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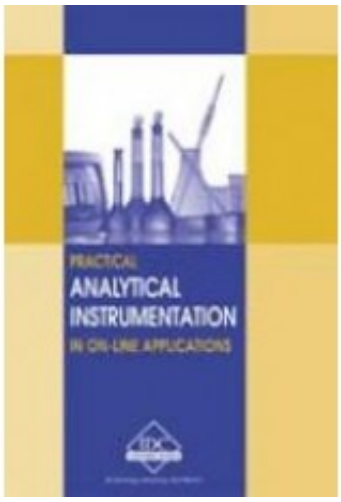
AI-E - Analytical Instrumentation



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Short Description

This manual will 'demystify' the world of analytical measurement and equip you with the knowledge required to understand, identify and confidently troubleshoot On-Line Analytical Measurement instrumentation in Process Control.

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This manual will offer you the vital knowledge that you need to multi-skill, reduce downtime, save your company money, and secure your value in the workplace.

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First Chapter

Chapter 1: Basic Chemistry

1

Basic Chemistry

Objectives

When you have completed this chapter you should be able to:

- Define the differences between elements, compounds and mixtures
- Explain the difference between organic and inorganic chemistry
- Describe the structure of an atom
- Show how the periodic table is formed and describe the different properties of elements
- Show how ions are formed and understand both covalent and ionic bonding
- Understand chemical formulae and the use of chemical equations
- Explain atomic weight and molar concentrations
- Discuss the difference between acids and bases and explain oxidation-reduction

1.1 Introduction

1.1.1 Elements, compounds and mixtures

All substances may be divided into three classifications: elements, compounds and mixtures.

The simplest forms of matter are ***elements*** — substances that cannot be split into simpler substances by a chemical reaction. As shown in Figure 1.1, there are over 100 known elements classified in the periodic table and these form the building blocks of all chemicals.

Figure 1.1

The periodic table

A ***compound*** is formed by two or more elements which are always combined in the same fixed ratio. Thus, for example, water is a compound of hydrogen and oxygen, shown by its chemical formula H_2O, which is always formed from two parts hydrogen and one part oxygen (Figure 1.2). Compounds are often difficult to split into their elements and can only be separated by chemical reactions.

Figure 1.2

Water (H_2O) — a compound formed from two parts hydrogen and one part oxygen.

The smallest particle of an element or compound that normally exists by itself and still retains its properties is called a molecule. Normally a molecule consists of two or more atoms — sometimes even thousands. However, as we shall see later, a molecule can also exist as a single atom called a ***monatomic molecule.***

Elements and compounds are pure substances whose composition is always the same. In reality, pure substances are rarely encountered and most are ***mixtures*** of compounds or elements that are not chemically combined and in which the proportions of each element or compound are not fixed (Figure 1.3).

Since the elements or compounds making up the mixture each keep their own properties they can usually be separated fairly easily by physical means.

When a mixture has the same properties and composition throughout, (e.g. a mixture of sugar and water in which the sugar is thoroughly dissolved in the

water) it is called a ***homogeneous***mixture or a ***solution***.

When the composition and properties of a mixture vary from one part to the other it is called ***heterogeneous***. This might take the form of a suspension in which fine particles of a solid are suspended in a liquid and are not dissolved. Another type of heterogeneous mixture is a two-phase mixture: e.g. a mixture of oil and water in which the oil floats on the water as a separate layer.

Figure 1.3

Various types of mixtures

1.1.2 Organic and inorganic chemistry

In the study of elements and their components, a distinction is made between what is termed organic and inorganic chemistry.

Originally organic chemistry concentrated on the study of substances found in living organisms. Now, however, it extends to cover all (with a few exceptions) of the compounds of carbon. The vast number of organic compounds (well over two million) include plastics, fibres, drugs, cosmetics, insecticides, foods, etc., and are made possible by the ability of the carbon atom to bond to itself and form a virtually unlimited chain or ring.

Inorganic chemistry is the study of that which is left over — those substances that do not form bonds with carbon.

1.2 Atomic structure

At one time the atom was considered to be the ‘fundamental particle’ — the

smallest bit of matter that could be conceived. And indeed, since all atoms of any given element behave in the same way chemically, the atom is the smallest entity to be considered from a chemical viewpoint.

In considering the basic construction of an atom it is usual to consider it as being composed of three elementary sub-atomic particles: protons, neutrons and electrons. It is the number of protons, neutrons and electrons that any atom contains that distinguishes one element from another.

The main mass of the atom comprises the nucleus, which consists of protons and neutrons. The proton has a positive charge and a relative mass of 1 whilst the neutron has a similar mass but no charge.

The nucleus is surrounded by a cloud of electrons each having a negative charge and a mass nearly 2000 times smaller than the proton. In its normal state, an atom has the same number of electrons as protons and is, therefore, electrically neutral.

The simplest structure is the hydrogen atom, which comprises a single proton and a single electron (Figure 1.4).

Figure 1.4

Basic structure of a hydrogen atom comprising a single proton and a single electron.

An element is determined by the number of protons in the nucleus — its ***atomic number.*** Since the atomic number defines the element, any atom with 6 protons

is carbon, irrespective of the number of neutron or electrons (normally 6 of each).

However, because the number of neutrons in the nucleus may not always be the same as the number of protons, an atom is also defined in terms of the total number of protons and neutrons in the nucleus — called its ***mass number*** (not to be confused with its atomic mass). Carbon, for example would normally have 6 protons (atomic number = 6) and 6 neutrons giving a mass number of 12. However, carbon can also exist in other forms, called ***isotopes***, in which the nucleus contains 7 or even 8 neutrons — giving a mass number of 13 or 14 respectively.

The three carbon isotopes are distinguished from one another by writing the mass number after the name of symbol of the element. Thus, as shown in Figure 1.5, carbon with 6 neutrons is called Carbon-12; with 7 neutrons is called Carbon-13; and with 8 neutrons is called Carbon-14.

Figure 1.5

The three isotopes of carbon which are distinguished from one another by writing the mass number after the name of symbol of the element.

Electron shells

With the electrons forming a cloud around the nucleus, the position of any electron is defined in terms of the probability of finding it at some distance from the nucleus. Consequently, it is convenient to visualise the electrons moving around the nucleus of an atom in the same way as planets move around the sun.

This solar-system model visualises the electrons arranged in definite shells or energy levels. Each shell has an upper limit to the number of electrons that it can accommodate and each is built up in a regular fashion from the first shell to a total of seven shells. The first shell can accommodate 1 or 2 electrons; the

second shell a maximum of 8; the third a maximum of 18; the fourth 32 and so on with successive shells holding still larger numbers.

In the study of chemistry, it is the electrons in the outermost shell — those which are added last to the atom's structure — that determine the chemical behavior of the atom. This outer shell is called the ***valance shell*** and the electrons in it are called ***valance electrons***. For the first two shells (the first 10 elements) matters are simple and each shell is filled before a fresh one is started. However, in later elements the outer shell develops before the previous one is completed.

Figure 1.6

The full periodic table

Chemical symbols

As shown in Figure 1.1, each element has its own unique symbol that, in most cases, is formed from one or two letters of the element’s English name: e.g. H for hydrogen; He for helium; Li for lithium. Note that the first letter is always capitalised and, where there is a second letter, this is always written in lower case. The symbols of some elements are derived from their Latin names (Table 1.1): Na for sodium from its Latin name Natrium; Au for gold from its Latin name Aurum; Pb for lead from its Latin name Plumbum; etc. An exception to this derivation is tungsten whose symbol W is derived from its German name Wolfram.

Table 1.2

Symbols of elements derived from their Latin names.

Element	**Atomic Number**	**Latin Name**	**Symbol**
Sodium	11	Natrium	Na

Potassium	19	Kalium	K
Iron	26	Ferrum	Fe
Copper	29	Cuprum	Cu
Silver	47	Argentum	Ag
Tin	50	Stannum	Sn
Antimony	51	Stibium	Sb
Gold	79	Aurum	Au
Mercury	80	Hydrargyrum	Hg
Lead	82	Plumbum	Pb

1.3 Periodic table

The periodic table (Figure 1.1) is an arrangement of the elements, in order of their increasing atomic numbers, in which a wide range of chemical and physical information is arranged in a systematic way.

As shown, there are seven rows, called ***periods***, with the atomic number increasing by one element from left to right.

The vertical columns or groups are numbered using roman numerals and separate the elements into families having the same number of electrons in the outer shell and similar chemical properties.

As shown in Figure 1.7, about 75% of the elements are made up of what are called metals. Except for mercury, metals are solid and are characterised by high conductivity (both electrical and thermal); high malleability (the ability to be formed or hammered into different shapes); and high ductility (the ability to be drawn into a thin wire).

Figure 1.7

About 75% of the elements are made up of metals

Moving to the right, the elements gradually become less metallic and, on the extreme right (Figure 1.8), are termed non-metals. Non-metals can be solid (carbon being the most commonly observed) liquid (bromine) or gas (oxygen, nitrogen) and generally have poor conductivity, malleability and ductility.

Figure 1.8

Non-metal elements

Somewhere in between the metallic and non-metallic elements are the metalloids (Figure 1.9) that behave mainly like non-metals except that their electrical conductivity, although not good, is closer to metals. These elements are thus often termed semiconductors.

Figure 1.9

The metalloid or semiconductors elements

1.4 Properties of elements

Elements to the extreme left of the periodic table (Figure 1.10), in Group I are, with the exception of hydrogen*, called ***alkali metals*** — metals that react with water to form alkaline solutions. All have only one valence electron (one electron in their outer shell) which is easily lost in reactions. Indeed, moving down the group from lithium, sodium, potassium, rubidium, caesium, and francium, their reaction with water becomes increasingly more violent and all need to be stored under oil because of this reactivity.

*Hydrogen owes its location in Group I to its electron configuration rather than its chemical properties.

Figure 1.10

Group I — the alkali metals

The metals of Group II (Figure 1.11) have two fairly loosely bound valance electrons and, although they are also strongly reactive, are not as reactive as Group I elements. Group II elements tend to be found as naturally occurring mineral deposits in the ground or in the sea and are, therefore called the ***alkaline earth metals***.

Figure 1.11

Group II — the alkali earth metals

At the far right hand side of the periodic table (Figure 1.12) are the Group VIII (also know as Group O) elements that form the noble or inert gases. The term noble indicates that the element is chemically inert or inactive.

Figure 1.12

Group VIII — the noble or inert gases

Noble gases – helium, neon, argon, krypton, xenon and radon – all have a full outer shell which accounts for their extreme stability and unwillingness to form compounds. Indeed, at normal temperatures, the lighter noble gases form no compounds whatsoever and exist as monatomic (single-atom) molecules.

In contrast, gases such as hydrogen, nitrogen, oxygen, fluorine, and chlorine react with each other to form ***diatomic*** (two-atom) molecules (Figure 1.13) e.g. H_2, N_2, O_2, F_2, and Cl_2. The Non-metallic elements bromine and iodine also exist as diatomic molecules: Br_2 and I_2.

Figure 1.13

Hydrogen exists as a two-atom or diatomic molecule (H_2)

Another important group that needs to be considered is Group VII – the halogens (Figure 1.14). The elements in this group – fluorine, chlorine, bromine, iodine and astatine – are all non-metals and are characterised by having seven valence electrons.

Figure 1.14

Group VII — the halogens

1.5 Formation of ions

Earlier we stated that the nature of the element is determined by its atomic number – the number of protons within the nucleus – and that it can gain or lose electrons. We also saw how the electrons in an atom are arranged in shells.

Because of the increasing distance of successive shells from the nucleus, the outer electrons are further away from the nucleus and are thus held less tightly. The result is that less energy is required to remove an electron from the 2nd shell than from the 1st shell and still less to remove an electron from the 3rd shell than the 2nd shell. Thus, referring to the periodic table, the energy required to remove an electron from the outer shell of an atom decreases from the top to the bottom (Figure 1.15).

Figure 1.15

The energy required to remove an electron from the outer shell of an atom increases from left to right and decreases from the top to the bottom

In addition, elements to the left of the table have loosely held valence electrons that are easily lost. Now, moving from left to right, as electrons are added to the outer shell, an effectively increasing charge binds them more and more tightly to the nucleus.

It can thus be seen that it is very difficult for elements in the upper right-hand corner to lose electrons and indeed elements with nearly completed shells will tend to attract electrons.

Figure 1.16 shows a sodium atom (atomic number 11) in which the first and second shells are complete and there is one valence electron. Assume now that the atom loses the electron in its outmost shell. What will be the result?

Figure 1.16

Basic structure of a sodium atom

Firstly, since the nucleus has been unaffected and it still has 11 protons (as well as 11 neutrons) it will continue to remain sodium.

The main effect will be that the total charge of the atom will no longer be neutral but will be unbalanced by the absence of the negatively charged electron. The result is that the atom will now have a net positive charge. Since, by definition, an atom is neutral, the change in its charge by losing the electron has, in effect created a new particle called an ***ion***. A positively charged ion is called a ***cation*** (pronounced CAT-ion).

The loss of the electron (e^-) from the sodium atom creates an ion with a net charge of +1 and the particle's change in status from a sodium atom to a sodium cation (Figure 1.17) could thus be indicated by the symbol $Na^{1+.}$ In practice the 1 is implied and the symbol is thus written Na^+.

Figure 1.17

Formation of sodium cation

If a magnesium atom (atomic number 12) with *two* valence electrons (Figure 1.16) should lose them, then the resulting cation will be unbalanced by the absence of *two* electrons and thus have a net positive charge of +2. In this case the particle's change in status from a magnesium atom to a magnesium cation (Figure 1.18) is indicated by the symbol Mg^{2+}.

Figure 1.18

Basic structure of a magnesium atom

Figure 1.19

Formation of magnesium cation

If we examine the structure of a chlorine atom (atomic number = 17), as depicted in Figure 1.20, it can be seen that the outer (third) shell contains only 7 electrons. And if it should capture an electron and make its outer shell complete (Figure 1.21) its overall charge will become negative. A negatively charged ion is called an anion (pronounced AN-ion).

Figure 1.20

Basic structure of a chlorine atom

Figure 1.21

Formation of chlorine anion

The gain of the electron (e^-) into the outer shell of the chlorine atom, creates an ion with a net charge of -1 and the particle's new status as a chlorine anion is indicated by the symbol Cl^- -- again with the 1 being implied.

1.6 Bonding

Earlier, we described a compound as a combination of two or more elements. The elements that are combined to form compounds are held together by bonding forces called ***chemical bonds.*** The two major bonding forces are ***ionic bonding*** and ***covalent bonding.***

1.6.1 Ionic bonding

Ionic bonding is based on the fact that opposite charges attract!

We have already seen how Group I and II elements have loosely held valence electrons that are easily lost and how elements with nearly completed shells will tend to attract electrons.

Thus a sodium atom with a single valence electron will give it up easily to, for example, a chlorine atom with 7 valence electrons (Figure 1.22).

Figure 1.22

Sodium atom gives up an electron easily to a chlorine atom with 7 valence electrons

The sodium cation, with a net charge of +1 and a chlorine anion having a net charge of -1 are attracted to each other and thus form an ionic bond. This ionic bond, formed between a sodium cation (Na^+) and a chlorine anion (Cl^-), results in the compound sodium chloride (Na^+Cl^-) or common salt (Figure 1.23). In practice the ionic charges are omitted from the formula which then becomes NaCl.

Figure 1.23

The ionic bond formed between a sodium cation (Na^+) and a chlorine anion (Cl^-) results in the compound sodium chloride (Na^+Cl^-)

Another example of an ionic compound formed in this manner is that of magnesium and oxygen. Here, a magnesium cation (Mg^{2+}) having a net charge of +2, combines with an oxygen anion (O^{2-}) having a net charge of -2. The ionic bonding results in the compound magnesium oxide ($Mg^{2+}O^{2-}$) — normally written as MgO.

Ionic compounds thus exist as a collection of electrically charged positive and negative ions – with each positive ion surrounding itself with as many negative ions as it can, and each negative ion surrounding itself with as many positive ions as it can.

The resulting structure consists of a regular pattern of alternate positive and negative ions, in which no individual molecules can be identified. This regular arrangement of positive and negative ions continues indefinitely in three dimensions throughout the whole structure and is stacked together to form a crystal lattice (Figure 1.24).

Such ionic crystals are hard and brittle with high melting points. Because, at room temperature, the ions are bound and are not free to move, ionic compounds do not normally conduct electricity. However, when melted or dissolved in water, the ions are freed and the materials become conductive.

Figure 1.24

Ionic compounds exist as collections of ions stacked together to form a crystal lattice

The ionic compounds formed in this fashion between metals and non-metals are called ***salts***.

1.6.2 Covalent bonding

Covalent bonding is a more complex arrangement than ionic bonding. Here, the valence electrons are actually shared between the atoms so that each acquires a stable outer shell.

When two atoms of hydrogen are brought together their electrons begin to feel the attraction of both nuclei (Figure 1.25). As the distance continues to decease, there is an increasing probability of finding either electron near either nucleus and at some point, each hydrogen atom shares an electron and the two are thus bonded together to form an H_2 molecule. A less accurate, but more easily visualised, analogy is that the electrons form a figure-of-eight path (Figure 1.26) around the two nuclei to form the H_2 molecule.

Figure 1.25

When two hydrogen atoms are brought together, at some point a bond is formed and each hydrogen atom shares an electron with the other to form an H_2 molecule

Figure 1.26

The electrons can be visualised as forming a figure-of-eight path around the two nuclei to form an H_2 molecule

In ionic bonding the ions exist separately. In covalent bonding, however the net molecular charge is neutral. In the case of hydrogen, the covalent bond is formed by a single pair of electrons – with the pair usually connected by a single dash (-):

H - H

Another example of a single-pair covalent bond is chlorine (Figure 1.27). When

chlorine atoms approach each other (each with an electron valence of seven) covalent bonding occurs when a pair of electrons are shared (one from each atom) so that each atom now has a stable outer shell of 8 electrons. Again the molecule formed by this single-pair bond is represented by: Cl - Cl

Figure 1.27

Covalent bonding of chlorine atoms occurs when a pair of electrons is shared so that each atom now has a stable outer shell of 8 electrons

Yet another single-pair covalent bond can be formed by, for example, hydrogen and chlorine (Figure 1.28). Here, the pair is made up by one electron from each atom to form a stable outer shell for each. The resulting compound, hydrogen chloride (HCl) is depicted by: H - Cl

Figure 1.28

Single-pair covalent bond formed from hydrogen and chlorine

More than one pair of electrons can form a covalent bond. An oxygen molecule, for example, (with six valence electrons) is formed when two pairs of electrons are shared – again resulting in a stable outer shell of eight electrons for each atom. Here, the double pair is represented by a double dash (=):

O = O

In the case of nitrogen, with five valence electrons, a molecule is formed by a triple bond in which three pairs of electrons (three electrons from each atom) give rise to a stable outer shell for each atom. Here, the triple pair is represented by a triple dash (º):

Chemical formulae

The most commonly used chemical formula is the ***molecular formula***, which gives the actual composition of a molecule. The molecular formula H_2O, for example, indicates that a water molecule comprises two H atoms and one O atom. Similarly, the formula for ethene is C_2H_4 — indicating that an ethene molecule is made up of two carbon atoms and four hydrogen atoms.

At this point a distinction needs to be drawn between the molecular formula, stated above, and what is termed an ***empirical formula***.

Whilst the molecular formula gives the composition of a molecule, the empirical formula expresses the composition of a substance in terms of whole-number ratios.

Figure 1.29 shows the structure of an ethene molecule. The empirical formula would be written CH_2 — indicating the *ratio* of atoms i.e. there are two hydrogen atoms for each carbon atom. The molecular formula, on the other hand (written C_2H_4), indicates that a molecule of ethene comprises two carbon atoms and four hydrogen atoms.

For even more information the ***shortened structural*** formula is used. This shows the sequence of groups or atoms in a molecule. And for more information still, the ***full structural*** or ***displayed*** formula shows all the bonds (both single and double) that make up the molecule.

Figure 1.29

Empirical, molecular and displayed, formulae for ethene

It should be noted that in organic chemistry, even more information than that provided by the displayed formula is required. For example, ***isomers*** are compounds having the same molecular formula but different arrangements of atoms in their molecules.

Often, such compounds can only be distinguished from each other using ***stereochemical formulae*** that show the structure of the molecule in 3-D.

Thus, whilst the molecular formula for butene is C_4H_8 it has two different stereochemical formulae (Figure 1.30).

Figure 1.30

Stereochemical formulae illustrates the difference in the molecular formula for butene

We have already seen how some elements such as oxygen and nitrogen occur as simple molecules even when not combined with other elements. These give the formula O_2 and N_2respectively.

1.7 Chemical equations

A chemical equation gives a ‘before and after’ picture of a chemical reaction.

In its most basic form, it may be written out:

Sodium + Water ® Sodium hydroxide + Hydrogen

The two substances that produce the reaction, and are called ***reactants***, are written on the left hand side of the equation and the result or products of the reaction are written on the right hand side. The + sign stands for ‘react with’ and the arrow (®) stands for ‘reacts to yield’. Thus, the above equation indicates that sodium reacts with water to yield sodium hydroxide and hydrogen.

In practice, the names of the materials involved in the reaction are not written out in full but are replaced by their chemical formulae:

$Na + H_2O \rightarrow NaOH + H_2$

Whilst this equation shows the reaction that takes place, it does not convey the complete picture since closer examination shows that it is chemically unbalanced — i.e. the number of atoms on the one side is not the same as the other (Table 1.2).

Table 1.2

Atoms in formula do not balance

Formula	**Na**	**+**	**H_2 O**	**®**	**Na O H**	**+**	**H_2**
Number of atoms	1		2 1		1 1 1		2
Totals		4		1		5	

In order to balance the equation it may be rewritten as shown with the number in front of each equation, called the coefficient, indicating the number of atoms :

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

Now, an audit, as shown in Table 1.3, show that there is a balance.

Table 1.3

Atoms in formula now balance

Formula	**2(Na)**	**+**	**2(H_2 O)**	**®**	**2(Na O H)**	**+**	**H_2**
Number of atoms	2(1)		2(3)		2(3)		2
	2		6		6		2
Totals		8		=		8	

The equation may be extended even further by including what are termed state symbols after each formula that indicate the physical state of each molecule. The state symbols (written in brackets) are:

(s) = solid

(l) = liquid

(aq) = aqueous (solution in water)

(g) = gas

Thus, the sodium reaction with water would be:

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Finally, when studying electrolytes in solution, the chemical properties are best represented by an ionic equation which is only concerned with the ions of the participant substances in the reaction.

Thus the reaction:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

may be rewritten:

$Na^+OH^-(aq) + H^+Cl^-(aq) \rightarrow Na^+Cl^-(aq) + H_2O(l)$

Here, Na^+, OH^- , Cl^- and H^+ are all ions. Since Na^+ and Cl^- appear on both sides of the equation, they are uninvolved the ionic reaction and are thus omitted. Now the ionic equation is simply:

~~Na^+~~$OH^-(aq) + H^+$~~Cl^-~~$(aq) \rightarrow$ ~~Na^+~~ ~~Cl^-~~$(aq) + H_2O(l)$

$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$

1.8 Naming compounds

Many compounds have *trivial* names —names that give little information about the structure of the compound. These include names such as salt (NaCl), borax ($Na_2B_4O_7 \cdot 10H_2O$), chalk ($CaCO_3$), or even proprietary names such as Teflon ($F(CF_2)_nF$). In addition, there are other chemical compounds whose names are universally associated with a chemical formula (e.g. water (H_2O)). However, most of these names are often difficult to interpret. As a result, most compounds are named using a systematic internationally agreed system.

The compounds of metals and non-metals containing, for example, two different elements are named by first taking the name of the metallic element followed by the *main* part of the name of the non-metal, which is then modified with the suffix ***-ide***. Thus, the compound of sodium and chlorine takes the metallic element first (sodium) followed by the modified form of chlorine (chloride): i.e. sodium chloride (NaCl).

Other such compounds include:

CaS — calcium sulfide;

MgO — magnesium oxide;

SiN — silicon nitride; and

ZnS — zinc sulfide

When more than two atoms are involved use can be made of a prefix:

mono-	1	hexa-	6
di-	2	hepta-	7
tri-	3	octa-	8
tetra-	4	nona-	9
penta-	5	deca-	10

Thus we get:

CO — carbon monoxide;

CO_2 — carbon dioxide

NO_2 —nitrogen dioxide;

CS_2 — carbon disulfide;

SF_6 — sulfur hexafluoride;

$GeCl_4$ — germanium tetrachloride; and

N_2O_4 — dinitrogen tetraoxide.

Another frequently used suffix is ***-ate*** which usually indicates the presence of oxygen. Thus: nitrate, NO^{3-}; sulfate, SO_4^{2-}; and phosphate, PO_4^{3-} .

The suffix ***-ite*** indicates fewer oxygen atoms than in the corresponding *-ate* ion, with the prefix *hypo-* used with the suffix *-ite* indicating still fewer. The prefix *per-* indicates more oxygen, or less negative charge, than the corresponding -ate ion. Thus:

Chlorate ClO_3^-

Chlorite ClO_2^-

Hypochlorite ClO^-

Perchlorate ClO_4^-

Certain metals can be found in more than one ionic state. Iron, for example, occurs as either Fe^{2+} or Fe^{3+}. In such cases, the suffix *-ous* may be used to identify the lower state and *-ic* the higher state. Thus:

Fe^{2+} = ferrous ion

Fe^{3+} = ferric ion

Cu^+ = cuprous ion

Cu^{2+} = cupric ion

This system of denoting the lower and higher valency states of metal cations has, however, given way to the Stock System in which the oxidation number of the metallic element is indicated by Roman numbers in parenthesis placed immediately after the atom concerned.

The $FeCl_2$ is denoted Iron (II) chloride rather than ferrous chloride and $FeCl_3$ is denoted Iron (III) chloride rather than ferric chloride.

1.9 Atomic weight

Although it is customary to use the term ‘atomic weight’, the term ‘atomic mass’ is more appropriate. Whilst weight is the force exerted on the body by the influence of gravity, mass is a measure of the quantity of matter in a body independent of gravity.

Historically, oxygen was taken as a standard of mass measurement and the oxygen atom was assigned a value of 16.0000 ***atomic mass units*** (amu). On this basis, helium was found to have an atomic weight of 4.003 amu, fluorine 19.000, and sodium 22.997.

However, since the early 1960s, the isotope carbon-12 has been used as a standard and the amu is now defined as being 1/12th of an atom of carbon-12 in which:

$1 \text{ amu} = 1.6605665 \times 10^{-24} \text{ g}$

In reality the atomic weights based on carbon-12 are in close agreement with those based on natural oxygen.

Table 1.4 compares the atomic weights of the three subatomic particles which show that the atomic weight of the electron is nearly 4000 times less than that of the nucleus and can thus be ignored. In addition, the proton and neutron both have masses close to unity. Since the atomic number is defined as the number of protons in the nucleus, we would expect that the atomic weight would be just over twice that of the atomic number.

Table 1.4

Atomic weights of the three subatomic particles

Particle	**Atomic weight (amu)**
Proton	1.007276

Neutron	1.008665
Electron	0.0005486
Total	**2.0164896**

This, in fact, is shown in Table 1.5 which lists the atomic weights of various elements together with their atomic numbers.

Table 1.5

The atomic weights of various elements together with their atomic numbers.

Element	**Symbol**	**Atomic weight (amu)**	**Atomic number**
Hydrogen	H	1.008	1
Helium	He	4.003	2
Carbon	C	12.01	6
Oxygen	O	16	8
Sodium	Na	22.99	11
Chlorine	Cl	35.45	17
Nickel	Ni	58.7	28
Germanium	Ge	72.59	32
Platinum	Pt	195.1	78
Gold	Au	197	79
Uranium	U	238	92

How about the mass of a molecule?

In fact it’s really quite simple. The ***molecular weight*** or mass is merely the sum of the atomic weights of each element.

Thus, the molecular weight of water (H_2O) would be the sum of the atomic weights of the two hydrogen atoms (1 + 1) and one oxygen atom i.e. 1 + 1+ 16 = 18.

Because there are many substances that do not, in fact, comprise molecules (e.g. salts such as sodium chloride) the term ***formula weight*** is often used in place of molecular weight and is calculated in exactly the same way. Thus, the formula weight of sodium chloride (NaCl) would be the sum of the atomic weights of sodium (22.99) and chlorine (35.45) i.e. 22.99 + 35.45 = 58.44.

We saw earlier that an 'atomic mass unit' (amu) was defined as having a mass of:

$1 \text{ amu} = 1.6605665 \times 10^{-24} \text{ g}$

Alternatively we could say that there were:

$6.022 \times 10^{23} \text{ amu} = 1\text{g}$

The figure of 6.022×10^{23} is referred to as ***Avogadro's number*** and is termed a ***mole*** and is given the symbol ***mol***. A mole is a measure of the amount of a substance and 1 mol of any substance contains 6.022×10^{23} molecules or atoms.

The formal SI definition of a mole is:

"… the amount of any substance that contains as many particles as there are atoms in 12 g of carbon-12. When the mole is used the particles (atoms, molecules, ions, electrons, etc.) must be stated."

Thus:

One mole of carbon-12 *atoms* thus has a mass of 12 g.

One mole of oxygen *atoms* has a mass of 16 g.

One mole of oxygen *molecules* has a mass of 32 g.

1.10 Molar concentrations

Many chemical reactions are carried out in solution and the concentration is usually defined in terms of the number of moles of the substance (the solute) contained in 1 l of solution. This is called its molar concentration or molarity.

For example, if 10 g of NaCl is dissolved in distilled water to give 1 l of the solution, what is the solution molarity?

We have already determined that the formula weight of NaCl = 58.44 and thus, by definition:

58.44 g of NaCl = 1 mol

Then:

10 g of NaCl = 0.171 mol

This is the thus the amount of NaCl dissolved in 1 l of the solution and the molarity is 0.171 mol/l.

1.10.1 Acids and bases

Whilst in a purely covalent bond the electrons are shared symmetrically, in most cases the shared electrons tend to be closer to one atom’s nucleus that the other. Such bonds have a partial ionic character in which one part of the molecule has a net positive charge and the other a net negative charge. These molecules are said to be polar.

Figure 1.31 shows a molecule of water in which the shared electrons are more likely to be found around the oxygen atom. The result is that there is a net negative charge on the oxygen atom. And since the electrons spend less time orbiting the hydrogen atoms there is a net positive charge on each hydrogen atom.

Figure 1.31

In a water molecule the shared electrons are more likely to be found around the oxygen atom

It should be noted that, as distinct from ionic bonding, the net charges are less than 1+ or 1-, this being indicated by the symbol (d).

In pure water, a small number of molecules ionise — each forming a hydrogen ion (H^+) and a hydroxide ion (OH^-). This reaction is called ***self-ionisation***. Since the number of hydrogen and hydroxide ions is equal, the water is neutral. However, this balance can be upset by a number of compounds that dissolve or react with the water and produce either hydrogen ions or hydroxide ions.

Substances that react in this manner and produce hydrogen ions (H^+) in the solution are called ***acids*** and those that react and produce hydroxide ions are called ***bases***.

Another name used to describe the hydrogen ion (H^+) is ***proton*** and thus acids may also be described as proton donors and bases as proton acceptors.

In reality, the hydrogen ions do not exist on their own but are attached to the water molecules to become what are called hydroxonium ions (H_3O^+). This is shown in the reaction of hydrochloric acid (HCl) with water:

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Nevertheless, because only the hydrogen ion takes part in the reaction in a solution, the H+ ions may be considered as the active ingredient and, for all intents and purposes, the hydroxonium ion may be considered to be a hydrogen ion.

A base has been described as a substance that gives hydroxide ions (OH^-) when reacting or dissolving in water. Alternatively, it has been described as a proton acceptor. A base is, therefore, the chemical opposite to an acid. As a result, a base may be further described as a substance that will neutralise an acid by accepting its hydrogen ions.

Thus, in the right proportions, the reaction of hydrochloric acid (HCl) with sodium hydroxide (NaOH) gives:

$HCl + NaOH \rightarrow H_2O + NaCl$

resulting in a solution containing ordinary table salt.

When a base is dissolved in water the resulting solution contains more hydroxide ions than hydrogen ions and is termed an ***alkaline***. The determination of whether a solution is acidic or alkaline, and their relative strengths, is compared on a pH scale.

1.11 Oxidation-reduction

In our discussions on bonding, we saw how both ionic and covalent bonding involved a shift in electron density from one atom to another.

In the case of sodium chloride (NaCl), for example, an electron was transferred completely from Na to Cl to form the Na^+ and Cl^- ions (Figure 1.32). This shift in electron density, from one atom to another, is termed an ***oxidation-reduction*** reaction — usually shortened to ***Redox***reaction.

Oxidation refers to the *loss* of electrons during a reaction whilst ***reduction*** refers to the *gain* of electrons. Oxidation and reduction always occur together — with one substance accepting the electrons that another loses. Thus in the reaction of sodium chloride, sodium loses an electron and is therefore oxidised whilst the chlorine atom gains an electron and is said to be reduced.

Figure 1.32

Loss of electrons is called oxidation and gain of electrons is termed reduction

Although in the sodium chloride reaction, the sodium supplies the electron, and is thus oxidised, it acts as the reducing agent. Likewise the chlorine, which is reduced, acts as the oxidising agent.

A measure of the power of a substance to gain electrons is called the Redox potential. A reducing agent that readily loses electrons will have a negative potential whilst oxidising agents will have a positive potential.