6, the polarity of the molecule must be $S^{x+}(F^{x/6-})_6$ with $x \geq 2$. (For an explanation, click here http://bit.ly/fM3PNf or see Appendix 5.) Quantum-mechanical calculations give $x \sim 3$. This corresponds to the semipolar bond structure:

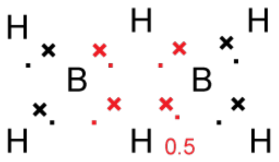
$$S^{3+}(\underset{0.5}{\text{-----}}F^{0.5-})_6$$

Note that the valency of the sulfur atom is still 6, but is made up of a covalency of 3 and an electrovalency of +3. The corresponding Lewis structure is

$$S\left(\ :\underset{..}{\ddot{F}}:\right)_6$$

with a space between the bonding pair and the sulfur atom to indicate polarity.

(iii) Modern theory pictures molecules like benzene and diborane as having pairs of electrons delocalized over several atoms. Lewis structures for such molecules can be drawn with fractional electron pairs, as in the example below. The fractions indicate that each pair of electrons spends a fraction of time between one pair of nuclei and a fraction between another pair.



Refinements (ii) and (iii) both apply to species like SO_4^{2-}. A simple bond formula for this can be drawn with 1½ bonds. A Lewis structure can therefore be drawn with 1½ bonding pairs:

$$[S(\ ::\underset{..}{\ddot{O}}:)_4]^{2-} \qquad : = \tfrac{1}{2}$$

I have again put a space between the bonding electrons and the sulfur atom to indicate polarity. In this case, to keep within an octet, the polarity must be $S^{x+}(O^{y-})_4$ with $4y - x = 2$ and $x \geq 2$. Quantum-mechanical calculations give $x \sim 2$. This suggests the structure

$$S^{2+}(\underset{1}{=\,=}O^{-})_4$$

with each sulfur-oxygen bond having an ionic component of ½ ($S^{½+}O^{-}$) and a covalent component of 1 (⅔ of a fully covalent 1½ bond), totalling 1½.

Exercises

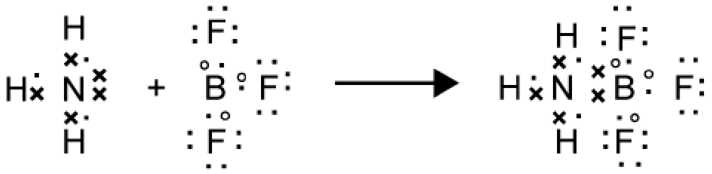
(i) Calculate the lowest charge the phosphorus atom can carry in PF_5.
(ii) Write a Lewis structure for CH_3NO_2, and calculate the lowest charge the nitrogen atom in this molecule can have.
(iii) Repeat this for the $[NO_3]^-$ ion, with fractional pairs.

(Click here for answers http://bit.ly/fFbGDB or see Appendix 1)

11.3 The dative bond

Ammonia gas (NH_3) reacts with boron trifluoride gas (BF_3) to give a colourless molecular solid, H_3NBF_3. This can be explained by adding a further postulate to 1–9 above:

10. A bond can be formed between an atom with a lone pair and an atom with an incomplete shell, e.g.



The boron atom now has an octet, and there is a new kind of bond between the nitrogen atom and the boron. This is similar to a covalent bond, but instead of one electron being supplied by each atom, both electrons come from the same atom, in this case the nitrogen.

The bond just described has been variously written and variously named. One way of writing it is

$$N \rightarrow B$$

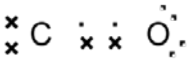
whence the name "dative" bond (Latin, *dare*, give). Another way of formulating it is to imagine first the transfer of one electron to give N^+ and B^- and then the formation of an ordinary covalent bond:

$$^{+}N{-}B^{-}$$

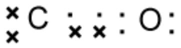
From this, it is sometimes called a "semipolar double bond" - a combination of a single ionic bond and a single covalent bond.

In practice, there can be little doubt that a dative bond is generally weaker than a double bond. In Me_3NBF_3, the N–B distance is about 1.6 Å, as compared with about 1.4 for a double bond and 1.6 for a single bond. The donation of the electron pair is evidently only partial - enough to form about half an ionic bond and half a covalent bond to give a bond order of about one. The symbol $^{+}X{-}Y^{-}$ for a donor bond thus needs to be used with care. For most purposes, the symbol $X \rightarrow Y$ is preferable, since it does not imply a particular bond order.

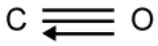
The dative bond has proved a mixed blessing to the concept of valency. On the one hand, it enables formulae to be drawn for a great many species that could not satisfactorily be formulated without it. An example is carbon monoxide, which when formulated as C=O does not do justice to the fact that the bond length is 1.13 Å, as compared with 1.22 Å for C=O in aldehydes and ketones. When written as a Lewis structure, however,



the possibility of the formation of a donor bond becomes evident, to complete the octet of the carbon atom:

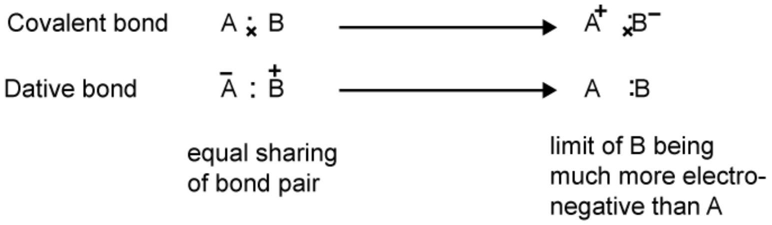


or



The shorter distance is now accommodated. Many other examples will be given in the chapter on coordination compounds (Chap. 13).

On the other hand, the dative bond is of indefinite order. The degree of donation is evidently dependent on the relative electronegativities of the donor and the acceptor, and this can vary widely. In the case of an ordinary covalent bond, this does not matter, since loss of covalency through unequal sharing of the bonding pair is compensated for by gain in electrovalency. In the case of the dative bond, however, it is not, and in the limit of unequal sharing there is no bond at all:



This means that dative bonds do not form everywhere where they might be predicted to on paper, so that dative bonding tends to be something that is invoked to explain the formulae of molecules once they are known, rather than a means of predicting the formulae of molecules yet to be made. Thus, for example, we can write down on paper a molecule of the formula

but no substance of this composition has ever been made. Presumably, the neon atom is too electronegative to part with its electrons.

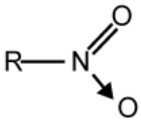
Exercise

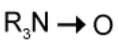
Write a Lewis structure for (i) CH_3NC; (ii) $[NNN]^-$

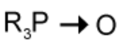
(Click here for answers http://bit.ly/ia1vYO or see Appendix 1)

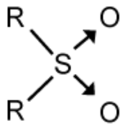
X=O or X→O?

Donor bonds allow atoms to preserve their octet where my treatment uses polar double bonds. For example:





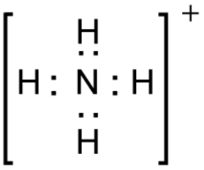




Here R = CH_3, F, O^-, etc. Lewis gave a dot formula of this type for $[SO_4]^{2-}$. The Oxford chemist N.V. Sidgwick extended this to other molecules. Most modern textbooks follow Sidgwick, at least for nitrogen compounds. However, quantum-mechanical calculations suggest that polar double bonds are a better approximation for most molecules (or even polar triple bonds as in CO if the symmetry allows it). Exceptions are molecules of the type R_3NO with weakly electronegative R groups (e.g. CH_3). For these a donor bond is better. [Note that the N–O bond in $(CH_3)_3NO$ is much longer (1.40 Å) than that in F_3NO (1.16 Å).]

Ammonium

The Lewis structure for the $[NH_4]^+$ ion can be derived by regarding it either (i) as a derivative of N^+ (with four valence electrons, forming covalent bonds to four hydrogen atoms), or (ii) as a derivative of NH_3 and H^+ (the lone pair on the nitrogen atom forming a dative bond with H^+). The result is the same:



$$\left[\begin{array}{c} \mathrm{H} \\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H} \\ \mathrm{H} \end{array}\right]^+$$

11.4 Isoelectronic principle

Systems are said to be "isoelectronic" (Greek *isos*, equal) if they have the same number of nuclei and the same number of electrons. Thus, Na^+ and F^- are isoelectronic with Ne, and the following constitutes an isoelectronic series:

$$O^{2-}, F^-, Ne, Na^+, Mg^{2+}, Al^{3+}$$

The isoelectronic principle states that, for small variations in nuclear charge at least, the arrangement of electrons in isoelectronic species is approximately same.

A simple example of this is provided by the OH^- ion. This is isoelectronic with the HF molecule, O^- having the same number of electrons as F. Now the bond formula for the HF molecule is

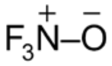
$$H–F$$

According to the isoelectronic principle, therefore, the bond formula of OH^- can be written

$$H–O^-$$

with F replaced by O^-.

This principle is particularly helpful in thinking about species containing dative bonds. Such species are often isoelectronic with, and close in nuclear charge to, stable species containing ordinary covalent bonds. Thus,



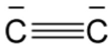
$$F_3\overset{+}{N}-\overset{-}{O}$$

is isoelectronic with CF_4, N^+ having the same number of electrons as C and O^- as F. Similarly

$$\overset{-}{C}\equiv\overset{+}{O}$$

is isoelectronic with N_2, C^- and O^+ having the same number of electrons as N. It is also isoelectronic with the cyanide ion and the acetylide ion

$$\overset{-}{C}\equiv N$$



$$\overset{-}{C}\equiv\overset{-}{C}$$

Thus, it seems that, if the parent species is stable enough, species that are isoelectronic with it will also be stable, provided that the nuclear charges do not differ too much. The last point is illustrated by the series N_2, CO, BF, BeNe, the third and fourth members of which do not exist as stable substances.

Exercise

Write down the formulae of as many species as you know to exist that are isoelectronic with CO_2.

(Click here for answers http://bit.ly/i0h05f or see Appendix 1)

11.5 Transition elements

Lewis's model can explain some of the valencies of transition elements. If their atoms have *N* valence electrons (*N* = group number), this accounts for the highest valencies up to group 8T. If a complete shell contains 18 electrons, this explains the formulae of many "nonclassical" compounds, considered in Chapter 13. A valence shell of 18 electrons corresponds to the filling of d, s, and p orbitals (3d, 4s, and 4p for first-row transition elements; 4d, 5s, and 5p for second-row; 5d, 6s, and 6p for third-row).

However, this leaves many valencies unaccounted for. To explain how these arise, Lewis suggested that transition-element atoms can have variable cores. Consider, for example, titanium. This has a valency of four, equal to the group number. Its atom therefore has four valence electrons. However, titanium also has a valency of three. In this valency, its compounds have similar structures to those of scandium, whose atom has three valence electrons. In trivalent compounds, therefore, a titanium atom behaves as if it has only three valence electrons, i.e. as if the fourth electron has become part of the core. In other words, the core of a titanium atom can be [Ar] or [$Ar3d^1$] (the configurations of Ti^{4+} and Ti^{3+} respectively) depending on how the atom is bound. Lewis structures can accordingly be drawn for transition-element compounds by specifying the charge on the core (in this case Ti^{4+} or Ti^{3+}).

The valencies of inner transition elements may also be understood in terms of variable cores and $\leq N$ valence electrons (on my group numbering).

11.6 Shapes of molecules

Lewis structures can be used to explain and predict the shapes of molecules. The basic assumption is that, if the core of an atom is effectively spherical (as for most atoms it is), groups of electrons in the Lewis shell (single bond pairs, double-bond quartets, fractional bond pairs, etc.) get as far apart as possible. Thus, two groups take up a linear arrangement, three a trigonal-planar one, four tetrahedral, five trigonal-bipyramidal, six octahedral, and so on.

For main-group atoms, lone pairs are included. For example, in an H_2O molecule, there are two bond pairs and two lone pairs round the oxygen atom. These take up a tetrahedral arrangement, making the molecule angular, as observed. For transition-metal atoms, lone pairs are excluded (Chap. 13).

This theory is called “valence-shell electron-pair repulsion (VSEPR) theory” or “electron-domain (ED) theory”. It is described in detail in most textbooks.

Further reading

“Modified Lewis theory”, *Chemistry Education: Research and Practice*, 2001, Vol. 2, pp. 67-72 (Part 1), 179-182 (Part 2) [http:/www.uoi.gr/cerp]; *Recent Research Developments in Inorganic Chemistry*, 2004, Vol. 4, pp. 1-11.

12 Compounds of higher order than two

Higher order compounds inevitably present a more complicated picture than binary compounds. It is possible, however, to introduce a certain amount of classification, as indicated below.

12.1 Limiting types

The limiting types of higher-order compounds are the same as the limiting types of binary compound, namely:

Metallic. Formed generally by the combination of metallic elements and having the characteristic properties of metallic elements.

Nonmetallic. Formed generally by the combination of nonmetals and having the characteristic properties of nonmetals.

Salt-like. Formed generally by the combination of metals and nonmetals, and having the characteristic properties of salt.

12.2 Metallic compounds

Metallic compounds of higher order than two are similar to those of order two.

Examples are the compounds $\sim FeCu_{13}Ni_6$ and $\sim FeCuNi_2$ formed in the iron-copper-nickel system.

12.3 Nonmetallic and salt-like compounds

These may be broadly divided into two types:

(i) *Simple*, whose structure can be explained by the same valency rules as for binary compounds.

(ii) *Complex*, whose structure cannot be so explained.

12.3.1 Simple nonmetallic compounds

These are similar to binary nonmetallic compounds.

Examples:	dichloromethane	CH_2Cl_2
	carbonyl chloride	$COCl_2$
	hydroxylamine	NH_2OH
	phosphoryl chloride	$POCl_3$
	thionyl chloride	$SOCl_2$
	dimethyl sulfate	$(CH_3)_2SO_4$

Exercise

Write down the simple bond formula of each of the above compounds.

(Click here for answers http://bit.ly/dXJgn7 or see Appendix 1)

Some compounds of this type can be conveniently treated as if they were compounds of lower order (Chap. 9).

12.3.2 Simple salt-like compounds

These are similar to binary salt-like compounds. They are of two types:

(i) simple pseudo-low-order compounds;

(ii) multiple compounds.

These will be discussed in turn.

(i) *Simple pseudo-low-order compounds*

Compounds of this type have already been discussed under pseudo-binary compounds (Chap. 9). They are compounds containing molecular ions obeying the valency rules, e.g., CN^-, SO_4^{2-}, $CH_3CO_2^-$.

(ii) *Multiple compounds*

These are salt-like compounds, formed by the combination of two or more simpler salt-like compounds, that contain the same ions in the molten state, or give the same ions in aqueous solution, as the compounds from which they are made.

An example is $KMgCl_3$. This is prepared by fusing $MgCl_2$ with KCl in the ratio 1:1. It is a colourless solid, dissolving in water to give a colourless solution. In the solid state, it is an insulator, but in the melt and in solution it is a good electrolytic conductor, with conductivities closely similar to the values that would be calculated for a mixture of $MgCl_2$ and KCl of the same composition. The solution in water gives all the characteristic tests for K^+, Mg^{2+}, and Cl^- ions, and each can be precipitated with the usual reagents. For example, one mole of $KMgCl_3$ gives three moles of AgCl on treatment with an excess of silver nitrate. The compound may thus be formulated $K^+Mg^{2+}(Cl^-)_3$. A similar compound can be made by fusing one mole of $MgCl_2$ with two moles of KCl. This may be formulated $(K^+)_2Mg^{2+}(Cl^-)_4$.

As here defined, multiple compounds represent a limiting type, with 100% ionic bonding. The category can be widened, however, to admit compounds that, while being predominately polar, have some degree of covalent or metallic bonding as well. In this wider sense, further examples are provided by the following minerals:

		Approximate constitution
Spinel	$MgAl_2O_4$	$Mg^{2+}(Al^{3+})_2(O^{2-})_4$
Perovskite	$CaTiO_3$	$Ca^{2+}Ti^{4+}(O^{2-})_3$
Magnetite	Fe_3O_4	$Fe^{2+}(Fe^{3+})_2(O^{2-})_4$

Multiple compounds are subdivided into double compounds, triple compounds etc. If compounds are salts, they are also called “multiple salts”. Multiple oxides are called “mixed oxides”.

Multiple compounds are named by a straightforward extension of the system used for binary compounds. The names of the electropositive constituents are cited first, followed by the names of the electronegative ones. Names of constituents are often cited in electronegativity order (EO), but IUPAC recommends alphabetical order (AO). The proportions of the constituents are indicated in the usual ways.

Example: EO: $NaFeO_2$ sodium iron dioxide, or sodium iron(III) oxide
AO: $FeNaO_2$ iron sodium dioxide, or iron(III) sodium oxide

Exercise

Name the following compounds:

(i) K_2MgCl_4; (ii) $KMgCl_3$; (iii) Fe_3O_4.

(Click here for answers http://bit.ly/i6elqN or see Appendix 1)

12.3.3 Complex nonmetallic and salt-like compounds

These are compounds, formed by the addition of two or more simple compounds, whose structure cannot be accounted for by the simple valency rules. Specifically, one or more of the atoms present are bound to more other atoms than the valency rules require.

They may be broadly divided into two types:

(i) *Coordination compounds.* These are compounds whose structure can be rationalized in terms of a characteristic number (or set of numbers) of atoms attached to the central atom. This number is called the “coordination number”.

(ii) *Loose compounds.* These are compounds whose structure cannot be rationalized in the above way. They are more easily dissociated into their components than type (i), and appear to be more loosely held together.

Coordination compounds are considered in detail in Chapter 13 and loose compounds in Chapter 14.

Notes

(i) Loose compounds are usually called “addition compounds”. However, this term has a wider meaning, covering some other types of compound formed by addition. Although my term “loose compound” is not in general use, it is sufficiently descriptive to be generally understood.

(ii) The term “complex compound” is often used more narrowly than the way I have used it here, being taken as synonymous with coordination compound. The way I have used it, however, accords with its literal meaning, viz. the opposite of a simple compound.

13 Coordination compounds

13.1 Basic theory

When aqueous ammonia is added to a solution of cobalt dichloride, $CoCl_2$, a blue precipitate forms of the corresponding hydroxide, $Co(OH)_2$, which dissolves on the addition of an excess of ammonia to give a solution that immediately begins to absorb oxygen and turn brown. From the oxidized solution, the following compounds can be isolated:

Composition	**Colour**
(I) $CoCl_3{\cdot}6NH_3$	orange yellow
(II) $CoCl_3{\cdot}5NH_3{\cdot}H_2O$	pink
(III) $CoCl_3{\cdot}5NH_3$	purple

A great many other compounds of this type can be prepared, (i) by starting with other cobalt salts, and (ii) by carrying out further reactions with the compounds first obtained. Among these other compounds are two other chlorides:

(IV) $CoCl_3{\cdot}4NH_3$	violet
(V) $CoCl_3{\cdot}4NH_3$	green

At first sight, the properties of compounds (I) - (V) are very puzzling:

(i) All of them fail to give a brown precipitate of $Co(OH)_3$ when treated with sodium hydroxide solution - a property expected of compounds containing the Co^{3+} ion. Only on boiling does a precipitate form.

(ii) All of them fail to give ammonium chloride when treated with concentrated hydrochloric acid - a reaction that would be expected of a compound containing ammonia. Only on boiling with sodium hydroxide is ammonia evolved.

(iii) While all of them give a precipitate of silver chloride when treated with silver nitrate in aqueous solution, the amount that is precipitated in the cold is in some cases less than expected, as shown in the table below. In these cases, the full amount is only obtained by leaving the solution to stand for a long time or by boiling it.

(iv) The five compounds give different numbers of ions in solution, as judged from (a) the electrical conductivities of their solutions in comparison with those of other electrolytes, (b) the extent to which they depress the freezing point of water. The numbers of ions judged to be present are shown in the table below.

Compound	**Moles of AgCl precipitated per mole**	**Number of ions present in solution per $CoCl_3$**
(I) $CoCl_3{\cdot}6NH_3$	3	4
(II) $CoCl_3{\cdot}5NH_3{\cdot}H_2O$	3	4
(III) $CoCl_3{\cdot}5NH_3$	2	3
(IV) $CoCl_3{\cdot}4NH_3$	1	2
(V) $CoCl_3{\cdot}4NH_3$	1	2

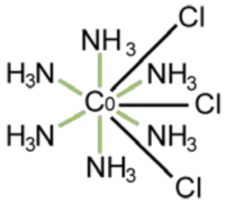
These properties, and those of many other compounds of a similar kind, were brilliantly rationalized by Alfred Werner in 1893. In this year, at the age of only 26, he proposed what is now referred to as his "coordination theory", for which he was awarded a Nobel Prize in 1913. Its principal postulates are as follows:

(1) An atom exhibits two types of valency, its ordinary valency (*V*), and a valency that determines the number of neighbouring atoms to which it is bound (the "coordination number").

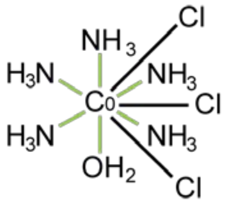
(2) An atom's ordinary valency is satisfied by other atoms or radicals; its coordination number is satisfied by atoms, radicals, or molecules.

(3) Bonds to neighbouring atoms are directed towards fixed positions in space.

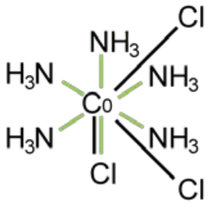
On the basis of postulates (1) and (2), Werner formulated compounds (I)–(V) as shown diagrammatically below. Ordinary valency bonds are designated by black lines (——) and bonds between neighbouring atoms by green lines (——). The cobalt atoms have their ordinary valency of three (as in CoF_3) and are given a coordination number of six. The other atoms are given coordination numbers to match (e.g. four for the nitrogen atom in NH_3, leaving one for the cobalt).



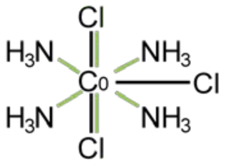
$CoCl_3{\cdot}6NH_3$



$CoCl_3{\cdot}5NH_3{\cdot}H_2O$



$CoCl_3{\cdot}5NH_3$



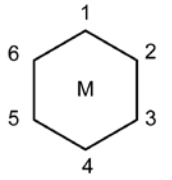
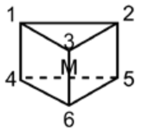
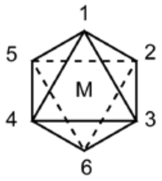
$CoCl_3{\cdot}4NH_3$

Now if in these formulations the single black lines are taken to be ionic bonds, and the green and double lines are taken to be bonds of a non-ionic character, the properties of compounds (I) - (V) given above are fully explained. Thus (I) and (II) would be expected to give three Cl^- ions in solution, (III) only two, and (IV) and (V) only one. This leads to the customary formulations:

(I)	$[Co(NH_3)_6]Cl_3$ containing the $[Co(NH_3)_6]^{3+}$ ion;
(II)	$[Co(NH_3)_5H_2O]Cl_3$ containing the $[Co(NH_3)_5H_2O]^{3+}$ ion;
(III)	$[CoCl(NH_3)_5]Cl_2$ containing the $[CoCl(NH_3)_5]^{2+}$ ion;
(IV), (V)	$[CoCl_2(NH_3)_4]Cl$ containing the $[CoCl_2(NH_3)_4]^+$ ion.

The existence of two isomers of $[CoCl_2(NH_3)_4]Cl$ was explained by Werner on the basis of postulate (3). Indeed, the fact that only two isomers of this formula were known led him to propose that the arrangement of atoms around the cobalt atom is an octahedral one, since other arrangements would lead to more than two isomers. This is shown in the following table.

Known isomers vs. the number theoretically possible for three different structures

Complex type	Number of known isomers	Number of isomers theoretically possible		
		 Planar	 Trigonal prism	 Octahedral
MA_5B	One	One	One	One
MA_4B_2	Two	Three (1,2; 1,3; 1,4)	Three (1,2; 1,4; 1,6)	Two (1,2; 1,6)
MA_3B_3	Two	Three (1,2,3; 1,2,4; 1,2,5)	Three (1,2,3; 1,2,4; 1,2,6)	Two (1,2,3; 1,2,6)

The absence of a third isomer of $[CoCl_2(NH_3)_4]Cl$ does not of course prove that the octahedral structure is correct. The third isomer may simply be much less stable or more difficult to isolate. Werner was able to prove, however, that the octahedral structure is the correct one by preparing a compound that would be expected to exist in optically active forms if the structure were octahedral, but not if it was planar or a trigonal prism, and showing that the compound can indeed be resolved into optically active isomers. This conclusion has been verified by X-ray crystallography.

Most metals can form some coordination compounds, but few form as many as trivalent cobalt. Others that do include trivalent chromium, and bi- and quadri-valent platinum. Trivalent chromium and quadrivalent platinum have the same coordination number and geometry as trivalent cobalt; bivalent platinum has a coordination number of four with the groups around it arranged in a square.

The complex part of a coordination compound may be a cation, an anion, or an uncharged molecule. For example:

complex cation	$[Co(NH_3)_6]^{3+}$
complex anion	$[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[Co(NO_2)_6]^{3-}$
neutral complex	$[CoCl_3(NH_3)_3]^0$, $[Co(NO_2)_3(NH_3)_3]^0$

Neutral complexes are frequently more soluble in nonpolar organic solvents than they are in water. When they do dissolve in water, they behave as non-electrolytes.

Exercise

(i) Interpret the following observations on the basis of Werner's coordination theory:

Compound	**Empirical formula**	**Moles of AgCl precipitated per mole on treatment with $AgNO_3$**	**Number of ions in solution per $PtCl_2$**
(I)	$PtCl_2{\cdot}4NH_3$	2	3
(II)	$PtCl_2{\cdot}2NH_3$	0	0
(III)	$PtCl_2{\cdot}2NH_3$	0	0
(IV)	$2KCl{\cdot}PtCl_2$	0	3

(ii) On mixing solutions of (I) and (IV) a green precipitate is formed, called Magnus's green salt. Suggest a formula for this, and comment on its relation to (II) and (III).

(Click here for answers http://bit.ly/hY34yC or see Appendix 1)

13.2 Terminology of coordination compounds

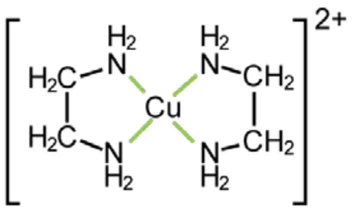
A species like $[Co(NH_3)_6]^{3+}$ is called a "coordination entity". The atom in the middle is called the "central atom", the attached groups are called "ligands" (Latin, *ligare*, bind), and the atoms by which they are attached, "coordinating" or "ligating" atoms. The ligands are said to be "coordinated" or "ligated" to the central atom. They are also said to be in the "coordination sphere" of the central atom.

Following Werner, the number of coordinating atoms around the central atom is called the "coordination number" of the central atom. This term is also used by crystallographers (Chap. 6). However, the latter use it to describe a particular structure, whereas Werner used it more as a valency. A better term for this purpose would be "coordinate valency".

A ligand containing more than one coordinating atom is called a multidentate (literally "many-toothed") ligand, the number of coordinating atoms being indicated by the terms "unidentate", "bidentate", etc. An example of such a ligand is ethylenediamine, usually abbreviated en:

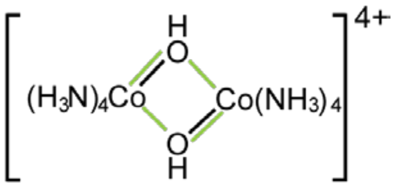
$$H_2N–CH_2–CH_2–NH_2$$

This can coordinate through its two nitrogen atoms in the same way as two molecules of CH_3NH_2 or NH_3. Thus, just as the addition of ammonia to a solution containing Cu^{2+} leads to the formation of the deep blue $[Cu(NH_3)_4]^{2+}$ ion, so the addition of ethylenediamine leads to the formation of the dark blue-violet $[Cu(en)_2]^{2+}$:



A multidentate ligand is said to function as a “chelate” ligand when it attaches itself to a central atom through more than one of its coordinating atoms, as in the example above. The resulting species is called a chelate. This comes from the Greek word for a crab’s claw (*khēlē*) and describes the way in which the ligand grasps the central atom between two or more of its coordinating members.

A ligand is said to function as a “bridging” ligand when it is attached to more than one coordinating centre. An example is the hydroxide ion in



Coordination entities of this sort are described as “polynuclear”, the number of central atoms being designated by the terms “mononuclear”, “dinuclear”, etc.

Note

As “nuclear” is a Latin word, it should properly have Latin numerical prefixes. However, the use of Greek prefixes is well established in this context (contrast “multinuclear” NMR). IUPAC also use Greek prefixes with “dentate” (“didentate”, etc.).

13.3 Nomenclature of coordination compounds

Coordination compounds are named according to the recommendations of IUPAC (see Chap. 7). The basic rules are as follows.

1. A coordination entity has a one-word name, formed from the name of the central atom and the names of the ligands.

2. If the entity is a cation or neutral, the usual name of the central atom is used (e.g. cobalt). If the entity is an anion, the name of the central atom is changed to end in -ate (e.g. cobaltate). For a few elements, Latin forms are used for anions (e.g. ferrate, cuprate).

3. Most neutral ligands have their usual names. A few have special names, e.g.

NH_3	ammine
H_2O	aqua

4. Anionic ligands have their usual names, modified to end in –o, e.g.

$CH_3CO_2^-$	acetato

A few have special names, e.g.

Cl^-	chloro
O^{2-}	oxo
OH^-	hydroxo
NO_2^- (coordinated through N)	nitro

5. The numbers of ligands are indicated by Greek numerical prefixes (di, tri, tetra, penta, hexa, etc.). Where these would create ambiguity, multiplicative prefixes (bis, tris, tetrakis, pentakis, hexakis, etc.) and brackets are used, e.g. bis(methylamine).

6. Ligands are listed first, in alphabetical order (e.g. tri<u>a</u>mminedi<u>b</u>romo<u>c</u>hloro), followed by the central atom.

7. There are alternative ways of indicating the overall stoicheiometry, as illustrated below for the compound $[CoCl(NH_3)_5]Cl_2$ (cf. Chap. 7).

(i) By specifying the oxidation number of the central atom,
e.g. pentaamminechlorocobalt(III) chloride

(ii) By specifying the charge on the coordination entity,
e.g. pentaamminechlorocobalt(2+) chloride

(iii) By specifying the proportions of the constituent ions,
e.g. pentaamminechlorocobalt dichloride

8. Bridging ligands are indicated by μ and separated by hyphens,
e.g. -μ-chloro-, -di-μ-hydroxo-

Exercise

Name the coordination compounds in the previous exercise.

(Click here for answers http://bit.ly/eaQNz5 or see Appendix 1)

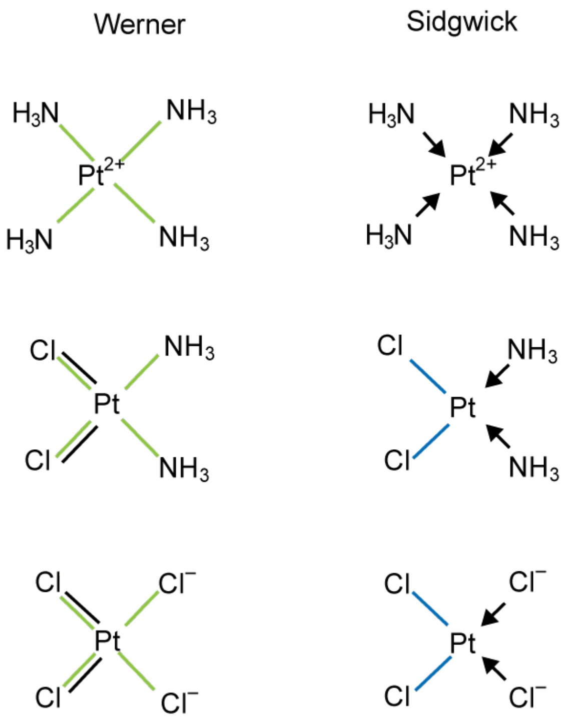
13.4 Bonding in coordination compounds

The bonding in coordination compounds is most easily described in the manner first proposed by the Oxford chemist N. V. Sidgwick in 1923. Sidgwick suggested that

(i) the bonds indicated by both a black and a green line (═) in the above formulae are ordinary covalent bonds,

(ii) the bonds indicated by a green line alone (—) are donor bonds, the ligand acting as the donor and the central atom as the acceptor.

This is illustrated below, where I have taken the single black lines in Werner's formulae to be ionic bonds and used my symbol for a covalent bond (Section 8.3):


Werner
Sidgwick
H3N
NH3
Pt2+
H3N
NH3
H3N
NH3
Pt2+
H3N
NH3
Cl
NH3
Pt
Cl
NH3
Cl
NH3
Pt
Cl
NH3
Cl
Cl⁻
Pt
Cl
Cl⁻
Cl
Cl⁻
Pt
Cl
Cl⁻

Sidgwick based his hypothesis on the following observations:

(i) All ligands thought to be bound by a dative bond possess at least one unshared pair of electrons, and no ligand is ever required to form more dative bonds than the number of lone pairs it has available.

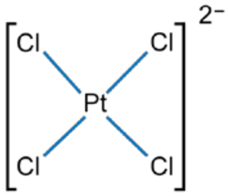
(ii) For many of the more stable coordination compounds (stable, that is, with respect to dissociation), the number of electrons calculated to be round the central atom on the above model is the same as the number of electrons round the atom of the next inert gas. For example:

$[Co(NH_3)_6]^{3+}$	Co^{3+} has	24 electrons
	$6NH_3$ donate	12 electrons
	Total	36 cf. Kr

This he called the “effective atomic number rule”. It is now called the “inert/noble gas rule”, or the “18-electron rule”. The latter is based on the number of outer electrons (i.e. electrons outside an [Ar], [Kr], or $[Xe4f^{14}]$ core):

$[Co(NH_3)_6]^{3+}$	Co^{3+} has	6 outer electrons
	$6NH_3$ add	12 electrons
	Total	18

Sidgwick recognized that, when the above formula for $[PtCl_4]^{2-}$ is drawn as a Lewis structure with only dots, all the Pt–Cl bonds are the same (Pt:Cl), as observed experimentally. He accordingly also wrote the formula (in my symbolism):

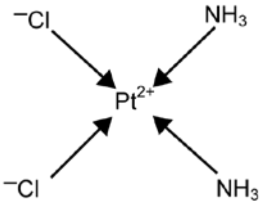


This effectively places the negative charge on the platinum atom.

Sidgwick’s understanding of the bonding in coordination compounds is accepted today in a slightly modified form. This is as follows:

(i) The bonds thought by Sidgwick as covalent bonds are now regarded as having some ionic character, in common with other electron-pair bonds between unlike atoms.

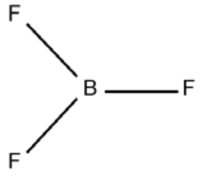
(ii) These bonds are replaced by their ionic-cum-dative equivalent, i.e. A–B is replaced by $A^+ \leftarrow B^-$. This gives for $[PtCl_2(NH_3)_2]$:



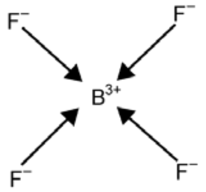
This is equivalent to taking all of the black lines in the earlier formulae as ionic bonds and all of the green lines as dative bonds.

The merit of the modern formulation is that it represents all the coordinate bonds in the same way. Its disadvantage, however, is that it exaggerates the extent to which it is necessary to go beyond a simple formulation, and creates inconsistencies of the type illustrated below:

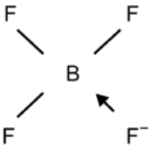
Formula of BF_3



Formula of BF_4^-



For many purposes, it is better to use Sidgwick's formulae, with his covalent bonds reckoned as polar (—— in my symbolism):

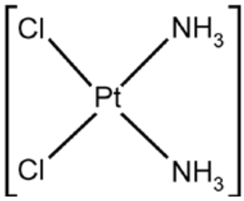


Notes

(i) The extent to which a ligand donates its electrons varies widely. Quantum-mechanical calculations indicate that in some complex ions the degree of donation is small (e.g. in $[AlF_6]^{3-}$ it is only ~15%). In these cases, most of the coordinate bonding comes from the attraction between the positive charge on the central atom and the negative charge on the coordinating atoms. (Neutral ligands are polar with a negative charge on the coordinating atom. For example, the charge on the N atom of NH_3 is about -0.8.)

(ii) The 18-electron rule is of limited applicability among classical coordination compounds. It holds for octahedral cobalt(III) and platinum(IV) complexes, but not chromium(III) (15 electrons) or square-planar platinum(II) (16 electrons). Classical compounds of transition elements are best treated as containing variable cores (Chap. 11). Complexes containing >18 outer electrons, e.g. octahedral nickel(II) (20), can be understood in the same way as main-group compounds with >8 outer electrons: i.e. polarity of the coordinate bonds reduces the number of electrons round the central atom.

(iii) Modern chemists often represent coordination entities by simple single-stroke formulae (Chap. 6), e.g.



Exercise

Write a bond formula for each of the following species:

(i) $[CoCl(NH_3)_5]^{2+}$; (ii) $[SiF_6]^{2-}$; (iii) $[Co(ox)_3]^{3-}$ (ox = oxalate, $C_2O_4^{2-}$).

(Click here for answers http://bit.ly/edB8Ce or see Appendix 1)

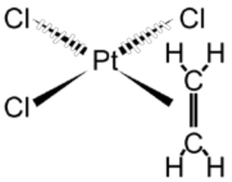
13.5 Nonclassical coordination compounds

Transition elements form coordination compounds with some ligands that bind weakly, if at all, to main-group electron-pair acceptors (e.g. BF_3). The principal ligands of this type are carbon monoxide and unsaturated hydrocarbons. Some examples of compounds are:

Nickel carbonyl, $Ni(CO)_4$. This is made by passing carbon monoxide over nickel powder. It is a colourless liquid, boiling at 43 °C. The $Ni(CO)_4$ molecule is tetrahedral. The C–O bond length is 1.15 Å, which is similar to that in CO (1.13 Å), and shorter than that in aldehydes and ketones (typically 1.22 Å). This suggests that the molecule should be formulated $[Ni(\leftarrow CO)_4]$, with zero-valent nickel, rather than $Ni(=C=O)_4$, with octovalent. However, the strength of the bonds compared with the weakness of bonds between CO and main-group acceptors indicates some enhancement of the bonding.

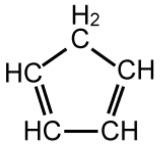
Iron pentacarbonyl, $Fe(CO)_5$. This is made by heating iron powder with carbon monoxide in an autoclave (at 200 °C and 200 atm). It is a yellow liquid, boiling at 103 °C. The molecule is trigonal bipyramidal, with a C–O distance of 1.15 Å, as in $Ni(CO)_4$.

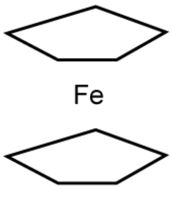
Ziese's salt. This can be made by shaking a solution of $K_2[PtCl_4]$ in aqueous hydrochloric acid with ethylene. It forms yellow crystals, which X-rays show contain square-planar $[PtCl_3(C_2H_4)]^-$ ions with the C_2H_4 bound sideways on:



Since C_2H_6 does not form a similar compound, the presumption is that the C_2H_4 molecule is bound to the platinum atom by one of the electron pairs from the double bond. This may be indicated: $Pt \leftarrow \|$, where $\|$ represents the double bond. There may again be some enhancement of the bonding.

Ferrocene, $Fe(C_5H_5)_2$. This can be made by several methods, starting from cyclopentadiene, C_5H_6 (below left). It forms brown crystals, melting at 173 °C. X-rays show that, instead of each C_5H_5 radical being bound to the iron atom through one carbon atom (>CH—Fe—CH<), the rings are bound face on, producing a "sandwich" structure (below right). The rings display aromatic reactivity, undergoing substitution rather than addition.





The molecule is most easily formulated with integral bonds in the rings (as above left with $-CH_2-$ replaced by $-CH<$). There is then one Fe—C bond to each ring and two Fe←|| bonds. However, the Fe–C and C–C bond lengths are all the same. Therefore a better formulation is with equal ring bonds, of value 1.4 (the average of three single bonds and two double). There are then five Fe--$_{0.2}$--C bonds to each ring (a single bond shared between five linkages) and five Fe<--$_{0.4}$--¦| bonds.

Compounds of this type conform to the 18-electron rule better than classical coordination compounds. Thus:

$Ni(CO)_4$: a nickel atom has 10 outer electrons; each CO molecule donates 2 electrons; the total number of electrons is therefore $10 + 4 \times 2 = 18$.

$Fe(CO)_5$: an iron atom has 8 outer electrons; the total number of electrons is therefore $8 + 5 \times 2 = 18$.

$Fe(C_5H_5)_2$: Fe has 8 outer electrons; each C_5H_5 radical shares its unpaired electron to form one Fe—C bond or five Fe--$_{0.2}$--C bonds (see above), and donates four electrons to form two Fe←|| or five Fe<--$_{0.4}$--¦| bonds; the total number of electrons in the molecule is therefore $8 + 2 \times (1 + 4) = 18$.

The platinum atom in $[PtCl_3(C_2H_4)]^-$ has only 16 electrons, but this number is characteristic of square-planar complexes (the “16-electron rule”).

Note that the shapes of $Ni(CO)_4$ and $Fe(CO)_5$ are determined by the bonding electrons alone (contrast main-group molecules, Chap. 11).

Further reading

“Valency”, *Journal of Chemical Education*, 1997, Vol. 74, pp. 465–470.

This gives a modern version of Werner’s theory, and an alternative treatment of nonclassical compounds (by introducing a “nonclassical” valency).

[Note that the correct relation between coordinate valency and Werner’s “auxiliary” or “secondary” valency (p. 468, col. 1, para. 3 up) is: secondary valency = coordinate valency – primary valency *used in coordination*.]

14 Loose compounds and solutions

14.1 Solutions

Solutions are important in chemistry. They may be divided into two types: (i) normal and (ii) abnormal.

14.1.1 Normal solutions

These are where solute, solvent, and solution all have the same character:

Character	**Bonding**
metallic	metallic
nonmetallic, molecular	covalent/van der Waals
nonmetallic, framework	covalent
salt-like	ionic

Examples of normal solutions are alloys, petrol, and mixed salts. The solute and solvent have to be sufficiently alike for a solution to form (iron does not dissolve in sodium, paraffin oil in water, etc.).

Note

A "normal" solution used to refer to its concentration, but this usage has now been dropped.

14.1.2 Abnormal solutions

These are where solute, solvent, and solution do not all have the same character. Examples are:

- solutions of salt-like substances in molecular ones (e.g. sodium chloride in water);
- solutions of molecular substances having similar properties to the previous type (e.g. hydrogen chloride in water);
- solutions of metals in molecular substances (e.g. sodium in liquid ammonia).

I will consider these in turn.

Solutions of salt-like substances in molecular ones

Sodium chloride dissolves in water despite the fact that the latter is molecular. The solutions are good conductors of electricity, and undergo electrolysis in the same way as molten sodium chloride except that hydrogen is formed at the cathode (sodium reacts with water to give hydrogen). The freezing points of the solutions are approximately twice those expected for the presence of NaCl molecules (the factor approaches 2.00 at low concentrations). The solutions evidently contain Na^+ and $Cl^−$ ions like sodium chloride itself (Chap. 5).

Given the strong Coulombic attraction between Na^+ and $Cl^−$ ions in solid sodium chloride, it is at first sight surprising that the latter should dissolve in water. The reason must be that the H_2O molecule is very polar. We saw in Chapter 5 that the charge distribution is approximately $(H^{0.4+})_2O^{0.8-}$. Thus if H_2O molecules surround the Na^+ ions with $O^{0.8-}$ pointing towards them and the Cl^- ions with $H^{0.4+}$ pointing towards them, considerable Coulombic attraction is generated, enough presumably to dissolve the ions.

For some cations, this attraction may be supplemented by some degree of dative bonding. For example, violet solutions of chromium(III) salts behave as if they contain relatively tightly bound $[Cr(H_2O)_6]^{3+}$ ions, analogous to $[Cr(NH_3)_6]^{3+}$ ions. Thus, if a solution containing a Cr^{3+} ions and b H_2O molecules is added to water enriched with $H_2{}^{18}O$ and some water is distilled from the mixture, the $^{18}O{:}^{16}O$ ratio in this corresponds to rapid exchange, not with all the H_2O molecules in the original solution, but with $(b - 6a)$.

Solutions of salt-like substances do not always contain simple hydrated ions. For example, some solutions of chromium(III) salts are green. These contain complexes with the anions of the salt, e.g. $[CrCl_2(H_2O)_4]^+$. Freezing points of copper sulfate solutions indicate that, except at very low concentrations, most of the salt is present, not as Cu^{2+} and $SO_4{}^{2-}$ ions, but as $[CuSO_4(H_2O)_n]$:

Concentration	**Proportion as [$CuSO_4$aq]**
0.001 M	15%
0.01 M	50%
0.1 M	80%

When solutions containing only simple hydrated ions are required, salts of weakly coordinating cations (e.g. K^+) or anions (e.g. ClO_4^-, BF_4^-) must be used.

Water is a particularly good ionizing solvent, but there are others. Among the most important are liquid NH_3 (b.p. –33 °C), liquid HF (b.p. 19.5 °C), 100% CH_3CO_2H (b.p. 118 °C), 100% H_2SO_4 (b.p. 320 °C), and 100% HSO_3F (b.p. 163 °C).

Salt-like solutions of molecular substances

Anhydrous hydrogen chloride is a gas. However, it dissolves in water to give solutions that are very like sodium chloride solutions. That is, they conduct electricity and undergo electrolysis, giving hydrogen at the cathode and chlorine at the anode. Their freezing points are also approximately twice those expected for the presence of HCl molecules. The solutions evidently contain hydrated H^+ and Cl^- ions. They will be discussed further in Chapter 17.

Solutions of metals in liquid ammonia

Sodium dissolves in liquid ammonia. Dilute solutions are blue, concentrated ones are bronze-coloured. The solutions conduct electricity. The other alkali metals and the alkaline earth metals also dissolve in liquid ammonia, giving solutions of the same colour.

Since sodium metal comprises Na^+ ions and electrons (Chap. 5), the solutions may contain solvated Na^+ ions and electrons. This is supported by the fact that other metals give solutions of the same colour, the colour being due to solvated electrons. The formation of the latter seems to be due to the slowness of the expected reaction:

$$Na + NH_3 \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

The solutions are indeed metastable, and catalysts soon give $NH_2^- + \tfrac{1}{2}H_2$.

14.2 Loose compounds

These are formed between the components of some solutions. They may be divided into two classes: (i) molecule-molecule compounds; (ii) salt-molecule compounds.

14.2.1 Molecule-molecule compounds

When chlorine is passed into water cooled in ice, pale greenish-yellow crystals of chlorine hydrate separate. Chemical analysis gives its composition as approximately $Cl_2{\cdot}7H_2O$. An X-ray examination of its structure gives its ideal formula as $3Cl_2{\cdot}23H_2O$ or $Cl_2{\cdot}7.67H_2O$. When gently warmed the crystals melt and in the dark evolve pure chlorine. The association between the chlorine molecules and the water molecules is evidently very weak.

Similar compounds are formed with other solutes and solvents, and between other molecular compounds generally.

Bonding

Compounds of this type seem generally to be held together by means of the same sort of forces by which the parent compounds are held together, viz. van der Waals' forces, plus forces arising from any polarity that the molecules may have. In some cases, however, these forces may be supplemented by varying degrees of dative bonding, leading in the limit to compounds of the coordination type.

As we have seen, the water molecule has considerable polarity, whence the low volatility of water. In a compound like $3Cl_2{\cdot}23H_2O$, the main force operating seems to be the attraction between the dipoles of the water molecules, forming a cage around the chlorine molecules. Such compounds are called "clathrate" compounds (Latin *clathratus*, meaning "enclosed by cross bars of a grating").

14.2.2 Salt-molecule compounds

The best-known examples of these are some of the salt hydrates. For example, sodium sulfate crystallizes from water at room temperature in the form of large crystals of $Na_2SO_4{\cdot}10H_2O$. These readily lose their water of crystallization, efflorescing in air to a powder of anhydrous Na_2SO_4. The water molecules are evidently only relatively loosely associated with the ions of the salt.

Not all salt hydrates are, of course, loose compounds. For many of them the association of at least some of the water molecules is much stronger. An instructive example is provided by the compound $CrCl_3{\cdot}6H_2O$, which exists in three forms.

(i) A dark green form, made by crystallizing the anhydrous chloride from water. One mole of this loses two moles of water when placed over concentrated sulfuric acid, and precipitates only one mole of AgCl to start with when treated with silver nitrate solution.

(ii) A greyish-blue form, made by refluxing a solution of (i) for some time, then cooling the solution in ice and saturating it with hydrogen chloride. This does not lose water over sulfuric acid, and immediately precipitates all of its chloride on treatment with silver nitrate.

(iii) A light green form, made by adding ether saturated with hydrogen chloride to the mother liquor from the preparation of (ii) and passing in hydrogen chloride. One mole of this loses one mole of water over sulfuric acid, and immediately precipitates two moles of AgCl with silver nitrate.

The properties of (i) - (iii) suggest the following formulations:

(i) $[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$

(ii) $[Cr(H_2O)_6]Cl_3$

(iii) $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$

All three contain coordinated water molecules; (i) and (iii) contain loosely held water as well. $CrCl_3$ also forms a brown, ether-soluble trihydrate, $[CrCl_3(H_2O)_3]^0$.

Similar compounds to salt hydrates are formed with other solvents. In all cases, a broad distinction can be drawn between coordinated solvent molecules and loosely associated ones, but the line between the two categories is not a sharp one.

Bonding

Loose compounds of the salt-molecule type seem to depend for their formation on the polarity of the molecular component, enabling it to be attracted electrostatically to the ions of the salt (positive poles to anions, negative to cations). This attraction can vary in strength, leading to the spectrum of types from loose compounds to coordination compounds indicated above.

As discussed for salt-molecule solutions, the forces of attraction between the ions and the molecules cannot be trivial since the ions have to move away from each other to make room for the molecules, and this entails a loss of Coulombic energy. The formation of salt hydrates must be due to the high polarity of the water molecule, producing strong forces of attraction between ions and molecules. A “loose” compound is not so much one in which the bonding between components is weak, but one in which the *net* bonding is weak (i.e. the difference in energy between reactants and products is low).

Nomenclature of loose compounds

Loose compounds are named as illustrated below:

$Na_2SO_4 \cdot 10H_2O$	sodium sulfate decahydrate
or	sodium sulfate—water (1/10)

15 Types of chemical reaction

15.1 General types

1 Combination

This is when two or more elements or compounds unite to form a single compound. For example:

$$2Mg + O_2 \rightarrow 2MgO$$

$$KCN + S \rightarrow KSCN$$

$$K_2O + SO_3 \rightarrow K_2SO_4$$

2 Decomposition

This is when a compound breaks up into two or more elements or simpler compounds. For example:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

$$NH_4NO_3 \xrightarrow{heat} 2H_2O + N_2O$$

$$2FeSO_4 \xrightarrow{heat} Fe_2O_3 + SO_3 + SO_2$$

A reversible decomposition is called a “dissociation”. Examples:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$2HI \rightleftharpoons H_2 + I_2$$

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

3 Displacement

This is when one element replaces another in a compound, or one compound replaces another in a larger compound. For example:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

$$Zn + CuSO_4 \xrightarrow{aq} Cu + ZnSO_4$$

$$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$$

4 Double decomposition

This is when two compounds interact by exchange of parts to produce two new compounds. The parts may be atoms or radicals. Examples:

$$AgNO_3 + NaCl \xrightarrow{aq} AgCl + NaNO_3$$

$$PCl_3 + 3AgF \rightarrow PF_3 + 3AgCl$$

$$SnCl_4 + 4PhMgCl \rightarrow SnPh_4 + 4MgCl_2$$

5 Addition

This is combination viewed from the point of view of one of the reactants, which has further atoms or groups of atoms added to it. For example:

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

$$2PCl_3 + O_2 \rightarrow 2POCl_3$$

$$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O$$

In each example, the first reactant is said to have atoms or groups of atoms from the second added to it.

6 Substitution

This is displacement or double decomposition viewed from the point of view of one of the reactants, in which one atom or radical is replaced by another atom or radical. For example:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

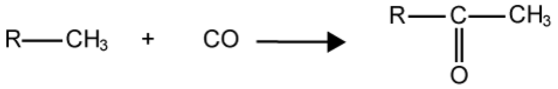
These are double decompositions:

$$CH_3{-}H + Cl{-}Cl \rightarrow CH_3{-}Cl + H{-}Cl$$

$$C_6H_5{-}H + HO{-}NO_2 \rightarrow C_6H_5{-}NO_2 + H{-}OH$$

7 Insertion

This is an addition reaction in which an atom or group of atoms is inserted between two atoms initially bound together. An example is the reaction



which takes place when R is one of a number of transition-metal radicals, e.g. $Mn(CO)_5$.

8 Isomerization

This is when a substance changes into another form with different properties but the same molecular formula. For example:

$$CH_2{=}CH{-}CH_2{-}CH_3 \xrightarrow{\text{catalyst}} CH_3{-}CH{=}CH{-}CH_3$$

$$\text{red } HgI_2 \xrightarrow{\text{heat}} \text{yellow } HgI_2$$

The different forms are called “isomers” (Greek *isos*, equal), and the phenomenon of the existence of different forms “isomerism”.

A rapidly reversible isomeric change is called a “tautomeric” change. The different forms are called “tautomers”, and the phenomenon “tautomerism”.

An isomeric change in the case of an element is called an “allotropic” change. The different forms are called “allotropes”, and the phenomenon “allotropy”.

9 Polymerization

This is when a substance changes into another substance with the same composition but a much higher molecular mass. For example:

$$nC_2H_4 \xrightarrow{\text{heat, pressure, catalyst}} (–CH_2–CH_2–)_n$$

The product of such a reaction is called a “polymer”, and the starting material the corresponding “monomer” (Greek *polus*, much; *meros*, share; *monos*, alone).

The term polymerization is also used for processes in which a polymer is formed, not from the monomer, but from other reactants of low molecular mass. This usage is somewhat misleading, but is well established.

10 Oligomerization

This is similar to polymerization except that the product contains only a small number of monomer units (Greek *oligos*, small). For example

$$3C_2H_2 \xrightarrow{\text{heat, catalyst}} C_6H_6$$

The degree of oligomerization is specified by the numerical prefixes di, tri, etc., as in dimer, trimerize, etc.

15.2 Some special types of reaction

There are many special types of reaction. Among the more important are the following.

Precipitation

This is when an insoluble solid is formed in a reaction taking place in solution. For example

$$NaCl + AgNO_3 \xrightarrow{aq} AgCl\downarrow + NaNO_3$$

$$K_2SO_4 + BaCl_2 \xrightarrow{aq} BaSO_4\downarrow + 2KCl$$

These are both double decompositions.

Precipitation reactions are popular in analytical chemistry, providing both characteristic tests for different ions, and also, when the precipitate is sufficiently insoluble, a means of determining the amount ("gravimetric analysis").

Neutralization

This is a reaction between an acid and a base. It is discussed under "Acids, bases and salts" (Chap. 16).

Hydrolysis

This is a double decomposition involving water as one of the reactants. This splits into H and OH or 2H and O. Examples:

$$POCl_3 + 3H_2O \rightarrow 3HCl + PO(OH)_3$$

$$CH_3CO_2CH_3 + H_2O \rightarrow CH_3CO_2H + CH_3OH$$

$$SOCl_2 + H_2O \rightarrow 2HCl + SO_2$$

Redox reactions

These are discussed separately under the heading "Oxidation and reduction" (Chap. 17).

Solvation

This is an addition reaction between a solute and a solvent. For example:

$$Na_2SO_4 + 10H_2O \rightarrow Na_2SO_4{\cdot}10H_2O$$

$$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O$$

$$MgBr_2 + 2Et_2O \rightarrow MgBr_2{\cdot}2Et_2O$$

The product of such a reaction is called a "solvate". If the solvent is water the adduct is called a "hydrate", and the process "hydration".

Complexation

This is an addition reaction that leads to the formation of a coordination entity (Chap. 13).

Exercise

(i) Give an example of each of the types of reaction referred to above, other than the examples cited.

(ii) Classify each of the following reactions:

(a) $NaNH_2 + C \xrightarrow{heat} NaCN + H_2$

(b) $2Pb(NO_3)_2 \xrightarrow{heat} 2PbO + 4NO_2 + O_2$

(c) $SO_2 + Cl_2 \rightarrow SO_2Cl_2$

(d) $NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

(e) $Ba(NO_3)_2 + H_2SO_4 \xrightarrow{aq} 2HNO_3 + BaSO_4$

(f) $P_4O_{10} + 6PCl_5 \rightarrow 10POCl_3$

(Click here for answers http://bit.ly/gBxNSm or see Appendix 1)

16 Acids, bases, and salts

16.1 Classical conception

Acids

Acids are substances having the following properties:

1. Sour taste.
2. Ability to dissolve substances that water will not, e.g. zinc, iron.
3. Ability to turn blue litmus red.
4. Ability to react with alkalis, the characteristic properties of each substance disappearing ("neutralization").

Examples:

Acetic acid, CH_3COOH

The 100% acid is called "glacial acetic acid" because it freezes at 17 ºC.

Hydrochloric acid

The concentrated acid is normally about 35% HCl (by mass). Anhydrous HCl is a gas, condensing to a liquid at –85 ºC.

Nitric acid

The concentrated acid is normally about 70% HNO_3.

Sulfuric acid

The concentrated acid is normally about 96% H_2SO_4.

Alkalis

Alkalis are substances having the following properties:

1. Solubility in water.
2. Solutions feel soapy.

3. Solutions turn red litmus blue.
4. Ability to neutralize acids.

Examples:

“Soda”, sodium carbonate, Na_2CO_3.

“Potash”, potassium carbonate, K_2CO_3.

“Caustic soda”, sodium hydroxide, NaOH.

“Caustic potash”, potassium hydroxide, KOH.

Ammonia

Concentrated ammonia solution normally contains about 35% NH_3.

Soda and potash liberate carbon dioxide on treatment with acids - a further feature of the latter.

Bases

Bases are substances having the following property:

1. Ability to neutralize acids.

They thus include alkalis, but constitute a larger class, including also sparingly soluble substances that neutralize acids.

Examples:

“Limestone”, “chalk”, calcium carbonate, $CaCO_3$.

“Quicklime”, calcium oxide, CaO.

“Slaked lime”, calcium hydroxide, $Ca(OH)_2$.

Note

Quicklime is formed from limestone by heating.

Slaked lime is formed from quicklime by adding water.

Soda and potash, once made by leaching ashes with water, can be converted into the caustic varieties by treatment with milk of lime, a suspension of slaked lime.

Exercise

Write balanced equations for these processes.

(Click here for answers http://bit.ly/iclRIc or see Appendix 1)

Salts

Salts are neutral substances (i.e. having neither the properties of an acid nor those of a base) formed by the reaction of certain acids with certain bases.

Example:

Sodium chloride, NaCl, formed by the reaction of hydrochloric acid with sodium hydroxide:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Note the use of the word “certain”. Sodium acetate, formed by the reaction of acetic acid with sodium hydroxide,

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

is *not* neutral. Its solution turns red litmus blue, and it is therefore a base. When acetic acid is “neutralized” with sodium hydroxide (in the sense defined above), less sodium hydroxide is required than that needed to convert all the acetic acid into sodium acetate.

Note

Some substances can function as both an acid and a base. For example, aluminium hydroxide can react with both hydrochloric acid and sodium hydroxide:

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$$

Substances of this type are called amphoteric (Greek *ampho*, both).

A useful distinction

A useful distinction can be drawn between a substance that is an acid or a base and one that *becomes* an acid or base on contact with water.

Thus, sulfur trioxide dissolves in water to give a solution with acidic properties. This solution is identical, however, with that obtained by dissolving sulfuric acid in water. Thus, sulfur trioxide is not so much an acid but an "acid former":

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Similarly, quicklime is better regarded as a base-former than a base:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Acid-base character of oxides

Most nonmetal oxides are acid-formers (hence Lavoisier's name for oxygen: Greek *oxus*, acid, -gen, former). Exceptions are N_2O and NO, which give neutral solutions in water.

Metal oxides vary from being base-formers (e.g. Na_2O, CaO) to acid-formers (e.g. CrO_3, Mn_2O_7). This variation is determined mainly by the number of oxygen atoms (n) per metal atom:

low n	base-former
intermediate n	amphoteric or neutral
high n	acid-former

So, for example, MnO is basic, MnO_2 is weakly amphoteric, and Mn_2O_7 is acidic. A second factor is the electronegativity of the metal (e.g., CaO is basic, ZnO is amphoteric).

16.2 Stoicheiometric conception

This is based on a shift in the concept of "neutralization", from the complete disappearance of properties characteristic of acids and bases, to the achievement of an exact balance between the number of moles of acid and the equivalent number of moles of base. For the reaction between hydrochloric acid and sodium hydroxide mentioned in the previous section, the neutral point and the equivalence point are the same, but for the reaction between acetic acid and sodium hydroxide, they are not.

On the stoicheiometric conception, an *acid* may be defined as a compound of general formula H_nA that undergoes the transformation

$$H_nA + nNaOH \rightarrow Na_nA + nH_2O$$

when treated with a solution of sodium hydroxide. Here n is called the "basicity" of the acid, and A is any radical. (Note that A may contain further H's, as in the acetate radical.)

Similarly, a *base* may be defined as a compound of formula $B(OH)_m$ that undergoes the transformation

$$mHCl + B(OH)_m \rightarrow BCl_m + mH_2O$$

when treated with hydrochloric acid, m being the "acidity" of the base.

A *salt* is the product of the reaction between an acid and a base according to the appropriate stoicheiometric equation,

$$mH_nA + nB(OH)_m \rightarrow B_nA_m + mnH_2O.$$

"Neutralization" in this sense is a species of double decomposition.

On this scheme, sodium acetate is now a salt, and not a base. Similarly, sodium carbonate becomes a salt - a salt of the acid "carbonic acid", H_2CO_3, formed by dissolving carbon dioxide in water:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

$$H_2CO_3 + 2NaOH \rightarrow Na_2CO_3 + 2H_2O$$

The reaction between sodium carbonate and an acid now falls into a different class from "neutralization" (in the new sense). It now becomes a displacement reaction - the displacement of a weak acid by a strong acid from one of its salts:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3$$

This is followed by the partial decomposition of the H_2CO_3, but the displacement part of the reaction holds for a salt of any weak acid:

$$NaX + HCl \rightarrow NaCl + HX$$

On the stoicheiometric conception of neutralization, we can now talk about the step-wise neutralization of a polybasic acid and the formation of "acid salts" and "neutral salts", e.g. $KHSO_4$ and K_2SO_4. Similarly, for a polyacidic base: e.g. $Cu(OH)_2$ forms $Cu(OH)Cl$ and $CuCl_2$, the former being a "basic" salt.

The stoicheiometric conception of acids, bases, and salts is based on different types of observation from the classical conception (those that lie behind chemical formulae and equations) and sits rather loosely on the observations that lie behind the latter. Sodium carbonate, having given us the name "alkali", now becomes a salt. Care is needed to keep the two systems distinct.

16.3 Electrolytic conception

When soluble in water, compounds that are acids, bases, or salts on the above definitions are generally good electrolytes. Thus, hydrochloric acid, sodium hydroxide, and sodium chloride each behave in solution as if there are two ions per formula unit, and in electrolysis, as if each ion carries a single charge:

$$HCl: \quad H^+ + Cl^-$$

$$NaOH: \quad Na^+ + OH^-$$

$$NaCl: \quad Na^+ + Cl^-$$

Acetic acid behaves as if it is partly dissociated into two ions according to the equilibrium

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Sodium carbonate behaves as if it is dissociated into Na^+ and CO_3^{2-} ions, with the CO_3^{2-} ions partly reacting with the water according to the equilibrium

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

The latter reaction belongs to the class called "hydrolysis" (see Chap. 15).

These facts suggest the association of acidity with the aqueous H^+ ion and basicity with the aqueous OH^- ion. An acidic solution is then one that contains more H^+ ions than pure water does and a basic solution one that contains more OH^- ions. Pure water has a very slight conductivity, attributed to low concentrations of H^+ and OH^- ions (~10^{-7} M at 25 ºC), arising from a small degree of self-ionization:

$$H_2O \rightleftharpoons H^+ + OH^-$$

An acidic solution accordingly has $[H^+] > 10^{-7}$ M at 25 ºC and an alkaline one $[OH^-] > 10^{-7}$ M.

Based on this association, it is possible to produce definitions of acids, bases, and salts that go some way to harmonizing the classical and stoicheiometric schemes:

> An *acid* is a compound that ionizes in water to give H^+ ions.
>
> A *base* is a compound that ionizes in water to give OH^- ions.
>
> A *salt* is a compound that, when it ionizes, does not give H^+ ions as the sole positive ions, or OH^- ions as the sole negative ions.

On these definitions:

1. Sodium carbonate is a salt (as on the stoicheiometric scheme), but can be also be described as a base-former (cf. the classical scheme).

2. Potassium hydrogen sulfate is both a salt (as on the stoicheiometric scheme) and an acid (as on the classical scheme), and can continue to be called an "acid salt".

3. Neutralization (classical sense) is bringing the concentration of H^+ and OH^- back to their values in pure water.

4. Neutralization in the stoicheiometric sense is unchanged.

16.4 Equations for acid-base reactions

Neutralization (stoicheiometric sense)

In the case of the reaction between a strong (i.e. completely dissociated) acid and a strong base, the equation for the reaction may be simplified as exemplified by the following:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$\therefore\ (H^+ + Cl^-) + (Na^+ + OH^-) \rightarrow (Na^+ + Cl^-) + H_2O$$

$$\therefore\ H^+ + OH^- \rightarrow H_2O$$

That the reaction does not involve the counter-ions is demonstrated experimentally by the fact that the heat of neutralization of a strong acid by a strong base is the same per mole of H^+ for all such acids and bases.

In the case of a reaction involving a weak acid or base, the simplified equation for the reaction is best written in terms of the unionized species. The process of simplification is then exemplified by:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

$$\therefore\ CH_3COOH + (Na^+ + OH^-) \rightarrow (CH_3COO^- + Na^+) + H_2O$$

$$\therefore\ CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

Displacement

Displacement reactions can be simplified similarly, e.g.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3$$

$$\therefore\ (2Na^+ + CO_3^{2-}) + (2H^+ + 2Cl^-) \rightarrow (2Na^+ + 2Cl^-) + H_2CO_3$$

$$\therefore\ CO_3^{2-} + 2H^+ \rightarrow H_2CO_3$$

$$CH_3COONa + HCl \rightarrow NaCl + CH_3COOH$$

$$\therefore\ (CH_3COO^- + Na^+) + (H^+ + Cl^-) \rightarrow (Na^+ + Cl^-) + CH_3COOH$$

$$\therefore\ CH_3COO^- + H^+ \rightarrow CH_3COOH$$

In using equations like this, care needs to be taken to distinguish between those that refer to processes taking place on mixing solutions and those that refer to processes taking place within a single solution. For example, the simplified equation for the displacement of acetic acid from sodium acetate by hydrochloric acid

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

looks, on the face of it, like the reverse of that representing the dissociation of acetic acid

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The two processes are, however, different, one taking place on mixing solutions, the other taking place within a solution:

$$\begin{gathered} CH_3COO^-\ \text{(in solution A)} + H^+\ \text{(in solution B)} \rightarrow \\ CH_3COOH\ \text{(in the solution obtained by mixing A \& B)} \end{gathered}$$

$$\begin{gathered} CH_3COOH\ \text{(in solution A)} \rightleftharpoons \\ CH_3COO^-\ \text{(in solution A)} + H^+\ \text{(in solution A)} \end{gathered}$$

The equation

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

tends to disguise the fact that the process this represents involves the displacement of a weak acid by a strong acid from a salt of the weak acid, and one must be careful not to get confused.

16.5 Further aspects

Aqueous ammonia as a base

Aqueous ammonia is a base in the classical sense, but poses problems on the stoicheiometric scheme. On this scheme, it is necessary to postulate the formation of ammonium hydroxide by the reaction

$$NH_3 + H_2O \rightarrow NH_4OH$$

the NH_4OH being the base and NH_3 the base-former. Unfortunately, no evidence for the formation of a species of formula NH_4OH has been obtained.

On the electrolytic scheme, however, it is not necessary to postulate the intermediate formation of NH_4OH. The properties of aqueous ammonia can be well accounted for in terms of the equilibrium

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

On this scheme, NH_3 is again a base-former - it is the solution that is basic, as if there *were* a base of formula $NH_4^+OH^-$.

Note, however, that tertiary alkyl amines, NR_3, on treatment with an alkyl halide, RX, give quaternary ammonium salts, $[NR_4]X$, analogous to ammonium salts, $[NH_4]X$, and these, on treatment with moist silver oxide, give the corresponding hydroxides

$$2[NR_4]X + Ag_2O + H_2O \rightarrow 2[NR_4]OH + 2AgX$$

These are very strong alkalis.

On the nature of the hydrogen ion in solution

While the hydration of all ions is acknowledged, special attention has been paid to the hydration of the hydrogen ion, for the following reason:

Anhydrous acids, unlike anhydrous bases and salts, are not ionic. For example, hydrogen chloride is a gas, and its molecules have a low polarity ($H^{0.2+}Cl^{0.2-}$, Chap. 5). While molten sodium hydroxide and sodium chloride are good electrolytic conductors, liquid hydrogen chloride scarcely conducts electricity at all:

	κ(m.p.)/$\Omega^{-1}m^{-1}$
sodium hydroxide	210
sodium chloride	360
hydrogen chloride	$\sim10^{-7}$

A few anhydrous acids are good conductors (e.g. 100% sulfuric acid), but this is unusual.

Thus, in the case of the hydrogen ion, it looks as though hydration is essential for its formation. Put another way, it looks as if the H^+ ion cannot exist on its own, but only in association with one or more water molecules.

The number of water molecules that it is associated with in a particular solution is difficult to determine. That one molecule is enough for its formation, however, can be demonstrated by examining the hydrates of strong acids like hydrochloric, nitric, and sulfuric. The lowest hydrates of these are as follows:

hydrochloric acid	$HC1\cdot H_2O$	m.p. −15 ºC
nitric acid	$HNO_3\cdot H_2O$	m.p. −38 ºC
sulfuric acid	$H_2SO_4\cdot H_2O$	m.p. 9 ºC

In the liquid state, these of course conduct electricity, and their structures in the solid state have been shown to be $H_3O^+Cl^-$, $H_3O^+NO_3^-$, and $H_3O^+HSO_4^-$ respectively.

In view of the above, some chemists insist that the hydrogen ion in water should not be called the hydrogen ion, but the hydroxonium ion, and should not be written as H^+ but as H_3O^+. In doing this they recognize that the H_3O^+ ion will be hydrated further, but believe that no formulation less than this will do justice to the difference in properties between anhydrous and aqueous acids. In practice, however, most chemists continue to write H^+, and to call it the hydrogen ion. Whether the latter approach is lazy or the former pedantic is a matter for discussion.

Some chemists further insist that compounds like HCl, HNO_3, and H_2SO_4 should not strictly be called acids. The true acids are $(H_3O)Cl$, $(H_3O)NO_3$, and $(H_3O)HSO_4$, and HCl, HNO_3, and H_2SO_4 are really acid-formers. On this basis, the latter should not be called hydrochloric acid, nitric acid, and sulfuric acid, but hydrogen chloride, hydrogen nitrate, and hydrogen sulfate. Few chemists would go as far as this, though “hydrogen chloride” has become the generally accepted name for anhydrous HCl.

IUPAC nomenclature

For other than very common oxoacids, IUPAC prefer to name acids as compounds of H^+, e.g. hydrogen chloride. For common oxoacids, however, they recommend the traditional name, or a more systematic alternative, e.g.

	Traditional name	**Alternative**
H_2SO_3	sulfurous acid	trioxosulfuric acid oxosulfuric(IV) acid
H_2SO_4	sulfuric acid	tetraoxosulfuric acid oxosulfuric(IV) acid

Most users stick to the traditional names.

16.6 Lowry-Brønsted conception of acids and bases

This is a broader conception than those we have discussed so far. It is one that gets over the distinction between acids and acid-formers or bases and base-formers, though it does so at the expense of other difficulties.

On this scheme,

an *acid* is a molecule or ion that supplies protons (i.e. a proton donor);

a *base* is a molecule or ion that accepts protons (i.e. a proton acceptor).

This means that the molecules HCl, HNO_3, and H_2SO_4 are now acids, not acid-formers:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ etc.}$$

Similarly, the species CO_3^{2-} and NH_3 are now bases and not base-formers:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \text{ etc.}$$

Further, the ion H_3O^+ is itself an acid, the ion OH^- is a base, and the H_2O molecule is *both* an acid *and* a base. These functions can all be seen in the self-ionization

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

On the Lowry-Brønsted scheme, an acid-base reaction effectively involves a competition for protons representable by an equilibrium of the type

$$HX^x + Y^y \rightleftharpoons X^{x-1} + HY^{y+1}$$

where x and y represent the charges on HX and Y respectively. Here X^{x-1} is called the “conjugate base” of the acid HX^x, and HX^x the “conjugate acid” of the base X^{x-1}. For example, NH_4^+ is the conjugate acid of NH_3, and CH_3COO^- is the conjugate base of CH_3COOH, and the reaction between them involves the competition between the two bases (NH_3, CH_3COO^-) for the proton:

$$NH_4^+ + CH_3COO^- \rightleftharpoons NH_3 + CH_3COOH$$

Advantages of the Lowry-Brønsted scheme are as follows:

(i) It takes in acid-formers and base-formers.

(ii) It is applicable to other solvents besides water. For example, in liquid ammonia, NH_4^+ acts as a proton donor, NH_2^- acts as a proton acceptor, and NH_3 functions in both ways. The Lowry-Brønsted definitions thus apply unchanged.

Disadvantages of the scheme are:

(i) It loses the category of salt. The scheme is essentially dualistic in character, and has no place for a third category. Sodium chloride is regarded merely as an aggregate of ions, one of which (Na^+) is neutral, and the other (Cl^-) a base - the conjugate base of HCl.

(ii) The scheme also loses the idea of neutralization. Though the latter could be defined as the complete transfer of a proton from an acid to a base (cf. the stoicheiometric conception), it would include some processes for which the name neutralization hardly seems appropriate, e.g.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

In view of the disadvantages, it can be questioned whether it is worth trying to extend the ideas of acid and base in the way that Lowry and Brønsted do. Chemistry might be better served if the classification of molecules and ions according to their ability to accept or donate protons – which is undoubtedly a very useful classification – were to be divorced from the classification of substances into acids and bases, and be given a terminology of its own. In fact, such terminology lies readily to hand, the terms “proton donor” and “proton acceptor” being entirely suitable for this purpose.

Note

IUPAC are trying to dissuade chemists from calling H^+ a proton. A proton is strictly $^1H^+$. Ordinary samples of acid contain 99.985% of $^1H^+$ and 0.015% of $^2H^+$. IUPAC recommend the following names:

H	hydrogen	^1H	protium	^2H	deuterium	^3H	tritium
H^+	hydron	$^1H^+$	proton	$^2H^+$	deuteron	$^3H^+$	triton

Exercise

Classify each of the following compounds on each of the four schemes given above (classical, stoicheiometric, electrolytic, Lowry-Brønsted):

(i) NaCN; (ii) NH_4Cl; (iii) $NaHCO_3$.

(Click here for answers http://bit.ly/hStxuL or see Appendix 1)

16.7 Solvent-system conception of acids and bases

The electrolytic conception of acids and bases can be extended to other ionizing solvents by means of the following definitions:

> An *acid* is a compound that ionizes to give the cation natural to the solvent.
>
> A *base* is a compound that ionizes to give the anion natural to the solvent.

The ions “natural” to a solvent are those produced in its self-ionization. For some of the more important ionizing solvents, these are as follows.

Solvent	**Cation**	**Anion**
H_2O	H_3O^+	OH^-
NH_3	NH_4^+	NH_2^-
HF	H_2F^+	HF_2^-
CH_3CO_2H	$CH_3CO_2H_2^+$	$CH_3CO_2^-$
H_2SO_4	$H_3SO_4^+$	HSO_4^-
HSO_3F	$H_2SO_3F^+$	SO_3F^-
N_2O_4	NO^+	NO_3^-
BrF_3	BrF_2^+	BrF_4^-

Thus, NH_4Cl is an acid in liquid ammonia, KNH_2 is a base, $KHSO_4$ is a base in 100% sulfuric acid, etc.

This extension of the ideas of acids and bases is a very useful one, and does not stretch the original conception too much. Note, however, that substances can change their character in going from one solvent to another. Thus, NH_4Cl is a salt in water, but an acid in liquid ammonia. Similarly, $KHSO_4$ is an acid salt in water, and a base in 100% H_2SO_4. A third example is CH_3COOH, which is an acid-former in water

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

and a base-former in sulfuric acid

$$CH_3COOH + H_2SO_4 \rightleftharpoons H_3CO_2H_2^+ + HSO_4^-$$

This being so, it is best to specify the solvent as well as the class of substance, at least when the solvent is not water, e.g.

NH_4Cl	ammonia acid
$KHSO_4$	sulfuric-acid base

16.8 Other conceptions of acids and bases

The remarks made at the end of the section on the Lowry-Brønsted definition apply with even greater force to two other definitions that have been proposed for acids and bases, namely:

	"Acid"	**"Base"**
Lux-Flood	oxide ion accepter	oxide ion donor
Lewis	electron-pair acceptor	electron-pair donor

These take us a long way from the original conceptions of acid and base, and might be better divorced from these ideas completely. At the very least, they should only be used in a qualified way, as in the expressions "Lewis acid" and "Lewis base".

For further details about these two definitions, see textbooks.

17 Oxidation and reduction

17.1 Basic theory

The word “oxidation” originally meant the gain of oxygen by an element or compound, and “reduction” the loss of oxygen, as in the processes:

$2Mg + O_2 \rightarrow 2MgO$ oxidation of magnesium (1a)
$2H_2 + O_2 \rightarrow 2H_2O$ oxidation of hydrogen (1b)
$4\sim FeO + O_2 \rightarrow 2Fe_2O_3$ oxidation of iron monoxide (1c)
$Mg + H_2O \rightarrow MgO + H_2$ oxidation of magnesium, reduction of water (1d)

There are, however, other processes that are similar to the above, for example:

$Mg + Cl_2 \rightarrow MgCl_2$ (2a)
$H_2 + Cl_2 \rightarrow 2HCl$ (2b)
$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$ (2c)
$Mg + 2HCl \rightarrow MgCl_2 + H_2$ (2d)

There is a close parallel between reactions (1a) - (1d) and (2a) - (2d), not only in terms of the equations for the reactions, but also in terms of the nature of the reactants and products. Thus in (1a) and (2a) magnesium metal combines with a nonmetal to form a product that is electrically salt-like.

The basis of the similarity of (1a) - (1d) and (2a) - (2d) is that chlorine is an electronegative element like oxygen. Thus (1a) - (1d) and (2a) - (2d) may be classed together if we extend the idea of oxidation and reduction as follows:

Oxidation: net gain of an electronegative group or net loss of an electropositive one.

Reduction: net loss of an electronegative group or net gain of an electropositive one.

Here “net” means “after allowance for difference in valency”, so that in

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

there are no net gains or net losses (e.g., each magnesium atom gains two electronegative atoms, but loses one with twice the valency). On these definitions, assignments corresponding to those given for (1a) - (1d) may be made for (2a) - (2d). In addition, complementary assignments can be made for (1a) - (1c) and (2a) - (2c) corresponding to those for (1d) and (2d), e.g. for (1a)

$2Mg + O_2 \rightarrow 2MgO$ oxidation of magnesium, reduction of oxygen

In (1d) and (2d), the oxygen and chlorine are unchanged: they gain an equivalent amount of magnesium to the hydrogen they lose.

In the case of (1a) and (2a), the similarity between the two reactions has an even deeper basis. Both MgO and $MgCl_2$ are predominantly ionic compounds, so that (1a) and (2a) may be written:

$$2Mg + O_2 \rightarrow 2Mg^{2+}O^{2-} \quad (1a')$$

$$Mg + Cl_2 \rightarrow Mg^{2+}(Cl^-)_2 \quad (2a')$$

In both processes, each magnesium atom loses two electrons, while each oxygen or chlorine atom gains electrons. This suggests the definitions:

Oxidation: loss of one or more electrons by an atom or radical.

Reduction: gain of one or more electrons by an atom or radical.

These definitions are of limited applicability, however, as can be seen from reactions (1b) and (2b). Neither H_2O nor HCl is ionic, so that this new definition does not apply. Both molecules are, however, polarized, and if this polarization is imagined to be complete, the new definitions can then be used:

$2H_2 + O_2 \rightarrow 2H_2O \dashrightarrow 2(H^+)_2O^{2-}$	oxidation of hydrogen, reduction of oxygen	(1b')
$H_2 + Cl_2 \rightarrow 2HCl \dashrightarrow 2H^+Cl^-$	oxidation of hydrogen, reduction of chlorine	(2b')

The dashed arrows here refer to the mental process of imagining the polarization being taken to the limit. The resulting charges are what we have previously called "polar numbers" or "oxidation numbers". In terms of these, oxidation and reduction may be defined as follows:

Oxidation: an increase in the oxidation number of an atom or radical.

Reduction: a decrease in the oxidation number of an atom or radical.

These definitions are equivalent to those given earlier in terms of net gains or net losses of electronegative or electropositive species. They have the advantage of being easier to use, but suffer from being very artificial when applied to other than ionic compounds.

Notes

(i) As now defined, oxidation and reduction always go together. Oxidation-reduction reactions are accordingly called "redox" reactions. The species that effects the oxidation is called the oxidizing agent, and is itself reduced in the reaction; the other species is called the reducing agent, and is itself oxidized.

(ii) On the new definitions, gain or loss of oxygen continues to be oxidation or reduction, except

  (a) when the oxygen displaces, or is displaced by, another electronegative species, as in

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

  (b) when the oxygen is in combination with fluorine, where gain of oxygen corresponds to reduction of fluorine and loss to oxidation.

(iii) Organic chemists sometimes speak of loss of hydrogen as oxidation and gain of hydrogen as reduction. This is acceptable, as long as the hydrogen is electropositive relative to the species that is gaining or losing it, as is the case with organic compounds. In relation to metals like sodium or potassium, gain of hydrogen corresponds to oxidation.

(iv) The retention of the word "oxidation" in the broader definitions is unfortunate, especially when we have to speak of loss of oxygen as an oxidation, as we do in

$$2OF_2 \xrightarrow{\text{heat}} O_2 + 2F_2$$

It might have been better to have used the words "elevation" and "reduction" to describe the broader categories, and "oxidation" and "deoxidation" to describe the original ones. As it is, whenever chemists wish to differentiate the latter from the former, they have to use the terms "oxygenation" and "deoxygenation".

17.2 Half equations

When the compounds involved are ionic, the equation for a redox reaction can be divided into two half equations, one representing the reduction of the oxidizing agent and the other the oxidation of the reducing agent. Thus equation (2a) or (2a') can be divided into

$$Mg \rightarrow Mg^{2+} \text{ (in } MgCl_2\text{)} + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ (in } MgCl_2\text{)}$$

Note that this can *only* be done when the compounds are ionic: it *cannot* be done in the case of an equation like (1b) or (2b).

The division of equations for redox reactions into half equations is most useful for reactions in solution. This is because ions in solution are relatively independent of each other (e.g. the freezing points of dilute solutions correspond to the number of ions present).

Consider the reaction

$$\mathrm{Mg(s) + Cl_2(aq) \rightarrow MgCl_2(aq)}$$

If the ions in solution are independent, this equation may be written

$$\mathrm{Mg(s) + Cl_2(aq) \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)}$$

This may then be written as the sum of

$$\mathrm{Mg(s) \rightarrow Mg^{2+}(aq) + 2e^{-}}$$
$$\mathrm{Cl_2(aq) + 2e^{-} \rightarrow 2Cl^{-}(aq)}$$

with each process independent of the other. To the extent that ions in solution are independent of each other, therefore, redox reactions in solution can be rationalized in terms of half reactions.

The property that is most used for this purpose is the standard potential of the electrode at which the half reaction occurs in an electrochemical cell, E^o. This can be used to work out the direction in which a complete reaction will tend to go, since the more positive the value of E^o, the stronger the tendency for the half reaction to proceed in the direction of taking up electrons. Thus, from the following values,

	E^o
$Mg^{2+} + 2e^- = Mg$	–2.34 V
$Cl_2 + 2e^- = 2Cl^-$	1.36 V

we can see at once that the second half reaction has a greater tendency to proceed from left to right than the first, so that the complete reaction

$$Mg + Cl_2 = Mg^{2+} + 2Cl^-$$

will tend to go in the direction written.

Notes

(i) In the context of E^o values, half reactions are always written as reductions, with electrons on the left.

(ii) Standard electrode potentials only tell us about the direction in which a reaction will *tend* to proceed. We must never forget that it is possible for a reaction to be energetically feasible but immeasurably slow.

(iii) Standard electrode potentials only relate to standard conditions. For ions in solution, these are standard pressure (1 bar) and a concentration of 1 M (1 mol dm^{-1}). Allowances must be made under other conditions.

(iv) The whole procedure depends on ions in solution being independent. This does not hold at high concentrations and where there is complexing.

(v) Other than in examinations, chemists only occasionally need to predict the direction of a redox reaction. An alternative to *remembering* that positive values of $E°$ favour uptake of electrons is to look up the values for reactions you know tend strongly to proceed to the left or the right, e.g.

$K^+ + e^- = K$	–2.93 V
$F_2 + 2e^- = 2F^-$	+2.87 V

If you set the equations you are considering between these, e.g.

$K^+ + e^- = K$	-2.93 V
$A^+ + e^- = A$	-1.0 V
$X^+ + e^- = X$	$+1.0$ V
$F_2 + 2e^- = 2F^-$	$+2.87$ V

you can see at once that X^+ will oxidize A as F_2 oxidizes K.

Exercise

From a table of standard electrode potentials given in a textbook, predict the direction of the following reaction

$$2Fe^{2+} + X_2 = 2Fe^{3+} + 2X^-$$

for X = Cl, Br, and I.

(Click here for answers http://bit.ly/fl8wZ6 or see Appendix 1)

17.3 On the balancing of equations for redox reactions

Equations for redox reactions in solution are best balanced via the appropriate half equations. These are combined in such away as to eliminate the electrons in them. For example, for the dissolution of aluminium in acid, the half equations are

$$Al \rightarrow Al^{3+} + 3e^-$$

$$2H^+ + 2e^- \rightarrow H_2$$

so that the first must be multiplied by 2 and the second by 3 to give

$$2Al \rightarrow 2Al^{3+} + 6e^-$$

$$6H^+ + 6e^- \rightarrow 3H_2$$

which on addition give

$$2Al + 6H^+ \rightarrow 2Al^{3+} + 3H_2$$

Balancing of half equations

Half equations can be routinely balanced by one of the following two procedures. Whichever procedure is chosen, the result can be checked by applying the other one.

Procedure A

1. Write down the reactant(s) and product(s).
2. Balance the main element(s).
3. Balance oxygen atoms with H_2O molecules.
4. Balance hydrogen atoms with H^+ ions.
5. Balance charges with electrons.

Procedure B

1. Write down the reactant(s) and product(s).
2. Balance the main element(s).
3. Work out the number of electrons from the change in oxidation number of the main element.
4. Balance oxygen atoms with H_2O molecules.
5. Balance hydrogen atoms with H^+ ions.

As an example of the application of these procedures, consider the reduction of dichromate to chromium(III) in acid solution. Procedure A gives:

Step (1): $Cr_2O_7^{2-} \rightarrow Cr^{3+}$
Step (2): $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Step (3): $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Step (4): $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Step (5): $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Procedure B begins similarly, but after (2), the oxidation number of the chromium in $Cr_2O_7^{2-}$ is determined (+6), and from this, the number of electrons required in the equation:

$$2Cr^{6+} + 6e^- \rightarrow 2Cr^{3+}$$

The final steps of Procedure B are thus:

Step (3): $Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}$
Step (4): $Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Step (5): $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Note that both procedures lead to equations containing H^+ ions. For reactions in alkaline solutions, it is as well to eliminate these by adding $n$$OH^-$ ions to each side of the equation, where n is the number of H^+ ions. You can then replace $nH^+ + nOH^-$ on one side of the equation by nH_2O, leaving nOH^- on the other side.

For analytical purposes, it is not necessary to specify the species in the equation with complete precision, and rigour in this respect is sometimes relaxed in the interests of simplicity. Thus, green solutions of chromium(III) do not strictly contain Cr^{3+}, but Cr^{3+} complexed with whatever anion is present; for simplicity, however, the species is written as Cr^{3+}. Unfortunately, there do not seem to be any rules governing these simplifications, and what is or is not acceptable tends to be somewhat arbitrary. In the above examples, Cr^{3+} is accepted without question: Cr^{6+} for $Cr_2O_7^{2-}$ would be frowned upon.

Exercise

Write a balanced equation for each of the following reactions:

(i) The oxidation of HCO_2H with MnO_4^- in acid solution.

(ii) The oxidation of I^- with IO_3^- in strong hydrochloric acid (product ICl_2^-, simplified to I^+).

(iii) The oxidation of H_2O_2 with MnO_4^- in acid solution.

(iv) Aerial oxidation of $Fe(OH)_2$ to $Fe(OH)_3$ in alkaline solution.

(v) The oxidation of HCO_2^- with MnO_4^- in alkaline solution (the MnO_4^- is reduced to MnO_2).

(vi) The oxidation of CuSCN with IO_3^- in strong hydrochloric acid (products Cu^{2+}, SO_4^{2-}, HCN, and I^+).

(Click here for answers http://bit.ly/gKISKI or see Appendix 1)

18 Further study

I have designed this course to be a general introduction to the study of inorganic chemistry proper. This comprises the chemistry of the elements and various special topics - organometallic compounds, bioinorganic chemistry, solid-state chemistry, solution chemistry, and others. For some topics, you will need additional background material, but you should get most of this from courses in the other branches of chemistry, including theoretical chemistry.

I hope you have found this course helpful, and will enjoy your further studies.

Comments on the course

If you have any queries or suggestions about the course, please contact the author,
P.G.Nelson@hull.ac.uk

If you have any comments about the Web site, please contact the publisher.

Appendix 1 Hints and answers

A1.1 Answers to questions and exercises, Chapters 1 - 5

Section 2.3

(1) Main uses:

Platinum: jewellery, catalysis
Gold: money, jewellery
Silver: jewellery, photography (non-digital), electronics (as electrical conductor)
Uranium: nuclear energy
Mercury: manufacture of sodium hydroxide
Tin: tin plate
Molybdenum: in steels
Copper: electrical conductor, alloys (brass, bronze)

(2) For other measures of importance, see Further Reading.

Section 3.1

(a) Yellow
(b) Orange

Section 3.2

Most chemists classify these elements as follows:

Carbon: nonmetal
Phosphorus: nonmetal
Arsenic: semimetal
Antimony: metal
Selenium: nonmetal
Iodine: nonmetal

Section 4.4

(i) Water, H_2O: colourless liquid, b.p. 100 °C
Hydrogen peroxide, H_2O_2: colourless liquid, b.p. 150 °C
(ii) Carbon monoxide, CO: colourless gas, b.p. −192 °C
Carbon dioxide, CO_2: colourless gas, sublimes −78 °C

(iii) Ammonia, NH_3: colourless gas, b.p. −33 °C
Hydrazine, N_2H_4: colourless liquid, b.p. 114 °C
Hydrogen azide, HN_3: colourless liquid, b.p. 37 °C (explosive)
(iv) Phosphorous oxide, P_4O_6: colourless solid, m.p. 24 °C, b.p. 174 °C
Phosphoric oxide, P_4O_{10}: white solid, sublimes 300 °C
(v) Hydrogen sulfide, H_2S: colourless gas, b.p. −61 °C
Hydrogen polysulfides, H_2S_{2-6}: yellow liquids
(vi) Sulfur dioxide, SO_2: colourless gas, b.p. −10 °C
Sulfur trioxide, SO_3: white solid, m.p. 17 °C, b.p. 45 °C
(vii) Sulfur dichloride, SCl_2, dark red liquid, b.p. −59 °C
Polysulfur dichlorides, $S_{2-100}Cl_2$: orange liquids
(viii) Sulfur tetrafluoride, SF_4: colourless gas, b.p. −38 °C
Sulfur hexafluoride, SF_6: colourless gas, sublimes −64 °C
Disulfur decafluoride, S_2F_{10}: colourless liquid, b.p. 30 °C

Nomenclature will be discussed in Section 7.5.

Section 4.5

(i) Calcium chloride, $CaCl_2$
(ii) Aluminium chloride, $AlCl_3$
(iii) Copper monochloride, CuCl
Copper dichloride, $CuCl_2$
(iv) Calcium oxide, CaO
Calcium peroxide, CaO_2
(v) Aluminium oxide, Al_2O_3
(vi) Iron monoxide, ~FeO
Triiron tetraoxide, Fe_3O_4
Diiron trioxide, Fe_2O_3
(vii) Dicopper oxide, Cu_2O
Copper monoxide, CuO

Alternative names for (iii), (vi), and (vii) will be explained in Section 7.5.

Section 5.1.2

(i) SiC, SiO_2
(ii) AB_2C_2

Section 5.2

[For hints, see Appendix A1.2.]

In the following answers, E' refers to the energy per mole of Na^+ and Cl^- ions.

(i) $E = -e^2/4\pi\varepsilon_0 r$
(ii) $E' = -Le^2/4\pi\varepsilon_0 r$
(iii) $E = -2{\cdot}586e^2/4\pi\varepsilon_0 r$, $E' = -1{\cdot}293Le^2/4\pi\varepsilon_0 r$
(iv) Equations differ only in numerical factor (1.000, 1.293, or 1.748).
(v) NaCl(g): $E' = -589$ kJ mol^{-1}
Na_2Cl_2(g): $E' = -718$ kJ mol^{-1}
NaCl(c): $E' = -864$ kJ mol^{-1}

Section 5.3

$(Na^+)_2K^+(e^-)_3$

Strength of binding about the same as in Na^+e^- or K^+e^- (one metallic electron per atom).

A1.2 Hints for exercises, Section 5.2

(i) Use the Coulomb equation for the energy between two charges, q_1 and q_2, a distance d apart:

$$E = q_1q_2/4\pi\varepsilon_0 d$$

Here ε_0 is the permittivity of a vacuum, a constant.

(ii) Multiply by the Avogadro constant, L.

(iii) Include the repulsion between like charges. Remember that one mole of Na^+ and Cl^- ions gives ½ mole of $(Na^+Cl^-)_2$ molecules.

A1.3 Answers to questions and exercises, Chapters 6 - 9

Section 6.3

(i) $[SiC_{4/4}]_\infty$
(ii) $[SiO_{4/2}]_\infty$

Section 7.1

Series in order of decreasing electropositive character (values in volts):

Cations: K (–2.92), Ca (–2.87), Na (–2.71), Mg (–2.34), Al (–1.67), Zn (–0.76), Fe (–0.44), Sn (–0.14), H (0.00), Cu (+0.34)
Anions: I (+0.53), Br (+1.07), Cl (+1.36), F (+2.85)

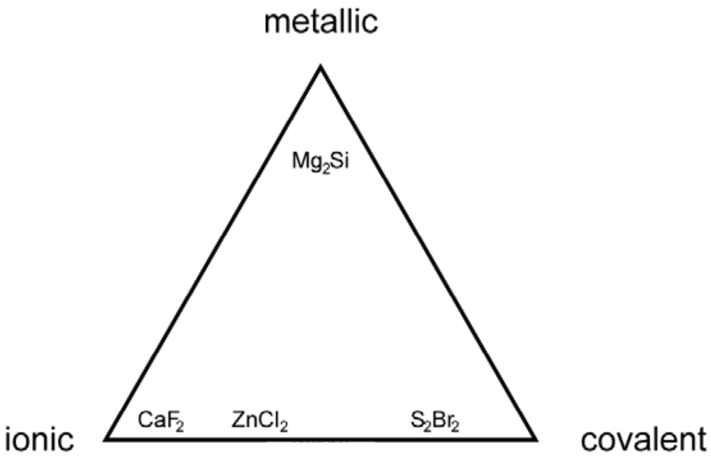
Section 7.3, first exercise

For the elements in the previous exercise, Pauling's electronegativities give:

K (0.8), Na (0.9), Ca (1.0), Mg (1.2), Al (1.5), Zn (1.6), Fe/Sn (1.8), Cu (1.9), H (2.1), I (2.5), Br (2.8), Cl (3.0), F (4.0)

The order is the same as in the previous exercise, except for inversions between Na and Ca, and Cu and H.

Section 7.3, second exercise



Section 7.4

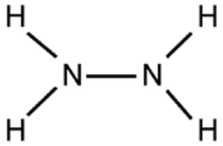
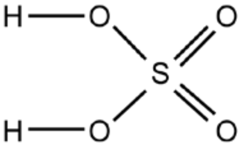
(i) H, +1; C, –4
(ii) Fe, +2; Cl, –1
(iii) Na, +1; H, –1
(iv) Si, +4; O, –2
(v) C, +4; O, –2; Cl, –1
(vi) H, +1; O, –2; N, –1
(vii) H, +1; O, –1
(viii) Si, +4; C, –4 [by analogy with (i) and (iv)]

Section 7.5

(i) tin tetrachloride *or* tin(IV) chloride
(ii) oxygen difluoride *or* oxygen(II) fluoride
(iii) dimagnesium stannide

Section 8.1

(i)

(a)	
(b)	O=N–O–N=O
(c)	H–O–N=O
(d)	

(ii) 2/3

Section 8.2

The data give, respectively:
$[Hg^+]^2/[Hg^{2+}]$ = 680, 436, 246 M
$[Hg_2^{2+}]/[Hg^{2+}]$ = 114, 110, 124
The figures in the second set are more constant.

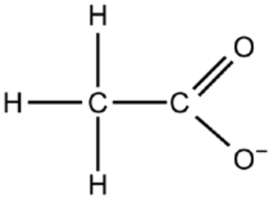
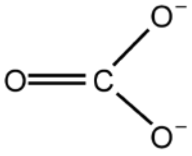
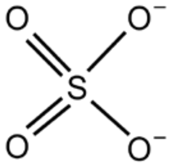
Section 8.4

(i) ECl_4, E_2Cl_6, etc.
(ii) ECl_4 only.

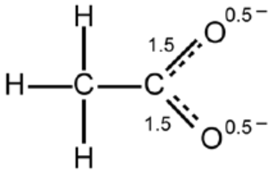
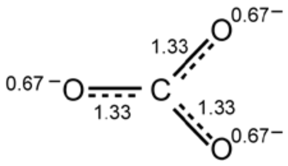
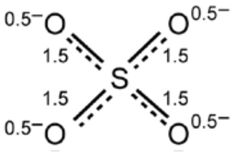
Section 8.5

Left to reader (add electrovalencies to covalencies).

Section 9.3

(i)	$^{-}$O–H
(ii)	$^{-}$S–C≡N
(iii)	
(iv)	
(v)	

Ions (iii), (iv), and (v) can also be drawn with non-integral bonds, as in Section 8.5:

(iii)	
(iv)	
(v)	

A1.4 Answers to questions and exercises, Chapters 10 - 12

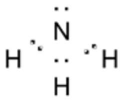
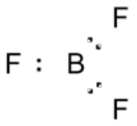
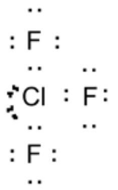
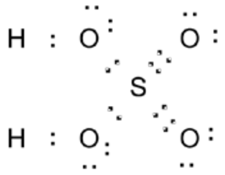
Section 10.1

Left to reader (see Sections 2.1 - 2.3).

Section 10.4

(i) Generalization holds with some exceptions.
(ii) Generalization holds.
(iii) Element 114 expected to be like lead, only somewhat more electropositive. Valencies = 2 and 4, with 2 much more stable.

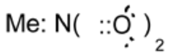
Section 11.1

(i)	(ii)	(iii)	(iv)	(v)	(vi)
			:N:::N:		

Section 11.2

(i) Lowest charge = +1

(ii)



Lowest charge = +1

(iii)

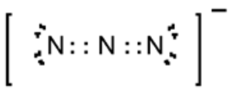
Lowest charge = +1

In (ii) and (iii), note that the bonding electrons are drawn closer to the oxygen atoms to indicate that the bonds are polarized away from the nitrogen atoms.

Section 11.3

(i)
Me:N:::C:

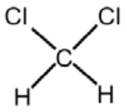
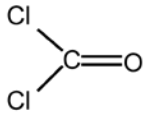
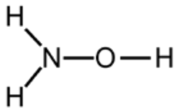
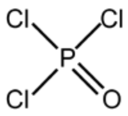
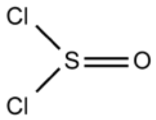
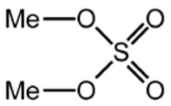
(ii)



Section 11.4

OCN^-, NO_2^+, CN_2^{2-}, FCN, N_2O, N_3^-

Section 12.3.1

dichloromethane	carbonyl chloride	hydroxylamine
		
phosphoryl chloride	thionyl chloride	dimethyl sulfate (Me = CH_3)
		

Section 12.3.2

(i) Dipotassium magnesium chloride
(ii) Potassium magnesium chloride
(iii) Triiron tetraoxide or iron(II) diiron(III) oxide

A1.5 Answers to questions and exercises, Chapters 13 - 18

Section 13.1

(i) Data explained with coordination number = 4 = square planar.
(I) = $[Pt(NH_3)_4]Cl_2$
(II), (III) = *cis* and *trans* $[PtCl_2(NH_3)_2]^0$
(IV) = $K_2[PtCl_4]$
(II) and (III) can be distinguished by reaction with a chelating agent (see Section 13.2). Chelating agents can replace ligands in a *cis* position, but not *trans*.
(ii) Magnus's green salt = $[Pt(NH_3)_4][PtCl_4]$
This has the same empirical formula as (II) and (III).

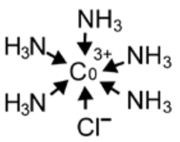
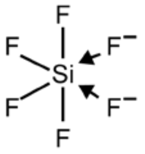
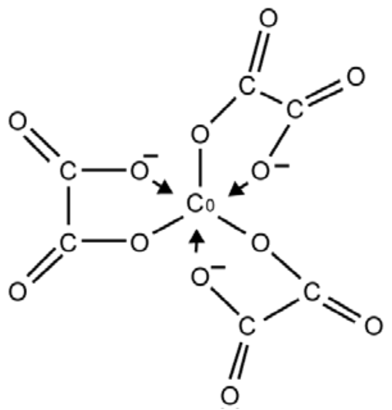
Section 13.3

These compounds are usually named as follows:

(I): tetraammineplatinum(II) chloride
(II), (III): *cis*- and *trans*-diamminedichloroplatinum(II)
(IV): potassium tetrachloroplatinate(II)
Magnus's green salt: tetraammineplatinum(II) tetrachloroplatinate(II)

Section 13.4

As explained in the text, the bond formula of a coordination entity can be written in two ways. The formula of (i) is drawn below in the modern way, of (ii) and (iii) in the older way.

(i)	(ii)	(iii)
		

Section 15.2

(i)

Combination	$2Na + Cl_2 \rightarrow 2NaCl$
Decomposition	$CaCO_3 \rightarrow CaO + CO_2$
Displacement	$2AgNO_3 + Cu \xrightarrow{aq} 2Ag + Cu(NO_3)_2$
Double decomposition	$Na_2CO_3 + CaCl_2 \xrightarrow{aq} CaCO_3(ppt) + 2NaCl$ $2NaCl + H_2SO_4 \rightarrow 2HCl(gas) + Na_2SO_4$
Addition	$C_6H_6 + 3H_2 \xrightarrow{catalyst} C_6H_{12}$ $ICl + Cl_2 \rightarrow ICl_3$
Substitution	$RCl + KCN \xrightarrow{aq\ alcohol} RCN + KCl$ $RCl + AgCN \xrightarrow{heat} RNC + AgCl$
Insertion	$S_2Cl_2 + nS \rightarrow S_{n+2}Cl_2$
Isomerization	yellow P $\xrightarrow{Hg}$ black P
Polymerization	$nCH_2{=}CHCl \rightarrow$ polyvinyl chloride (PVC)
Oligomerization	$3ClCN \rightarrow (ClCN)_3$ [with C_3N_3 ring]
Precipitation	$Na_2CO_3 + CaCl_2 \xrightarrow{aq} CaCO_3(ppt) + 2NaCl$ $Ca(OH)_2 + CO_2 \xrightarrow{aq} CaCO_3(ppt) + H_2O$
Neutralization	Chapter 16
Hydrolysis	$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$
Redox	Chapter 17
Solvation	$CuSO_4 + 5H_2O \rightarrow CuSO_4{\cdot}5H_2O$
Complexation	$AgCl + 2NH_3 \xrightarrow{aq} [Ag(NH_3)_2]Cl$

(ii)

- (a) displacement
- (b) decomposition
- (c) combination, addition
- (d) hydrolysis
- (e) double decomposition, precipitation ($BaSO_4$ is insoluble)
- (f) combination

Section 16.1

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + H_2O \rightarrow CaCO_3$$
$$M_2CO_3 + Ca(OH)_2 \rightarrow 2MOH + CaCO_3(ppt)$$

Section 16.6

	Classical	Stoicheiometric	Electrolytic	Lowry-Brønsted
(i) NaCN	base	salt	salt	CN^{-} = base
(ii) NH_4Cl	acid	salt	salt	NH_4^{+} = acid Cl^{-} = base
(iii) $NaHCO_3$	base	acid salt	salt	HCO_3^{-} = amph.

Section 17.2

$Fe^{2+} \rightarrow Fe^{3+}$ for X = Cl, Br
$Fe^{2+} \leftarrow Fe^{3+}$ for X = I

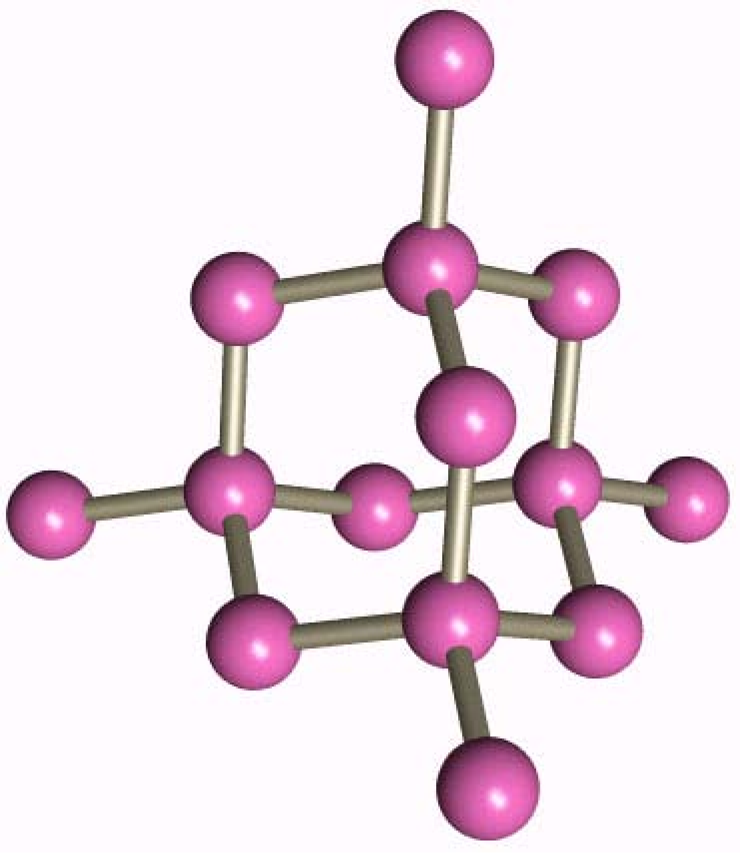
Section 17.3

(i)	$2MnO_4^{-} + 5HCO_2H + 6H^{+} \rightarrow 2Mn^{2+} + 5CO_2 + 8H_2O$
(ii)	$IO_3^{-} + 2I^{-} +6H^{+} \rightarrow 3I^{+} + 3H_2O$
(iii)	$2MnO_4^{-} + 5H_2O_2 + 6H^{+} \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$
(iv)	$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$
(v)	$2MnO_4^{-} + 3HCO_2^{-} + OH^{-} \rightarrow 2MnO_2 + 3CO_3^{2-} + 2H_2O$
(vi)	$4CuSCN + 7IO_3^{-} + 14H^{+} \rightarrow 4Cu^{2+} + 4SO_4^{2-} + 4HCN + 7I^{+} + 5H_2O$

Appendix 2 Pictures of structures

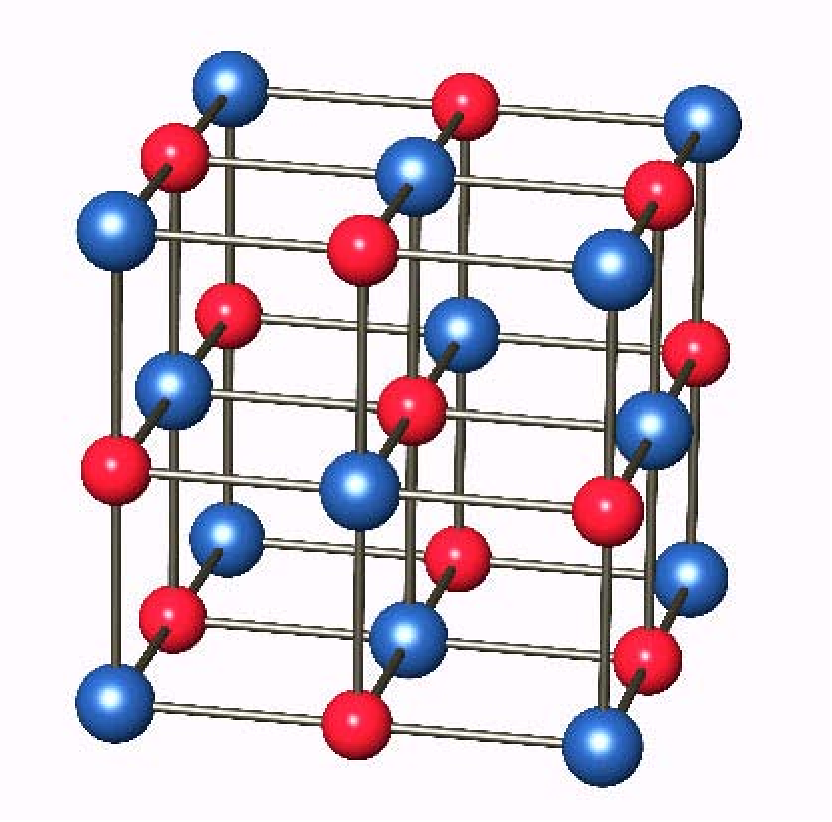
Structure of diamond

The picture below shows a small part of the structure of diamond. In a perfect crystal, the pattern continues in all directions as far as the faces. In the bulk of the crystal, each carbon atom is surrounded by four other atoms, at the corners of a tetrahedron.



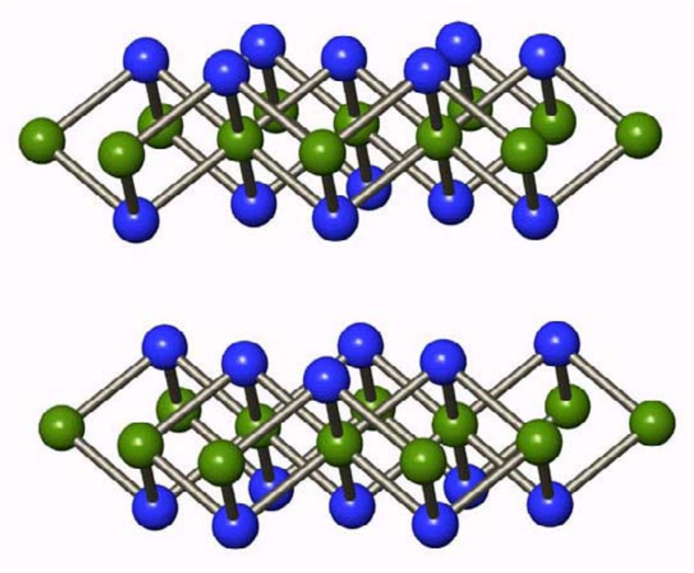
Structure of sodium chloride

The picture below shows the structure of a small part of a crystal of sodium chloride - the pattern continues in all directions until the faces of the crystal are reached. In the bulk of the crystal, each sodium ion (red) is surrounded by six chloride ions (blue), and each chloride ion by six sodium ions.



Structure of cadmium chloride

The picture below shows part of the structure of a crystal of $CdCl_2$. The layers in the picture continue longways and sideways, and the stack of layers upwards and downwards. Each cadmium "ion" (green) is surrounded by six chloride "ions" (blue), but each chloride ion has three cadmium ions on one side, and three chloride ions from the next layer on the other side.



Appendix 3

Pauling's electronegativities

Pauling reasoned that, if a bond A–B were completely covalent, the energy required to break it (B_{AB}) would be a mean (B_m) of the energies required to break A–A and B–B bonds, which must be covalent. Any difference between the actual bond energy and this mean must therefore be due to the polarity of the bond. He found that this difference ($B_{AB} - B_m$) increases the further apart A and B are in the electrochemical series, and is approximately given by the expression:

$$B_{AB} - B_m = C(\chi_A - \chi_B)^2$$

where χ_A has approximately the same value in all molecules containing A, and likewise χ_B. C is a constant chosen to produce a convenient scale of numbers. Pauling set $\chi_H = 0$, but later fixed the zero on his scale by comparison with Mulliken's values. (A plot of Pauling's original values against $A + I$ gives both Mulliken's constant k and Pauling's new zero, corresponding to $\chi_H = 2.1$.)

Note that it is not surprising that Pauling's method gives a similar series to the electrochemical series since bond energies largely determine the affinity between elements.

Appendix 4

Quantum theory of atomic structure

According to the quantum theory, electrons in atoms can be thought of as moving in diffuse shells. The shells differ in size and capacity. The size is indicated by a number ($n = 1, 2, 3, \ldots$) and the type by a letter:

Type	**Capacity**
s	2 electrons
p	6 electrons
d	10 electrons
f	14 electrons
…	…

The types of shell for different values of *n* are as follows:

n	**Types**
1	1s
2	2s, 2p
3	3s, 3p, 3d
4	4s, 4p, 4d, 4f
…	…

Motions within a shell are described as “orbitals”.

In atoms in their lowest-energy state, shells are generally filled in the following order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, …

For example, the electronic configuration of an argon atom (which has 18 electrons) is $1s^2 2s^2 2p^6 3s^2 3p^6$. Small deviations sometimes occur when shells are close in energy. For example, a chromium atom has the configuration $[Ar]4s^1 3d^5$ instead of $[Ar]4s^2 3d^4$, where [Ar] represents the configuration of an argon atom. The filling of shells corresponds to periods in the Periodic Table:

Period	Shells filled	Total capacity
1	1s	2
2	2s, 2p	8
3	3s, 3p	8
4	4s, 3d, 4p	18
5	5s, 4d, 5p	18
6	6s, 4f, 5d, 6p	32
7	7s, 5f, 6d, 7p	32

Further details may be found in textbooks on the quantum theory.

On the interpretation the theory, see my article:

“How do electrons get across nodes? A problem in the interpretation of the quantum theory”, *Journal of Chemical Education*, 1990, Vol. 67, 643-647.

Appendix 5

Electronic structure of hypervalent molecules

Explanation of charge distribution in SF_6

The following is a simple explanation of why x in $S^{x+}(F^{x/6-})_6$ must be ≥ 2:

A sulfur atom has 6 valence electrons and can form 2 covalent bonds to give an octet.
An S^+ ion has 5 valence electrons and can form 3 covalent bonds to give an octet, and one ionic bond (total 4 bonds).
An S^{2+} ion has 4 valence electrons and can form 4 covalent bonds to give an octet, and 2 ionic bonds (total 6 bonds).
An S^{3+} ion has 3 valence electrons and can form 3 covalent bonds and 3 ionic ones (total 6).
An S^{4+} ion has 2 valence electrons and can form 2 covalent bonds and 4 ionic ones (total 6).
An S^{5+} ion has one valence electron and can form one covalent bond and 5 ionic ones (total 6).
An S^{6+} ion has no valence electrons but can form 6 ionic bonds.

Thus, a sulfur atom can form 6 bonds provided that its charge is ≥ +2 (up to +6).

Extension to other molecules

This reasoning can be extended to other molecules. In the case of SF_6, the central atom does not have lone pairs (see picture in Section 11.1). When lone pairs are present, these must be taken into account. Consider, for example, SF_4. This has one lone pair (see picture). The charge on the sulfur atom in this case must be ≥ +1 (up to +4):

A sulfur atom cannot have only one lone pair.
An S^+ ion can have one lone pair and form 3 covalent bonds and one ionic one (total 4).
An S^{2+} ion can have one lone pair and form 2 covalent bonds and 2 ionic ones (total 4).
An S^{3+} ion can have one lone pair and form one covalent bond and 3 ionic ones (total 4).
An S^{4+} ion can have one lone pair and form 4 ionic bonds.
(Higher ions cannot have a lone pair in the valence shell.)

General formulation

Consider a molecule formed by an element A in main-group N of the Periodic Table ($N \geq 4$). What does the polarity have to be to keep within an octet? *Answer*: An A^{x+} ion has $N - x$ valence electrons, comprising l lone pairs and $N - x - 2l$ unpaired electrons. The latter can be shared with an equal number of unpaired electrons on other atoms to form covalent bonds. We want the total number of electrons ($= 2N - 2x - 2l$) to be ≤8. We must therefore have $x \geq N - 4 - l$. [There will be $N - x - 2l$ covalent bonds and x ionic ones, giving a total of $N - 2l$ ($= V$). The maximum value of V is N (when $l = 0$).]