General Principles of Chemistry

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Preface

General chemistry is a course often taught at introductory level in tertiary institutions. It is intended to serve as a broad introduction to a variety of concepts in chemistry.

This book has been written to help students have a better understanding of some of the topics that are usually covered in general chemistry. Efforts have also been made to present the text in a simple, easy-to-understand language with exercises, which are meant to make you have a good grasp of what you are going to learn.

We have adopted the use of diagrams throughout the book in order to make points clearer and minimize memorization. The overall goal of this text is to introduce the students to the relevance and excitement of chemistry as a discipline or pre-requisite course.

The following topics are discussed in the book namely; matter, atomic theory, quantum theory, periodic table, oxygen, hydrogen, chemical bonds, stoichiometry, and acids, bases and salts.

The book could serve as a useful companion for students pursuing a degree in the University, Polytechnic, College of Education, and other higher educational establishments.

We wish you an exciting time as you read through the book. Cheers!!!

Contributing Authors
2014

CHAPTER ONE

Matter

Matter is defined as

“that which has mass and occupies space.”

This definition seems simple enough, yet there are profound issues which surround it. For example, there is currently no generally accepted scientific theory for why mass exists. It can be defined,

“mass characterizes an object's resistance to a change in its motion.”

But why it exists cannot yet be demonstrated. Mass just is, it just exists. The mass is the amount of matter in an object, which is not the same thing as its weight. The weight is a measure of the gravitational force exerted on an object. As long as the gravity is uniform (earth’s surface), the weight does not change. Hence, we can freely use the word mass or weight; it does not make any difference. However, if the gravitational forces are not the same (earth vs. moon), the weight differs from the mass. For example, the same astronaut (same mass) weighs differently on earth and on moon.

As we look into it more, definitions start to become circular, as in the definition of space:

“space is that which is occupied by matter.”

So, any definition of space exists only if there is matter. Take the matter away and space ceases to exist. Of course, saying "take the matter away" is very easy to say. It is quite another thing to specify what is meant by it. The entire universe is made of two things: matter and energy. All living and non-living things are made up of matter.

Particulate Nature of Matter

All matter is particulate in nature. This basically means that between separate bits of matter there are spaces which contain no matter. In science it is called the “atomic nature of matter”. It is generally agreed that the Greek philosopher Leucippus and his student Democritus were the first to propose this idea, about 440 B.C. This “atomic theory” (to use a modern phrase) was opposed by Aristotle 100 years later, who taught that all space is filled with matter, that there are no empty spaces. Aristotle's ideas were accepted as correct by almost all educated people, until the early 1800’s, when atomic ideas began to be more generally accepted as correct.

Today, we know that there are many different particles which make up matter. Some are long-lasting, such as the proton. Others are very, very short-lived, such as the top quark. The primary “particle” in chemistry is the atom. However, you probably know that there is a substructure to an atom; that it is made of protons, neutrons and electrons. You may also know that protons and neutrons are each made of three quarks. There are many other particles beyond the proton and neutron, some containing two quarks and some containing three.

There are two other categories of particles which appear to NOT be made of quarks: electrons and neutrinos. As far as science is currently able to tell, there are three types of particles with no substructure that we can detect: quarks, electrons and neutrinos. It may be that someday we will learn the electron, for example, is made of still smaller pieces like an atom is made of protons, neutrons and electrons.

There is also a fairly sophisticated concept called “virtual particles”. While it is based on some concepts you have not yet learned, it is still fairly easy to describe in a general way. There is energy also in the universe, we are just ignoring it for the time being in this tutorial. Some of the energy can spontaneously merge to form a particle of matter. (Einstein showed that matter and energy can be converted, one into another.) These “virtual particles” exist for very, very small amounts of time, so small that we cannot detect them before that pop back into being the energy they were made from.

Since the universe is flooded with energy, this means that, in every square centimeter of the universe, are trillions and trillions and trillions of virtual particles popping into existence every fraction of a second and then going back to energy. “Empty” space is actually a boiling cauldron of particles. Even though individual particles cannot be detected, the effect can. If you want to look into this farther, look up the “Casimir Effect” as well as learn what “polarizability of the vacuum” or “quantum fluctuation of the vacuum” means. It may be that Aristotle was right all along.

The fundamental building block of matter is the atom. However, the term “atom” just refers to a building block of matter; it doesn't specify the identity of the atom. It could be an atom of carbon, or an atom of hydrogen, or any other kind of atom. Any atom is composed of a little nucleus surrounded by a “cloud” of electrons. In the nucleus there are protons and neutrons.

The atom is the basic building block for all matter in the universe. Atoms are extremely small and are made up of a few even smaller particles. The basic particles that make up an atom are electrons, protons, and neutrons. Atoms fit together with other atoms to make up matter. It takes a lot of atoms to make up anything. There are so many atoms in a single human body we won't even try to write the number here. Suffice it to say that the number is trillions and trillions (and then some more).

There are different kinds of atoms based on the number of electrons, protons, and neutrons each atom contains. Each different kind of atom makes up an element. There are 92 natural elements and up to 118 when you count in man-made elements.

Atoms last a long time, in most cases forever. They can change and undergo chemical reactions, sharing electrons with other atoms. But the nucleus is very hard to split, meaning most atoms are around for a long time.

Classification of Matter

The matter can be classified in two different ways; (a) according to its state, and (b) according to its composition.

Classification According to its States

Matter exists, at room temperature, in three different states namely: solid, liquid and gaseous states. Adsorption or evolution of heat results in the interconversion of these states. There are two other states of matter, plasma state and Bose-Einstein condensate, which occur at a very high temperature of 10^5 K and very low temperature of less than 10^{-7} K respectively.

Solids

Solids have a definite shape and a definite volume. Most everyday objects are solids: rocks, chairs, ice, and anything with a specific shape and size. The molecules in a solid are close together and connected by intermolecular bonds. Solids can be amorphous, meaning that they have no particular structure, or they can be arranged into crystalline structures or networks. For instance, soot, graphite, and diamond are all made of elemental carbon, and they are all solids. What makes them so different? Soot is amorphous, so the atoms are randomly stuck together. Graphite forms parallel layers that can slip past each other. Diamond, however, forms a crystal structure that makes it very strong.

Liquids

Liquids have a definite volume, but they do not have a definite shape. Instead, they take the shape of their container to the extent they are indeed “contained” by something such as beaker or a cupped hand or even a puddle. If not “contained” by a formal or informal vessel, the shape is determined by other internal (e.g. intermolecular) and external (e.g. gravity, wind, inertial) forces. The molecules are close, but not as close as a solid. The intermolecular bonds are weak, so the molecules are free to slip past each other, flowing smoothly. A property of liquids is viscosity, the measure of “thickness” when flowing. For example, water is not nearly as viscous as molasses.

Gases

Gas particles have a great deal of space between them and have high kinetic energy. If unconfined, the particles of a gas will spread out indefinitely; if confined, the gas will expand to fill its container. When a gas is put under pressure by reducing the volume of the container, the space between particles is reduced, and the pressure exerted by their collisions increases. If the volume of the container is held constant, but the temperature of the gas increases, then the pressure will also increase. Gas particles have enough kinetic energy to overcome intermolecular forces that hold solids and liquids together, thus a gas has no definite volume and no definite shape.

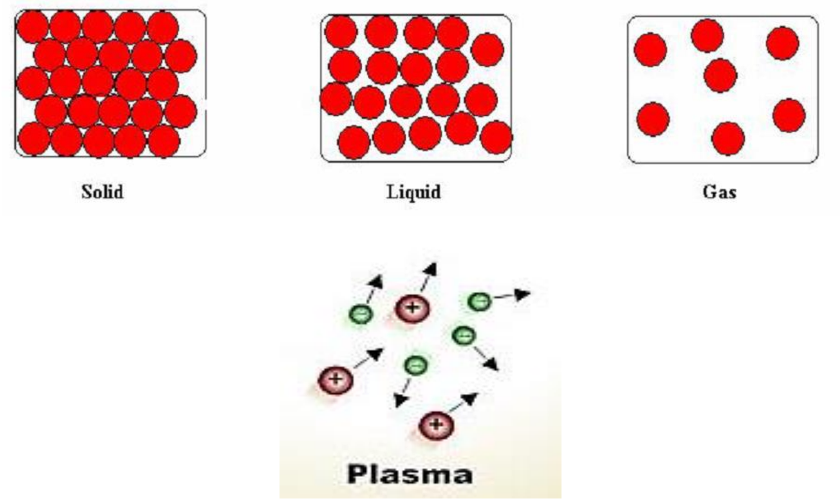


Figure 1.1*: Solid, liquid, gaseous and plasma states of matter*

Plasma

Plasma is not a common state of matter here on Earth, but may be the most common state of matter in the universe. Plasma consists of highly charged particles with extremely high kinetic energy. The *noble gases* (helium, neon, argon, krypton, xenon and radon) are often used to make glowing signs by using electricity to ionize them to the plasma state. Stars are essentially superheated balls of plasma.

Bose-Einstein Condensates

In 1995, technology enabled scientists to create a new state of matter, the **Bose-Einstein condensate** (BEC). Using a combination of lasers and magnets, Eric Cornell and Carl Weiman cooled a sample of *rubidium* to within a few degrees of absolute zero. At this extremely low temperature, molecular motion comes very close to stopping altogether. Since there is almost no kinetic energy being transferred from one atom to another, the atoms begin to clump together. There are no longer thousands of separate atoms, just one "super atom."

A BEC exists when matter is frozen to extremely low temperatures that are a tiny fraction of a degree above absolute zero. In this state, the atoms overlap into each other to form a wave. The BEC is a matter wave. If the wave was compressed, it would form a singularity. If enough mass was condensed into the singularity it could turn into a black hole. The occurrence of a black hole while making BEC would not need to be too much of a concern anyway because it would require a tremendous amount of energy to compress mass into the critical point.

A BEC is used to study quantum mechanics on a macroscopic level. Light appears to slow down as it passes through a BEC, allowing study of the particle/wave paradox. A BEC also has many of the properties of a superfluid – flowing without friction. BECs are also used to simulate conditions that might apply in black holes.

Classification According to its Composition

Matter is classified into two broad categories, namely, pure substances and mixtures. Mixtures can be separated into pure substances by physical methods. Pure substances are further divided into categories as elements and compounds. Similarly, mixtures are also classified into types; homogeneous mixtures and heterogeneous mixtures (see Figure 1.2).

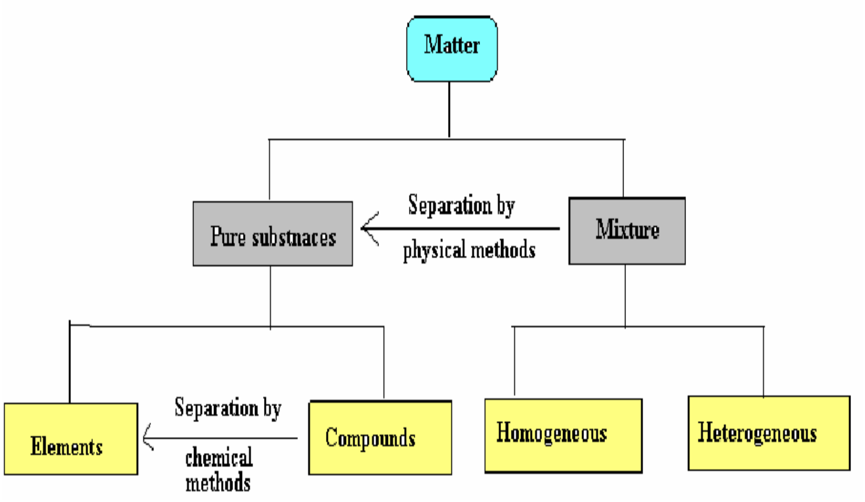


Figure 1.2*: Classification of matter according to its composition*

Chemical Substances

In *chemistry*, a chemical substance is a form of matter that has constant chemical composition and characteristic properties. It cannot be separated into components without breaking chemical *bonds*. Chemical substances can be *solids*, *liquids*, gases, *plasma*, *or Bose-Einstein Condensate*. Changes in *temperature* or *pressure* can cause substances to shift between the different phases of matter.

Element

An element is a chemical substance that is made up of a particular kind of atom and hence cannot be broken down or transformed by a chemical reaction into a different element. It is either discovered innature or synthesized in the laboratory in pure form that cannot be separated into simpler substances by chemical methods. All atoms of an element have the same number of *protons*, though they may have different numbers of *neutrons* and *electrons*. Currently, there are about 118 elements discovered; some are found in nature and some are man-made. The periodic table is the diagrammatic and systematic arrangement of the elements in the order of their increasing atomic numbers and according to their families. Basically, there are three main classes of elements namely: the metals, the non-metals and the metalloids. However, with reference to the periodic table, there are broadly classified, based on their chemical properties, as alkali metals, alkaline-earth metals, lanthanides, actinides, transition metals, post-transition metals, metalloids, polyatomic non-metals, diatomic non-metals and noble gases. In order to call it as an element, its properties must be unique; no two elements are alike.

Names and Symbols of Elements

The names of the elements are given by its inventor(s):

1. Some are named after the place like an element Berkelium (Bk) after its discovery in Berkeley (University of California, Berkeley);
2. Some are based on planet, like element Mercury (Hg) named after the planet mercury;
3. Some, given to honour the great scientist, like Curium (Cm) after Madame Curie.

Similarly, elements have symbols, which are the short-hand notations for elements consisting of one or two letters:

1. The first letter is always in upper case and the second one in lower case;
2. Most of the symbols are derived from their English names except few that are derived from their Latin names;

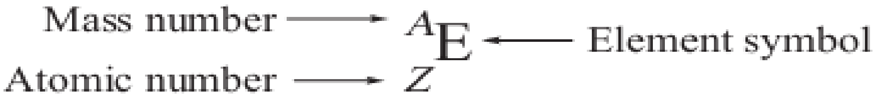
3. One-letter symbols are taken from the first letter of the name. The two-letter symbols are derived in various ways. Some symbols are derived by the combination of the first letter and the second letter (e.g. Ba for Barium), some are of the first letter and the third letter (e.g. Cl for chlorine), etc.

Atomic Number, Mass Number and Atomic Weight

It is possible to confuse these values, but they are quite distinct from one another. Atoms consist of a nucleus containing positively charged protons and electrically neutral neutrons, with electrons orbiting some distance away. Protons and neutrons are relatively heavy, and similar in weight, but electrons are very much lighter and contribute very little to the weight of an atom.

The number of protons in an atom defines what element it is. For example, carbon atoms have six protons, hydrogen atoms have one, and oxygen atoms have eight. The number of protons in an atom is referred to as the atomic number of that element. The number of protons in an atom also determines the chemical behaviour of the element.

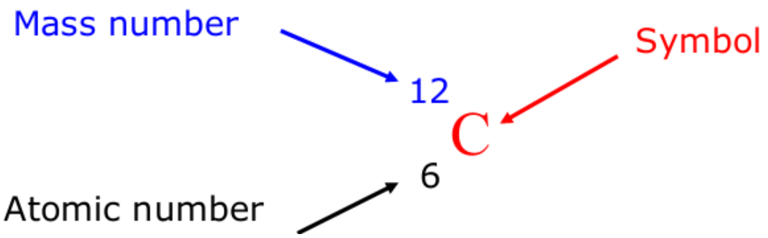
The mass number of an atom is the number of protons plus the number of neutrons and is nearly equal to the weight of the atom. The number of neutrons in an element can vary. Forms of an element with different numbers of neutrons are known as *isotopes*.



Mass number = A = number of protons + number of neutrons

Number of neutrons = A – Z

For instance, for a carbon atom, the atomic number and mass number are as presented below:



The atomic mass of an element is a weighted average of all the element's isotopes based on their natural abundance. The standard atomic weight is the average mass of an element in atomic mass units ("amu"). Though individual atoms always have an integer number of atomic mass units, the atomic mass on the periodic table is stated as a decimal number because it is an average of the various isotopes of an element. The atomic weight is usually determined as an average, based on the relative abundance of isotopes. Since some isotopes are unstable, changing over time into other elements, atomic weights can vary, and may be represented as a range, rather than a single value. Isotopes are usually represented with the atomic number at the bottom left of the chemical symbol, and the mass number, or approximate atomic weight, at the top right. For example, carbon-13 would be shown as $^{13}_{6}\mathrm{C}$.

Example 1
You are given a sample containing 98% *carbon-12 and 2% carbon-13.* What is the *relative atomic mass* of the element?

Solution

1. First convert the percentages to decimal values by dividing each percentage by 100. The sample becomes 0.98 carbon-12 and 0.02 carbon-13.

2. Next, multiply the atomic mass of each isotope by the proportion of the element in the sample:
   0.98 x 12 = 11.76
   0.02 x 13 = 0.26

3. For the final answer, add these together:
   11.76 + 0.26 = 12.02 g/mol

Note that:

1. The approximated *value of atomic mass is given on a periodic table* is given *in atomic mass units* or amu, but *for chemistry calculations*, atomic mass is usually written in terms of grams per mole or g/mol.
2. To calculate the *atomic mass of a single atom* of an element, add up the mass *of protons and neutrons.*

Example 2

Calculate the value of A_r for naturally occurring chlorine, if the distribution of isotopes is 75.77% $^{35}_{17}Cl$ and 24.23% $^{37}_{17}Cl$. Accurate masses for $^{35}_{17}Cl$ and $^{37}_{17}Cl$ are 34.97 and 36.96 respectively.

Solution

Relative atomic mass, A_r $\left(\frac{75.77}{100} \times 34.97\right) + \left(\frac{24.23}{100} \times 36.97\right) =$ 35.45 g/mol

Table 1.1: Names, symbols and origin of names of some elements

Element	Sym	Origin of name	Element	Sym	Origin of name
Aluminium	Al	the Latin name for alum, 'alumen' meaning *bitter salt*	Hydrogen	H	the Greek 'hydro' and 'genes' meaning *water-forming*
Americium	Am	Americas, the continent where the element was first synthesized	Iron	Fe	the Anglo-Saxon name *iren* (*ferrum* in Latin)
Antimony	Sb	the Greek 'anti – monos', meaning *not alone* (*stibium* in Latin)	Lead	Pb	the Anglo-Saxon *lead* (*plumbum* in Latin)
Argon	Ar	the Greek, 'argos', meaning *idle*	Magnesium	Mg	Magnesia, a district of Eastern Thessaly in Greece
Barium	Ba	the Greek 'barys', meaning *heavy*	Manganese	Mn	Either the Latin 'magnes', meaning *magnet* or from the *black magnesium oxide*, 'magnesia nigra'
Beryllium	Be	the Greek name for beryl, 'beryllo'	Mercury	Hg	Mercury, the first planet in the Solar System (Hg from former name *hydrargyrum,* from Greek *hydr*- water and *argyros* silver)
Boron	B	the Arabic 'buraq', which was the name for borax	Nitrogen	N	the Greek 'nitron' and 'genes' meaning *nitre-forming*
Bromine	Br	the Greek 'bromos' meaning *stench*	Oxygen	O	the Greek 'oxy' and 'genes' meaning *acid-forming*
Cadmium	Cd	the Latin name for the mineral	Phosphorus	P	the Greek 'phosphoros',

		calmine, 'cadmia'			meaning *bringer of light*
Calcium	Ca	the Latin 'calx' meaning *lime*	Potassium	K	the English word *potash* (*kalium* in Latin)
Californium	Cf	State of California, USA, where the element was first synthesized	Silicon	Si	the Latin 'silex' or 'silicis', meaning *flint*
Carbon	C	the Latin 'carbo', meaning *charcoal*	Silver	Ag	the Anglo-Saxon name *siolfur* (*argentum* in Latin)
Chlorine	Cl	the Greek 'chloros', meaning *greenish yellow*	Sodium	Na	the English word *soda* (*natrium* in Latin)
Copper	Cu	the Old English name *coper* in turn derived from the Latin 'Cypriumaes', meaning *a metal from Cyprus*	Sulfur	S	Either from the Sanskrit 'sulvere', or the Latin 'sulfurium', both names for sulphur
Curium	Cm	Pierre Curie, a physicist, and Marie Curie, a physicist and chemist	Tin	Sn	the Anglo-Saxon word *tin* (*stannum* in Latin, meaning *hard*)
Fluorine	F	the Latin 'fluere', meaning *to flow*	Zinc	Zn	the German, 'zinc', which may in turn be derived from the Persian word 'sing', meaning *stone*
Gold	Au	the Anglo-Saxon word *gold* (aurum in Latin, meaning *glow of sunrise*)	Zirconium	Zr	the Persian 'zargun', meaning *gold coloured*

Compound

In contrast to elements, compounds are composed of different type of atoms. More precisely, a compound is a chemical substance that consists of two or more elements. A pure chemical compound is a chemical substance that is composed of a particular set of molecules or ions that are chemically bonded.

The smallest representative for a compound (which means it retains characteristics of the compound) is called a molecule. In other words, a molecule is the smallest particle that has any of the properties of a compound. A molecule is formed when two or more *atoms* join together chemically. A compound is a molecule that contains at least two different *elements*. All compounds are molecules but not all molecules are compounds. Molecular *hydrogen* (H_2), molecular *oxygen* (O_2) and molecular *nitrogen* (N_2) are not compounds because each is composed of a single element. Water (H_2O), carbon dioxide (CO_2) and methane (CH_4) are compounds because each is made from more than one element. The smallest bit of each of these substances would be referred to as a molecule. For example, a single molecule of molecular hydrogen is made from two atoms of hydrogen while a single molecule of water is made from two atoms of hydrogen and one atom of oxygen.

The formula for a molecule must be neutral. When writing the formula for an ionic compound, the charges on the ions must balance, the number of positive charges must equal the number of negative charges. Molecules are composed of atoms that have “bonded” together. As an example, the formula of a water molecule is “H_2O”: two hydrogen atoms and one oxygen atom.

When the compound is formed, altogether a new substance is formed and the properties of which are quite different from its reacting elements. Compounds can be separated into elements using chemical methods but not the physical methods.

A chemical compound can be either atoms bonded together in molecules or *crystals* in which atoms, molecules or ions form a *crystallinelattice*. Compounds made primarily of carbon and hydrogen atoms are called organic compounds, and all others are called inorganic compounds. Compounds containing bonds between carbon and a *metal* are called organometallic compounds.

Compounds have properties different from the elements that created them. Water, for example, is composed of hydrogen and oxygen. Hydrogen is an explosive gas and oxygen is a gas that fuels fire. Water has completely different properties, being a liquid that is used to extinguish fires.

Chemical substances are often called ‘pure’ to set them apart from mixtures. A common example of a chemical substance is pure water; it always has the same properties and the same *ratio* of hydrogen to *oxygen* whether it is isolated from a river or made in a laboratory. Other chemical substances commonly encountered in pure form are *diamond* (carbon), gold, table *salt* (sodium chloride), and refined sugar (sucrose). Simple or seemingly pure substances found in nature can in fact be mixtures of chemical substances. For example, tap water may contain small amounts of dissolved sodium chloride and compounds containing iron, calcium, and many other chemical substances.

Chemical Mixtures

A mixture is a material *system* made up of two or more different substances, which are mixed but not combined chemically. A mixture refers to the physical combination of two or more substances in which the identities of the individual substances are retained.

Mixtures can be separated into their constituent parts by physical means (e.g. distillation of liquids or separating magnetic and non-magnetic solids using a magnet), and have many of the properties of their constituent parts (e.g. the element “oxygen” is part of the mixture “air” and some of the properties of air are due to the oxygen, albeit somewhat reduced compared with pure oxygen due to the presence of the other constituents of the mixture called “air”).

Mixtures can broadly be classified as heterogeneous and homogeneous mixtures. However, they take the form of *alloys*, solutions, suspensions, and *colloids*.

All mixtures have two parts, the “dispersing medium” and the “dispersed phase”. Generally speaking, the dispersed phase is in the smaller amount and is spread throughout the dispersing medium. In most cases, the dispersed phase is quite small in amount compared to the amount of the dispersing medium.

Heterogeneous Mixtures

A heterogeneous mixture is a mixture of two or more chemical substances (elements or compounds), where the different components can be visually distinguished and easily separated by physical means.

Examples include:

- mixtures of sand and water
- mixtures of sand and iron filings
- a conglomerate rock
- water and oil
- a salad
- trail mix
- mixtures of gold powder and *silver* powder

Homogenous Mixtures

A homogeneous mixture is a mixture of two or more chemical substances (elements or compounds), where the different components cannot be visually distinguished. The composition of homogeneous mixtures is constant. Often separating the components of a homogeneous mixture is more challenging than separating the components of a heterogeneous mixture.

Solutions

They are a special type of homogeneous mixtures in which one substance (called the “solute”) is dissolved in another substance (called the “solvent”), e.g. salt water is salt dissolved in water – in such a way that the salt no longer exists as solid particles within the water.

Suspensions

Suspensions are heterogeneous fluid mixtures containing solid particles large enough for sedimentation, which means that the particles (compare with the “solute” part of a solution) will eventually settle to the bottom of the container (unlike in the case of colloids, below), e.g. particles of sand in water.

Colloids

Colloids are heterogeneous mixtures in which one is substance microscopically dispersed evenly throughout another substance (for comparison, the size of the particles of “solute” are greater than in the case of a solution, but much smaller than in the case of a suspension). There are many naturally occurring colloids, e.g. milk. Colloids are very important in biology and medicine.

Table 1.2: Types of Colloids

		Dispersing Medium		
		Gas	***Liquid***	***Solid***
Dispersed Phase	***Gas***		Foam	Foam
	Liquid	Aerosol	Emulsion	Gel
	Solid	Aerosol	Sol	Solid Sol

Table 1.3: Examples of Colloids

		Dispersing Medium		
		Gas	***Liquid***	***Solid***
Dispersed Phase	***Gas***		shaving cream, whipped cream	foam rubber, sponge, pumice
	Liquid	fogs, clouds, aerosol can spray	mayonnaise, milk, face cream, hair gel	jelly, cheese, butter
	Solid	smoke, car exhaust, airborne viruses	Gold in water, milk of magnesia, river silt	alloys of metals (steel, brass

Alloys

They are mixtures in which the main element(s) are metal(s). A more technical definition of an alloy is “a partial or complete solid solution of one or more elements in a metallic matrix”. Common examples of alloys include bronze, brass and steels.

Physical and Chemical Changes

Physical Changes

A physical change is any change NOT involving a change in the chemical identity of the substance. Energy is absorbed or released during a physical change.

Many physical changes also involve the rearrangement of atoms most noticeably in the formation of crystals. Many chemical changes are *irreversible*, and many physical changes are *reversible*, but reversibility is not a certain criterion for classification. Although chemical changes may be recognized by an indication such as odour, colour change, or production of a *gas*, every one of these indicators can result from physical change.

In general, a physical change is reversible using physical means. For example *salt* dissolved in water can be recovered by allowing the water to evaporate.

Physical changes are attributed to:

1. **Phase change**. This involves moving between solid, liquid and gas involves only the amount of energy in the sample. There is no effect on the chemical identity of the substance. For example, water remains water, no matter if it solid, liquid or gas.
2. **Grinding something into a powder**. Or the reverse process of making a bigger lump of stuff, say by melting lots of small pellets of copper into one big piece.
3. **Magnetisation**. This change in no way affects the chemical identity of the element. Iron that is magnetized rusts just as easily as iron that is not magnetized.

Table 1.4: Processes involved in change of phases of matter

Change	**Name of change**
Solid to liquid	melting, fusion
Liquid to gas	boiling, evaporation
Solid to gas	sublimation
Gas to solid	deposition
Gas to liquid	condensation, liquefaction
Liquid to solid	freezing, solidification

The change of state from solid to liquid is called melting or fusion, while the reverse process is called freezing or solidifying. The melting point is the temperature at which a substance changes from solid to liquid. Conversely, freezing point is the temperature at which a substance changes from a liquid to solid. These two temperatures are essentially the same – which one is used depends upon whether the substance is being heated or being cooled.

The change of state from liquid to gas is called vaporisation or boiling, while the reverse process is called condensation. The boiling point is the temperature at which a substance changes from liquid to gas. Conversely, condensing point is the temperature at which a substance changes from a gas to liquid. When liquids gradually turn into gases at temperatures less than their boiling point, the process is called evaporation.

Some substances, like iodine and solid carbon dioxide, can go directly from solid to gaseous state without melting – this is known as sublimation. The reverse process of sublimation is called deposition.

Chemical Changes

A chemical change means that the reacting compound(s) are changed into new compounds. The actual atoms involved remain, but are simply rearranged into the new compounds. The rearrangement is called a chemical reaction.

For example:

$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

is a chemical reaction in which water is broken down into the hydrogen and oxygen which make it up. Notice how the amounts of hydrogen atoms (four) and oxygen atoms (two) do not change from one side of the arrow to the other. However, the arrangement of the atoms is different. Some chemical bonds (the one involved in the water) have been broken and some new chemical bonds (the one in hydrogen and oxygen) have been formed.

Thus, a chemical change is a process in which chemical bonds are broken and new ones are made. A process like grinding some salt crystals into a fine powder does not involve the breaking of chemical bonds and the formation of new ones, so it is a physical change. A chemical change always involves a change in the chemical relationship between the various substances involved.

This change is seen in the fact that some chemical bonds are broken and some bonds are newly made.

Another example of a chemical change is:

$$2N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

While all three substances are gases, the two reacting substances are quite different chemically from the product. This is because the bonds between the nitrogen atoms have been broken, as well as between the hydrogen atoms. In the place of these broken bonds has come something not present in the reactants, bonding between a nitrogen atom and some hydrogen atoms.

Separation of Mixtures

Most materials found in nature are in the form of mixtures. A separation process is used to transform a mixture into two or more distinct products. Components of mixtures are usually separated by physical means to give their purified forms. There are different physical methods which can be employed to separate mixtures. The particular technique chosen for any given mixture depends on the nature of the constituents.

This is done by considering that different components of the mixture may have different properties such as:

- size
- density
- solubility
- electrical charge
- boiling point

Depending on the raw mixture, various processes can be employed to separate the mixtures. Often, two or more of these processes must be used in combination to obtain the desired separation.

Evaporation

This method is used to separate components of soluble solid/liquid mixtures and volatile/non-volatile liquid mixtures. The principle governing this method is the fact that molecules of liquid substances when they gain heat, become gaseous and are lost from the surface. Note that the liquid, having vaporized is not collected but lost to the atmosphere. The other component (which is required), is then collected. An example is a mixture of sodium chloride and water.

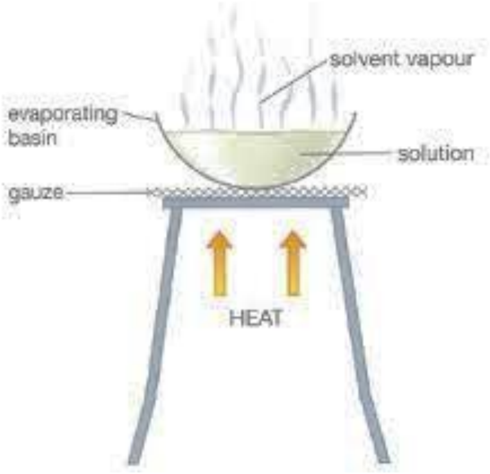


Figure 1.3: *Evaporation process*

Distillation

This is used to separate components of liquid/liquid mixtures and soluble solid/liquid mixtures. It involves heating the mixture, and the vapour formed is allowed to cool, liquefy and is collected as pure liquid. Thus, each component of the mixture is purified. The principle behind this method is based on the fact that when liquids are heated to their boiling points, they become gaseous, and when the gases are cooled, they change back to the liquid.

It is worthy of note that while evaporation is mostly used for solid/liquid mixtures, distillation is mostly used to separate liquid/liquid mixtures. Both evaporation and distillation involve gain of heat, and then vaporization. In evaporation, the vapour formed is allowed to escape into the atmosphere, while in distillation, the vapour is not lost but cooled, liquefied and collected as pure liquid. Distillation is used to purify solvents. There are two kinds of distillation – simple and fractional distillation.

Simple Distillation

This is used to separate mixtures of volatile/non-volatile liquids, or for mixtures of liquids whose boiling points are wide apart (by at least 100 ^{o}C). In other words, simple distillation is a method used for the separation of components of a mixture containing two miscible liquids that boil without decomposition and have sufficient difference in their boiling points. Examples of such mixtures are the mixture of water and ink, acetone and water. Simple distillation is applicable in the distillation of alcohol.

The distillation process involves heating a liquid to its boiling points, and transferring the vapours into the cold portion of the apparatus, then condensing the vapours and collecting the condensed liquid in a container. In this process, when the temperature of a liquid rises, the vapour pressure of the liquid increases. When the vapour pressure of the liquid and the atmospheric pressure reach the same level, the liquid passes into its vapour state. The vapours pass over the heated portion of the apparatus until they come into contact with the cold surface of the water-cooled condenser. When the vapour cools, it condenses and passes down the condenser and is collected into a receiver through the vacuum adapter.

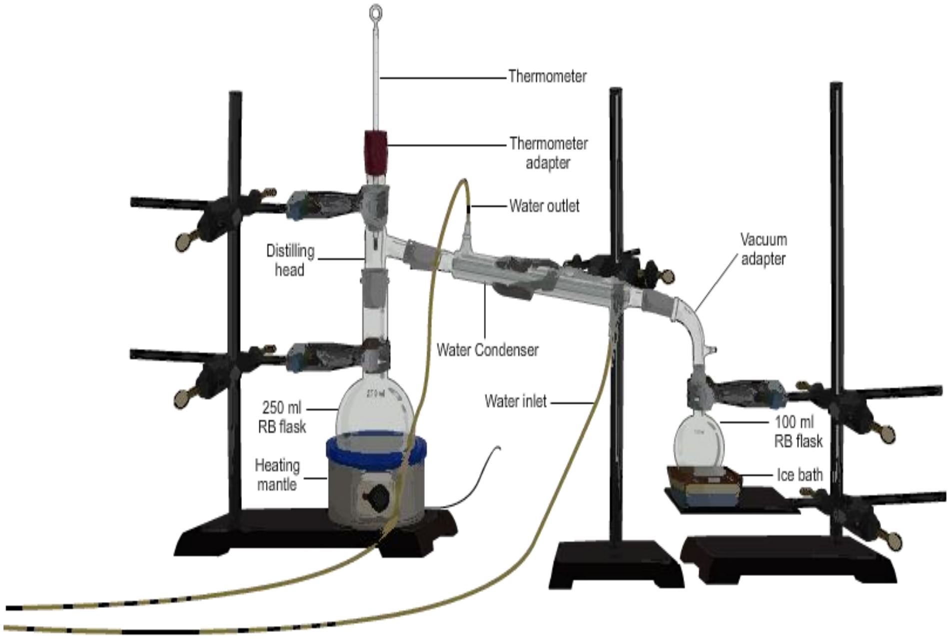


Figure 1.4: *Simple distillation set-up*

Fractional Distillation

This is used to separate a mixture of liquids whose boiling points are close (boiling point difference of not more than 20-30^oC). Examples of mixtures that can be separated by this method include: petroleum; alcohol and water; liquid air (a mixture of oxygen (b.pt 90 K), nitrogen (b.pt 77 K) and water (b.pt 100^oC)). The apparatus for fractional distillation is similar to that of simple distillation, except that a fractionating column is fitted in between the distillation flask and the condenser.

A simple fractionating column is a tube packed with glass beads. The beads provide surface for the vapours to cool and condense repeatedly. When vapours of a mixture are passed through the fractionating column, because of the repeated condensation and evaporation, the vapours of the liquid with the lower boiling point first pass out of the fractionating column, condense and are collected in the receiver flask. The other liquid, with a slightly higher boiling point, can be collected in similar fashion in another receiver flask.

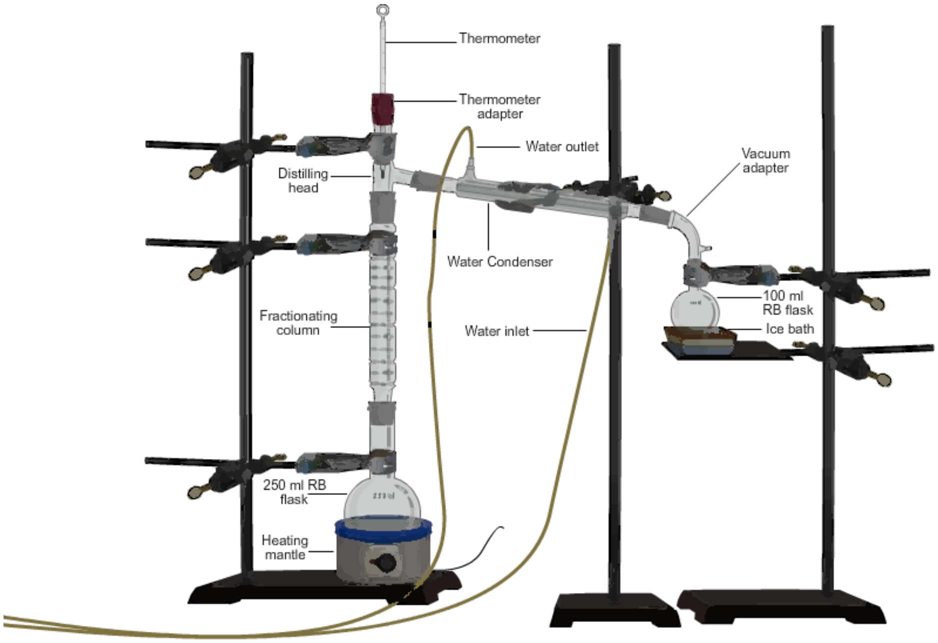


Figure 1.5: *A simple fractionating column*

Fractional distillation process is application in the separation of different fractions from petroleum products and separation of a mixture of methanol and ethanol.

Sublimation

Sublimation is suitable for solid mixtures containing solid substances that can vaporize directly when heated. Examples of such substances are iodine crystals, ammonium chloride, anhydrous aluminium chloride, anhydrous iron (III) chloride and benzoic acid. The vapour is cooled away from the other component(s) and collected as solid.

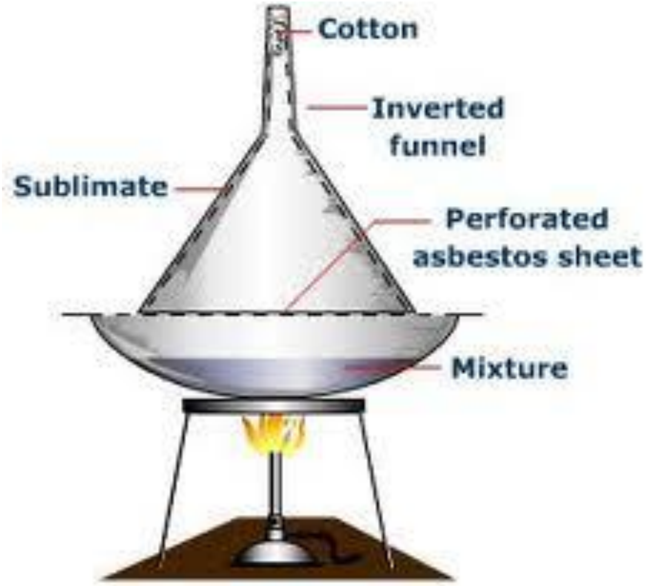


***Figure 1.6**: Sublimation set-up*

Dissolution

The principle behind this technique is that some solid substances are soluble in certain kind of solvent, while others are not. Hence, it is used generally to separate soluble substances from insoluble ones. For example, a mixture of sodium chloride crystals and sand – the sodium chloride is soluble in water while sand is not. Therefore, water is added to the mixture to dissolve sodium chloride while leaving the sand to settle.

Organic solvents generally dissolve organic substances, e.g. kerosene dissolves wax, grease, fats and oils. Inorganic solvents dissolve inorganic substances, and ionic solvents dissolve ionic substances. Common solvents for sulphur are: carbon (IV) sulphide, CS_2 and methylbenzene (toluene). Common solvents for iodine are: ether (ethoxyethane), alcohol, carbon tetrachloride, CCl_4 and potassium iodide.

Water soluble salts include all common trioxonitrates (V) of metals; all common salts of sodium, potassium and ammonium; all common tetraoxosulphates (VI), (except, barium tetraoxosulphate (VI) and lead (II) tetraoxosulphate (VI), and calcium tetraoxosulphate (VI) is sparingly soluble); and all common chlorides except those of silver, mercury (I) and lead.

Filtration

This is used to separate liquid components of mixtures from the solid components (which are in suspension). The principle of this technique is that the particles of liquid are small enough to pass through the filter material while those of solids are not. This implies that the solid particles are in suspension. If they were settled at the bottom, then the process would be decantation and not filtration. Decantation does not involve the use of filter materials; it is the run-off of the liquid component, leaving the solid behind. Decantation will come before filtration (depending on whether the mixture contains solid components which are large and heavy enough to settle).

Both filtration and decantation usually follow the process of dissolution. For instance, after the sodium chloride component of a mixture of sodium chloride and sand is dissolved in water, the liquid component (sodium chloride solution) is decanted (separation from sand), and then filtered to obtain clear sodium chloride solution.

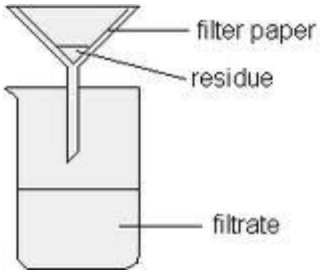


Figure 1.7*: Simple filtration process*

Crystallization

The principle of this method is based on the fact that soluble salts are only soluble to certain concentrations at a given temperature. Decrease in the temperature of their saturated solutions will see the salts forming out of the solution. It is used to obtain a soluble salt from its solution, and it involves heating the solution up to the point of saturation (for salts which crystallize with water of crystallization, e.g., $ZnSO_4.7H_2O$). Cooling the solution below this point results in the formation of the crystals from the solution.

For salts which do not crystallize with water, such as NaCl, their solutions are heated to dryness to produce them. The salts which crystallize with water are not heated to dryness, otherwise, their crystalline nature will be lost. To purify further, the salt can be recrystallized, that is, the crystals obtained is dissolved in hot distilled water and the process of crystallization is repeated.

It is noteworthy that crystallization needs evaporation (by heating) for the solution to become saturated. It is possible to separate a mixture of more than one water-soluble salt by crystallization. This is because the solutions of different substances attain saturation at different temperatures. A solution containing a mixture of different substances therefore crystallizes its components separately when cooled below the saturated points of the different components in solution - this is known as fractional crystallization.

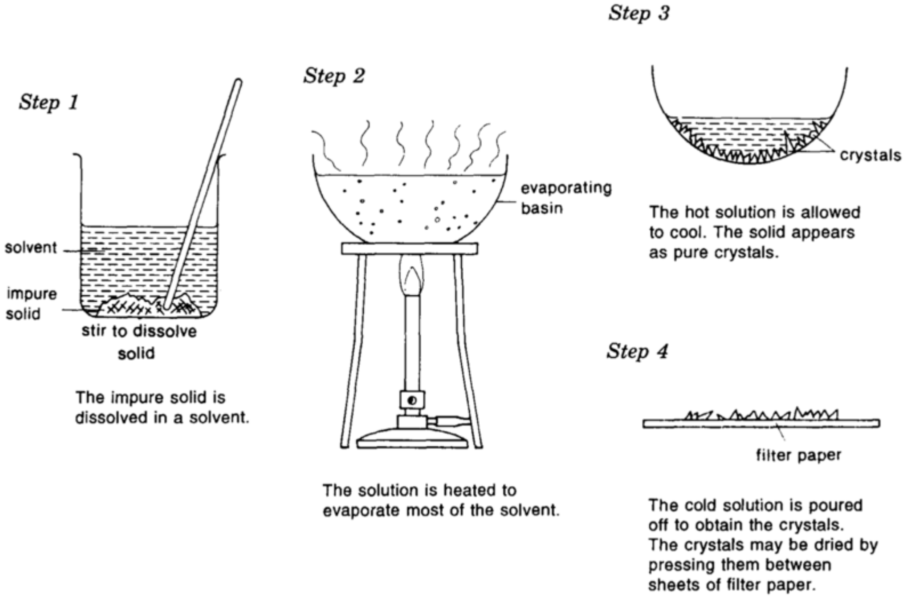


***Figure 1.8**: Schematic diagram of crystallisation process*

Chromatography

This method is mostly popular for the separation of coloured components of pigments (e.g. ink and paints). However, it is useful also in separating certain non-coloured components of mixtures. All chromatographic methods involve two phases, namely: stationary phase and mobile phase. Separation is based on the relative speed of the components of the mixture in-between the two phases.

If the stationary phase is a solid, the process is called adsorption chromatography. If the stationary phase is a liquid, the process is called partition chromatography.

Column Chromatography (Adsorption Chromatography)

The stationary (adsorbent) is a solid such as finely divided alumina and silica gel. The column is usually a glass tube with a tap at the bottom packed with the adsorbent and the mobile phase (the eluting solvent).

As the solvent travels down the column, it carries with it the different components, which travel down at different rates depending on the extent to which they are adsorbed. More strongly adsorbed components travel down more slowly than less adsorbed ones. Hence, components are separated based on their different degree of adsorption on to the stationary phase as they move down the column (which causes them to move at different speeds).

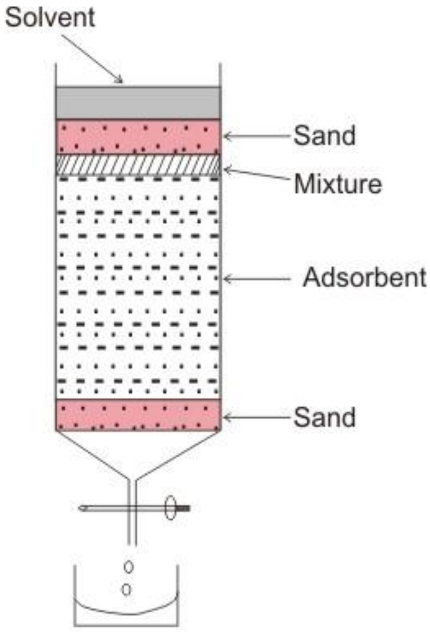


Figure 1.9*: Column chromatography set-up*

Paper Chromatography (Partition Chromatography)

Paper chromatography, also known as partition chromatography is a technique that involves the use of strips of filter paper. Notice that the stationary phase in paper chromatography is the moisture in the paper, and not the paper itself. This is an example of partition chromatography. Separation depends on the different degree of motion (i.e. speed) of the components of the mixture between the stationary water phase and the mobile chromatographic solvent (due to the different affinity the components have for both the stationary and mobile phases).

The material to be separated is applied as a spot near the bottom of the strip of paper. It is dipped into the solvent and the chromatogram left to develop. The solvent (e.g. propanone or ethanol) ascend the strip of paper by capillary action, and carries the solute along with it, different components travel at different rates depending on their relative affinity for both the mobile and stationary phrases.

This is ascending paper chromatography. A descending technique can be made by allowing the solvent to flow down the strip from a tray containing the solvent. Components of mixtures with greater affinity for the mobile phase than the stationary phase are separated first.

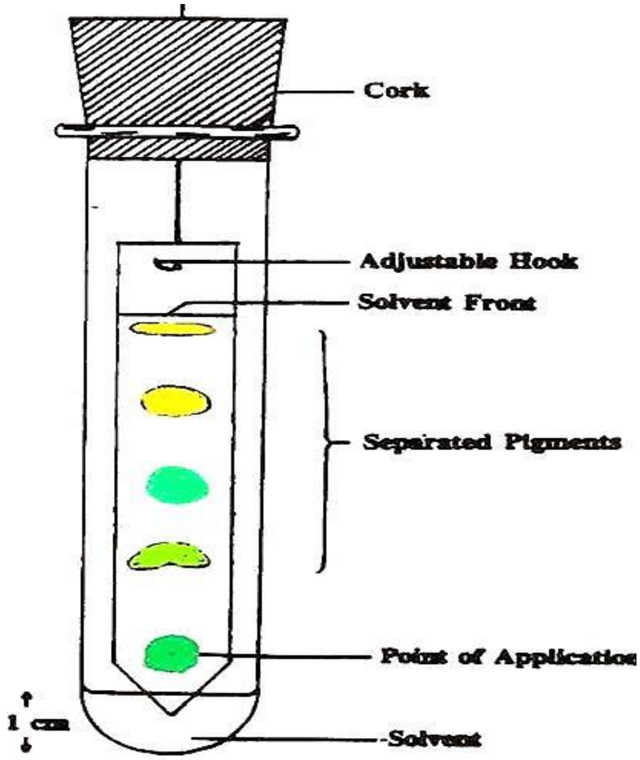


Figure 1.10: *Ascending paper chromatography set-up*

Precipitation

Precipitation is used to separate a salt which is soluble in one solvent, forming a mixture with that solvent, but become insoluble when another liquid which mixes well with the mixture but which does not dissolve the salt is added. The salt will therefore be precipitated from the solution and collected by filtration. For example, iron (II) tetraoxosulphate (VI) is soluble in water to form a mixture (i.e. a solution). When ethanol is added to the solution (ethanol is miscible with water), the iron (II) tetraoxosulphate (VI) will be precipitated from the solution as it is insoluble in ethanol.

Sieving

Sieving is used to separate solid mixtures whose components' particle sizes differ greatly. A sieve is used to make the separation. The particles of one component are small enough to pass through the sieve, while those of the other are not, and are therefore held onto the sieve, separated from the first. Notice that the principle of separation used here is the large difference in the particle size of the components of the mixture.

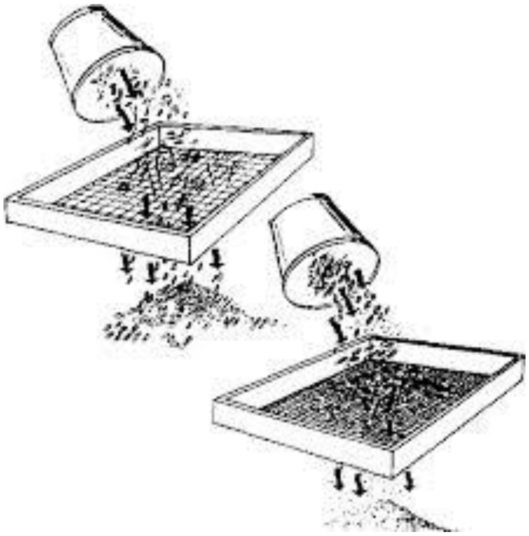


***Figure 1.11**: A simple sieving process*

Separating Funnel

It is used for the separation of components of a mixture between two immiscible liquid phases. One phase is the aqueous phase and the other phase is an organic solvent. This separation is based on the differences in the densities of the liquids. The liquid having more density forms the lower layer and the liquid having less density forms the upper layer. Applications of separating funnel include separating a mixture of oil and water, and a mixture of kerosene oil and water.

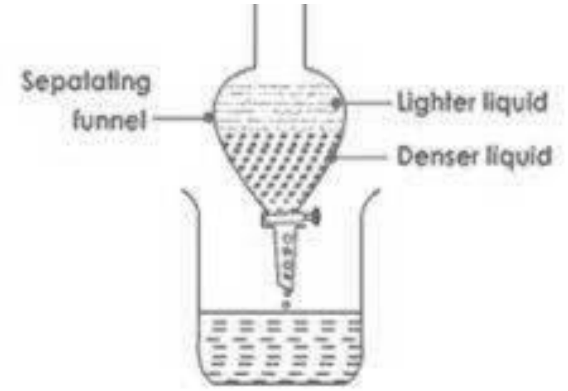


Figure 1.12: *Separating funnel*

Centrifugation

Sometimes the solid particles in a liquid are very small and can pass through a filter paper. For such particles, the filtration technique cannot be used for separation. Such mixtures are separated by centrifugation. So, centrifugation is the process of separation of insoluble materials from a liquid where normal filtration does not work well. The centrifugation is based on the size, shape, and density of the particles, viscosity of the medium, and the speed of rotation. The principle is that the denser particles are forced to the bottom and the lighter particles stay at the top when spun rapidly.

The apparatus used for centrifugation is called a centrifuge. The centrifuge consists of a centrifuge tube holder called rotor. The rotor holds balanced centrifugal tubes of equal amounts of the solid-liquid mixture. On rapid rotation of the rotor, the centrifuge tubes rotate horizontally and due to the centrifugal force, the denser insoluble particles separate from the liquid. When the rotation stops, the solid particles end up at the bottom of the centrifuge tube with liquid at the top.

Applications of centrifugation include:

1. Used in diagnostic laboratories for blood and urine tests.
2. Used in dairies and home to separate butter from cream.
3. Used in washing machines to squeeze water from wet clothes.

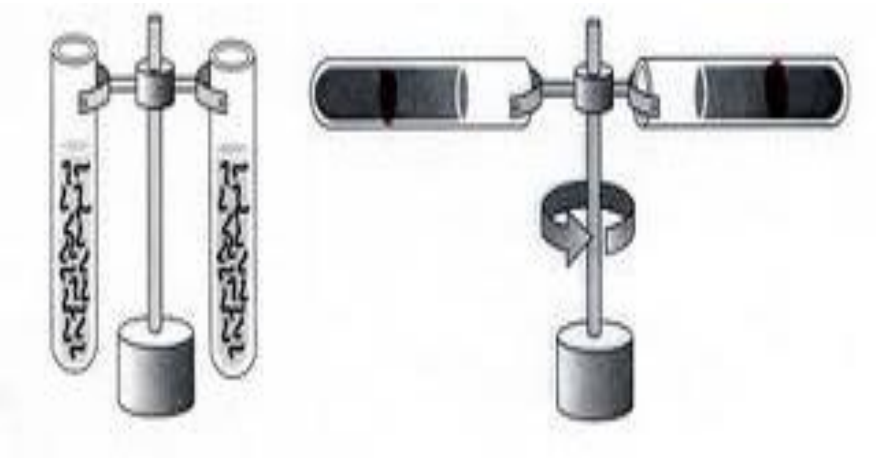


***Figure 1.13**: A Simple centrifugation process*

Study Questions

1. Identify the following states of matter:
    a. The volume is constant but does not depend on shape
    b. The particles are moving and colliding at the fastest rate
    c. Particle movement is restricted to the volume
    d. In this state of matter volume does not vary as temperature increases

2. True/False

a. Water is the only compound to be found in all three principal states of matter?

b. Chemical changes lead to the different states of matter in water?

c. During the variations between the different states, matter is lost?

d. Solid, liquid, and gas are the only states of matter?

3. In the followings, identify which is an element and which is a compound. (a) Silver metal (b) Table salt (c) Oxygen gas (d) Stainless steel (e) Iron.

4. Classify each of the following as homogeneous or heterogeneous mixture (a) Wine (b) Chicken soup (c) Unopened Carbonated soda (d) Creamy peanut butter (e) Minestrone soup.

5. Classify each of the following as an element, compound, or a mixture (a) Gold ring on your finger (b) Sugar (e) French salad dressing (d) Helium (e) Sand.

6. Label each process as a physical or chemical change:

   (a) perfume evaporating on your skin (b) butter melting (c) wood rotting (d) charcoal heating a grill (e) a hot glass cracking when placed in cold water (f) melting copper metal (g) burning sugar (h) mixing sugar in water (i) digesting food.

7. Which of the following would NOT be a physical change?

   (a) freezing water to make ice cubes (b) melting gold to make jewelry (c) burning gasoline in a lawnmower (d) boiling water for soup (e) tearing a piece of aluminum foil

8. Which of the following is NOT a physical change?

(a) grating cheese (b) melting cheese (c) fermenting of cheese (d) mixing two cheeses in a bowl

9. Which are physical and which are chemical changes?
   (a) boil (b) burn (combustion) (c) condense (d) corrode (e) crumple (f) ferment (g) melt (h) rust (i) crush (j) freeze (k) oxidize (l) tarnish (m) explode (n) grind (o) rot (p) vaporize (q) photosynthesis (r) sublimation

10. If a certain mixture is homogeneous, you would properly conclude that the physical properties and the composition:
    (a) are different from one part of the sample to another (b) vary smoothly from top to bottom of the sample (c) are the same in every small volume element from the sample (d) none of these

11. Label each process as a physical or chemical change:
    (a) hydrofluoric acid attacks glass (used to etch glassware) (b) A chef making a sauce with brandy is able to burn off the alcohol from the brandy, leaving just the brandy flavouring (c) Chlorine gas liquefies at -35 °C under normal pressure (d) hydrogen burns in chlorine gas

12. Label each process as a physical or chemical change:
    (a) fogging a mirror with your breath (b) breaking a bone (c) mending a broken bone (d) burning paper (e) slicing potatoes for fries (f) mixing sugar with coffee (g) frying chicken (h) a nail rusting (i) paper ripping (j) wood burning (k) mixing water and food colouring (l) food molding (rotting) (m) writing on paper (n) dyeing fabric

13. Is concrete a heterogeneous mixture?

CHAPTER TWO

Atomic Theory

Democritus first suggested the existence of the atom but it took almost two millennia before the atom was placed on a solid foothold as a fundamental chemical object by John Dalton (1766-1844).

John Dalton, a British school teacher, is the scientist credited for proposing the atomic theory. He published his theory about atoms in 1808. His findings were based on experiments and the laws of chemical combination.

Dalton's Theory

1. All matter consists of indivisible particles called atoms.
2. Atoms of the same element are similar in shape and mass, but differ from the atoms of other elements.
3. Atoms cannot be created or destroyed.
4. Atoms of different elements may combine with each other in a fixed, simple or whole number ratios to form compound atoms.
5. Atoms of same element can combine in more than one ratio to form two or more compounds.
6. The atom is the smallest unit of matter that can take part in a chemical reaction.

Modifications of Dalton's Atomic Theory

1. The indivisibility of an atom was proved wrong: an atom can be further subdivided into protons, neutrons and electrons.

However an atom is the smallest particle that takes part in chemical reactions.

2. According to Dalton, the atoms of same element are similar in all respects. However, atoms of some elements vary in their masses and densities. These atoms of different masses are called isotopes. For example, chlorine has two isotopes with mass numbers 35 and 37.
3. Dalton also claimed that atoms of different elements are different in all respects. This has been proven wrong in certain cases: argon and calcium atoms each have an atomic mass of 40 amu. These atoms are known as isobars.
4. According to Dalton, atoms of different elements combine in simple whole number ratios to form compounds. This is not observed in complex organic compounds like sugar ($C_{12}H_{22}O_{11}$).
5. The theory fails to explain the existence of *allotropes*; it does not account for differences in properties of charcoal, graphite, diamond.

Despite these modifications, credits are given to John Dalton because his:

1. The atomic theory explains the laws of chemical combination, and
2. He was the first person to recognize a workable distinction between the fundamental particle of an element (atom) and that of a compound (molecule).

Law of Conservation of Mass

The law of conservation of mass was formulated by Antoine Lavoisier (1743-1794) as a result of his combustion experiment, in which he observed that the mass of his original substance – a glass vessel, tin, and air – was equal to the mass of the produced substance – the glass vessel, “tin calx”, and the remaining air. He laid the foundation of the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton’s Atomic Theory of Matter.

The law of conservation of mass states that:

> *“the total mass present before a chemical reaction is the same as the total mass present after the chemical reaction.”*

The law of conservation of mass is also known as the “law of indestructibility of matter.” According to this law,

> *“during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.”*

Example

If heating 10 grams of $CaCO_3$ produces 4.4g of CO_2 and 5.6g of CaO, show that these observations are in agreement with the law of conservation of mass.

Solution

Mass of the reactants = 10 g Mass of the products = 4.4 + 5.6g = 10 g.

These observations are in agreement with the law of conservation of mass.

Law of Constant Proportion

Another French chemist, Joseph Proust, stated this law the following way:

> *"A chemical compound always contains the same elements combined together in the same proportion by mass."*

For example, pure water obtained from different sources such as a river, a well, a spring, the sea, etc., always contains hydrogen and oxygen together in the ratio of 1:8 by mass. Similarly, carbon dioxide (CO_2) can be obtained by different methods such as:

- Burning of carbon
- Heating of lime stone
- Applying dilute HCl to marble pieces

Each sample of CO_2 contains carbon and oxygen in a 3:8 ratio

Example

When 1.375 g of cupric oxide is reduced on heating in a current of hydrogen, the weight of copper remaining 1.098 g. In another experiment, 1.179 g of copper is dissolved in nitric acid and resulting copper nitrate converted into cupric oxide by ignition. The weight of cupric oxide formed is 1.476 g. Show that these results illustrate the law of constant proportion.

Solution

First experiment

- Copper oxide = 1.375 g
- Copper left = 1.098 g
- Oxygen present = 1.375 - 1.098 = 0.277 g

Second Experiment

- Copper taken = 1.179 g
- Copper oxide formed = 1.476 g
- Oxygen present = 1.476 - 1.179 = 0.297 g

Percentage of oxygen is approximately the same in both the above cases. So the law of constant composition is illustrated.

Law of Gaseous Volumes

This law, formulated by Gay Lussac, states that,

> *"the ratio between the volumes of gaseous reactants and products can be expressed in simple whole numbers."*

For example, in the following reaction, the ratio of volumes of hydrogen, chlorine, and hydrogen chloride is 1:1:2 (a simple ratio):

$$\begin{array}{ccccc} H_{2(g)} & + & Cl_{2(g)} & \rightarrow & 2HCl_{(g)} \\ 1\text{ vol} & & 1\text{ vol} & & 2\text{ vol} \end{array}$$

Law of Multiple Proportions

John Dalton (1803) stated:

> *"When two elements combine with each other to form two or more compounds, the ratios of the masses of one element that combines with the fixed mass of the other are simple whole numbers."*

Example

Carbon monoxide (CO): 12 parts by mass of carbon combines with 16 parts by mass of oxygen.

Carbon dioxide (CO2): 12 parts by mass of carbon combines with 32 parts by mass of oxygen.
Ratio of the masses of oxygen that combines with a fixed mass of carbon (12 parts): 16:32 or 1:2

Hydrogen and oxygen are known to form 2 compounds. The hydrogen content in one is 5.93%, and that of the other is 11.2%. Show that this data illustrates the law of multiple proportions.

Solution
In the first compound: hydrogen = 5.93%
Oxygen = (100 -5.93) = 94.07%

In the first compound the number of parts of oxygen that combine with one part by mass of hydrogen $\frac{94.07}{5.93}$ = 15.86 parts

In the second compound: hydrogen = 11.2%
Oxygen = (100 -11.2) = 88.88%

In the first compound the number of parts of oxygen that combine with one part by mass of hydrogen $\frac{88.8}{11.2}$ = 7.9 parts

Ratio of the masses of oxygen that combine with fixed mass of hydrogen: 15.86:7.9 or 2:1. This is consistent with the law of multiple proportions.

Law of Reciprocal Proportions

The law of reciprocal proportions was proposed by Jeremias Ritcher in 1792. It states that,

> *"If two different elements combine separately with the same weight of a third element, the ratio of the masses in*

> *which they do so are either the same or a simple multiple of the mass ratio in which they combine."*

For example, oxygen and sulphur react with copper to give copper oxide and copper sulphide, respectively. Sulphur and oxygen also react with each other to form SO_2.

Therefore,
in CuS,
Cu:S = 63.5:32

in CuO,
Cu:O = 63.5:16

Therefore,
S:O = 32:16
S:O = 2:1

Now in SO_2:
S:O = 32:32
S:O = 1:1

Thus, the ratio between the two ratios is the following:

$$\frac{2}{1}:\frac{1}{1} = 2:1$$

Discovery of Electrons

The first cathode-ray tube (CRT) was invented by Michael Faraday (1791-1867). Cathode rays are a type of radiation emitted by the negative terminal, the cathode, and were discovered by passing electricity through nearly-evacuated glass tubes. The radiation crosses the evacuated tube to the positive terminal, the anode.

Cathode rays produced by the CRT are invisible and can only be detected by light emitted by the materials that they strike, called phosphors, painted at the end of the CRT to reveal the path of the cathode rays. These phosphors showed that cathode rays travel in straight lines and have properties independent of the cathode material (whether it is gold, silver, etc.).

Another significant property of cathode rays is that they are deflected by magnetic and electric fields in a manner that is identical to negatively charged material. Due to these observations, J.J. Thompson (1856-1940) concluded that cathode rays are negatively charged particles that are located in all atoms. It was George Stoney who first gave the term electrons to the cathode rays.

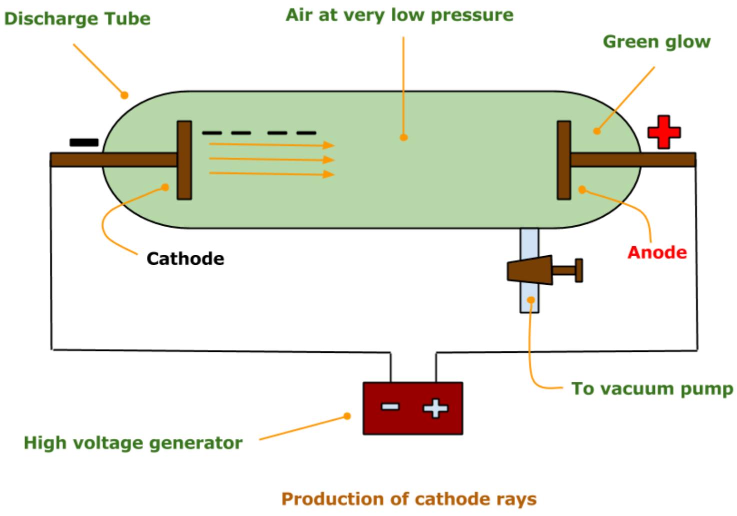


Figure 2.1*: Cathode ray tube*

J. J. Thomson measured the charge-by-mass-ratio $\frac{e}{m}$ of cathode ray particle using deflection in both electric and magnetic field.

$$\frac{e}{m} = -1.76\times108 \text{ coulomb per gram}$$

The cathode ray particle turned out to be 2000 times lighter than hydrogen.

Although $\frac{e}{m}$ ratio for electron was deduced by J.J. Thomson's Cathode Ray Tube experiment, Robert Millikan designed an experiment to measure the absolute value of the charge of electron.

In 1909, American physicist R. Millikan measured the charge of an electron using negatively charged oil droplets. The measured charge (e) of an electron is -1.60×10^{-19}Coulombs.

Using the measured charge of electron, we can calculate the mass of electron from e/m ratio given by J. J. Thomson's cathode ray experiment.

$$\frac{e}{m} = -1.76 \times 10^{8} \text{ Coulomb/gram}$$

$$m = \frac{e}{-1.76 \times 10^{8}}$$

Putting $e = -1.60 \times 10^{-19}$ Coulomb,

$$m = 9.1 \times 10^{-28}\text{gram}$$

Discovery of Protons

In 1909, Rutherford discovered proton in his famous gold foil experiment. In his gold foil experiment, Rutherford bombarded a beam of alpha particles on an ultrathin gold foil and then detected the scattered alpha particles in zinc sulphide (ZnS) screen (Figure 2.2).

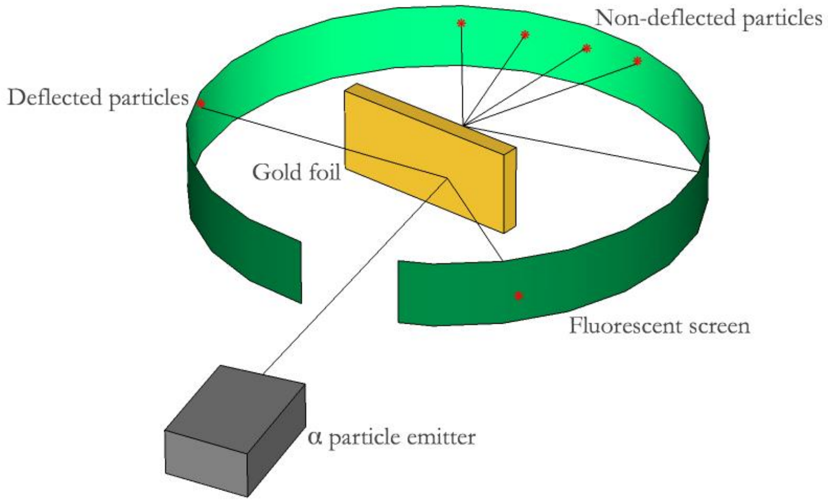


Figure 2.2*: Schematic gold foil experiment*

From his experiment, he observed that:

1. most of the particles pass through the foil without any deflection;
2. some of the alpha particles deflect at small angle;
3. very few even bounce back (1 in 20,000).

He, however, drew conclusion that:

1. most of the atom's mass and its entire positive charge are confined in a small core, called nucleus. The positively charged particle is called proton;
2. most of the volume of an atom is empty space;
3. the number of negatively charged electrons dispersed outside the nucleus is same as number of positively

charge in the nucleus. It explains the overall electrical neutrality of an atom.

Discovery of Neutrons

In 1920, Ernest Rutherford postulated that there were neutral, massive particles in the nucleus of atoms. This conclusion arose from the disparity between an element's atomic number (protons = electrons) and its atomic mass (usually in excess of the mass of the known protons present). James Chadwick was assigned the task of tracking down evidence of Rutherford's tightly bound “proton-electron pair” or neutron.

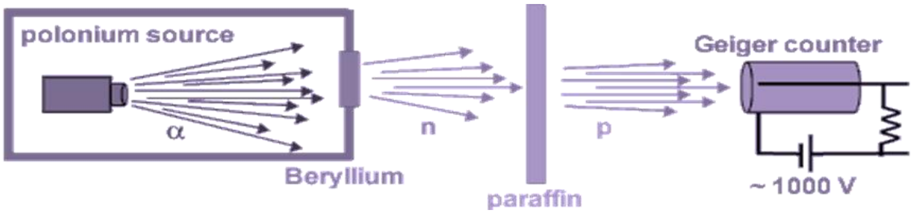


Figure 2.3*: Schematic diagram for the experiment that led to the discovery of neutrons by Chadwick*

In 1930 it was discovered that Beryllium, when bombarded by alpha particles, emitted a very energetic stream of radiation. This stream was originally thought to be gamma radiation. However, further investigations into the properties of the radiation revealed contradictory results. Like gamma rays, these rays were extremely penetrating and since they were not deflected upon passing through a magnetic field, neutral. However, unlike gamma rays, these rays did not discharge charged electroscopes (the photoelectric effect).

Irene Curie and her husband discovered that when a beam of this radiation hit a substance rich in protons, for example paraffin, protons were knocked loose which could be easily detected by a Geiger counter.

$$ {}^{9}_{4}Be + {}^{4}_{2}\alpha \rightarrow {}^{12}_{6}C + {}^{1}_{0}n $$

In 1932, Chadwick proposed that this particle was Rutherford's neutron. Using kinematics, Chadwick was able to determine the velocity of the protons. Then through conservation of momentum techniques, he was able to determine that the mass of the neutral radiation was almost exactly the same as that of a proton. This is Chadwick’s equation:

$$ n \rightarrow p + {}^{0}_{-1}e + \bar{v}_e $$

With Chadwick's announcement, Heisenberg then proposed the proton-neutron model for the nucleus. Rutherford was incorrect in his “proton-electron” pair – there were no “free electrons” in the nucleus. However, once free of the nucleus, evidence was mounting that these neutrons were unstable. By 1932, the products of beta decay had been thoroughly examined.

Table 2.1: Properties of electron, proton and neutron

Particle	**Symbol**	**Charge**	**Mass**
Electron	e^-	-1.60×10^{-19} C	9.1×10^{-31} kg
Proton	p^+ (H^+)	1.60×10^{-19} C	1.672×10^{-27} kg
Neutron	n^o	0.00 C	1.674×10^{-27} kg

Structure of the Atom

At the centre of the atom is the nucleus. The nucleus is made up of the protons and neutrons. The electrons spin in orbits around the outside of the nucleus. This is illustrated in Figure 2.4.

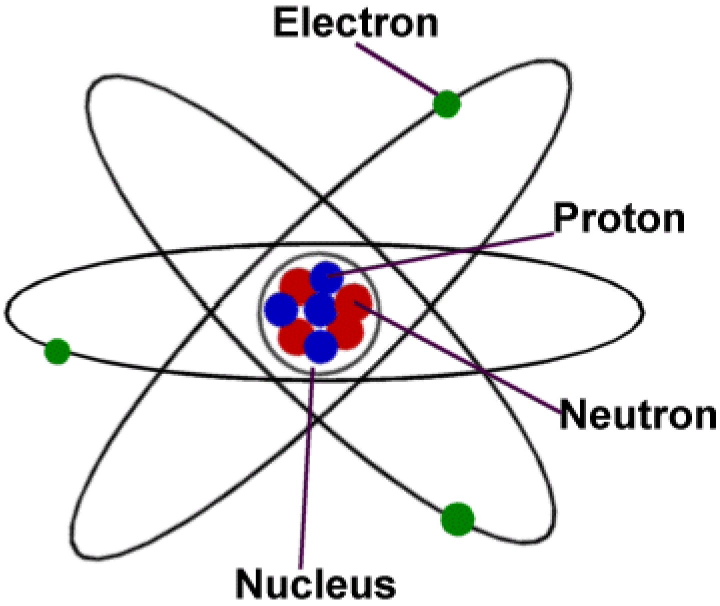


***Figure 2.4**: Schematic representation of an atom*

The Proton

The proton is a positively charged particle that is located at the centre of the atom in the nucleus. The hydrogen atom is unique in that it only has a single proton and no neutron in its nucleus.

The Electron

The electron is a negatively charged particle that spins around the outside of the nucleus. Electrons spin so fast around the nucleus, scientists can never be 100% sure where they are located, but scientists can make estimates of where electrons should be. If there are the same number of electrons and protons in an atom, then the atom is said to have a neutral charge. Electrons are attracted to the nucleus by the positive charge of the protons. Electrons are much smaller than neutrons and protons. They are about 1800 times smaller.

The Neutron

The neutron does not have any charge. The number of neutrons affects the mass and the radioactivity of the atom.

Isotopes

Isotopes are atoms of the same element that have a different number of neutrons in their nuclei. There are naturally occurring isotopes and isotopes that are artificially produced. Isotopes are separated through mass spectrometry (MS); MS traces show the relative abundance of isotopes vs. mass number (mass:charge ratio).

Isotopes are denoted the same way as nuclides, but they are often symbolized only with the mass numbers, because isotopes of the same element have the same atomic number. The term nuclide is used to describe particular isotopes, notably in cases where the nuclear rather than the chemical properties of an atom are to be emphasized. The lexicon of isotopes includes three other frequently used terms: isotones for isotopes of different elements with the same number of neutrons, isobars for isotopes of different elements with the same mass number, and isomers for isotopes identical in all respects except for the total energy content of the nuclei.

The number of neutrons in the nucleus of an atom can be calculated using the Atomic Number (Z) and the Mass Number (A): A - Z = number of neutrons (X stands for the symbol).

$${}^{A}_{Z}\mathrm{X}$$

Examples

Isotopes of Hydrogen

Most hydrogen atoms consist of just one proton and one electron, but some also have one or two neutrons (See Table 2.2).

Table 2.2: Composition of isotopes of hydrogen

Isotope	Protons	Electrons	Neutrons
${}^{1}_{1}\mathrm{H}$	1	1	1 - 1 = 0
${}^{2}_{1}\mathrm{H}$	1	1	2 - 1 = 1
${}^{3}_{1}\mathrm{H}$	1	1	3 - 1 = 2

Isotopes of Chlorine

Chlorine atoms contain 17 protons and 17 electrons. About 75 per cent of chlorine atoms have 18 neutrons, while about 25 per cent have 20 neutrons (See Table 2.3).

Table 2.3: Composition of isotopes of chlorine

Isotope	Protons	Electrons	Neutrons
${}^{35}_{17}\mathrm{Cl}$	17	17	35 - 17 = 18
${}^{37}_{17}\mathrm{Cl}$	17	17	37 - 17 = 20

Isotopes of Carbon

Carbon atoms exist naturally with 6, 7 or 8 neutrons. Carbon-12 and carbon-13 are stable. Carbon-14 is unstable, decaying with a half-life of about 5,700 years. It is produced in earth's atmosphere by cosmic ray bombardment of nitrogen-14 (See Table 2.4).

Table 2.4: Composition of isotopes of carbon

Isotope	Protons	Electrons	Neutrons
${}^{12}_{6}C$	6	6	12 - 6 = 6
${}^{13}_{6}C$	6	6	13 - 6 = 7
${}^{14}_{6}C$	6	6	14 - 6 = 8

Isotopes of Uranium

Uranium has three naturally occurring isotopes. These are uranium-234, uranium-235, and uranium-238. Since each atom of uranium has 92 protons, the isotopes must have 142, 143 and 146 neutrons respectively (See Table 2.5).

Table 2.5: Composition of isotopes of uranium

Isotope	Protons	Electrons	Neutrons
${}^{234}_{92}U$	92	92	234 - 92 =142
${}^{235}_{92}U$	92	92	235 - 92 =143
${}^{238}_{92}U$	92	92	238 - 92 =146

Isotopes can be classified as natural (found in nature) or man made (artificial or synthetic).

Isotopes can also be classified as stable or unstable. A stable isotope does NOT undergo radioactive (or nuclear) decay whereas an unstable isotope undergoes radioactive (or nuclear) decay. Unstable isotopes are also known as radioisotopes or radionucleides.

Natural and Artificial Isotopes

Most elements have naturally occurring isotopes. Percent natural abundances indicate which isotopes of any given element are predominant (occur in greater abundance) and which only occur in trace amounts. Mercury, for example, has seven naturally occurring isotopes: ^{196}Hg, ^{198}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{204}Hg, having the percent natural abundances of 0.146%, 10.02%, 16.84%, 23.13%, 13.22%, 29.80%, and 6.85%, respectively. It is clear that ^{202}Hg occurs with greatest abundance, and ^{200}Hg is the next most abundant, but the other isotopes only occur in small traces.

There are 20 elements with only artificially produced isotopes. The majority of these are heavier elements; the lightest elements with artificial isotopes are ^{43}Tc and ^{61}Pm. The other elements that only have artificial isotopes are those with atomic numbers of 84-88 and 89-103, otherwise known as the actinoids, but excluding ^{90}Th and ^{92}U.

Some naturally occurring and artificially produced isotopes are radioactive. The nucleus of a radioactive isotope is unstable; radioactive isotopes spontaneously decay, emitting alpha, beta, and gamma rays until they reach a stability, usually in the state of a different element. Bismuth ($^{209}_{83}$Bi) has the highest atomic and mass number of all the stable nuclides. All nuclides with atomic number and mass number greater than 83 and 209, respectively, are radioactive. However, there are some lighter nuclides that are radioactive. For example, hydrogen has two naturally occurring stable isotopes, ^{1}H and ^{2}H (deuterium), and a third naturally occurring radioactive isotope, ^{3}H (tritium).

Radioisotope Dating

The presence of certain radioisotopes in an object can be used to determine its age. Carbon dating is based on the fact that living plants absorb stable ^{12}C, ^{13}C and radioactive ^{14}C from the atmosphere, and animals absorb them from the plants. An organism no longer absorbs carbon after it dies, its age can be determined by measuring the ratio of ^{13}C to ^{14}C in the sample and extrapolating based on its decay rate.

In living organisms, the relative amount of ^{14}C in their body is approximately equal to the concentration of ^{14}C in the atmosphere. When an organism dies, it is no longer ingesting ^{14}C, so the ratio between ^{14}C and ^{12}C will decline as ^{14C} gradually decays back to ^{14}N. This slow process, which is called beta decay, releases energy through the emission of electrons from the nucleus or positrons.

After approximately 5,730 years, half of the starting concentration of ^{14}C will have been converted back to ^{14}N. This is referred to as its half-life, or the time it takes for half of the original concentration of an isotope to decay back to its more stable form. Because the half-life of ^{14}C is long, it is used to date formerly-living objects such as old bones or wood. Comparing the ratio of the ^{14}C concentration found in an object to the amount of ^{14}C in the atmosphere, the amount of the isotope that has not yet decayed can be determined.

Art forgeries are often detected by similar means. ^{137}Cs and ^{90}Sr do not occur naturally and are only present in the atmosphere today because of nuclear weapons. Any object created before July 1945, then, would have neither of these elements, so finding them through mass spectrometry or other means would indicate that it was created later.

Isotopic Masses, Percent Natural Abundance, and Weighted-Average Atomic Mass

Most elements occur as isotopes and different isotopes have different masses, thus, the atomic mass of an element is the average of the isotopic masses, weighted according to their naturally occurring abundances; this is the mass of each element recorded on the periodic table, also known as the relative atomic mass (A_r). Treating isotopic masses in weighted averages gives greater importance to the isotope with greatest percent natural abundance.

The atomic mass of an element based on percent natural abundance and isotopic masses is given as follows:

$$\begin{matrix}\text{atomic mass of}\\ \text{an element}\end{matrix} = \left(\begin{matrix}^{*}\text{fractional}\\ \text{abundance of}\\ \text{isotope 1}\end{matrix} \times \begin{matrix}\text{mass of}\\ \text{isotope 1}\end{matrix}\right) + \left(\begin{matrix}\text{fractional}\\ \text{abundance of}\\ \text{isotope 2}\end{matrix} \times \begin{matrix}\text{mass of}\\ \text{isotope 2}\end{matrix}\right) + \ldots$$

* fractional abundance is the percent abundance divided by 100%

For instance, bromine has two naturally occurring isotopes: bromine-79 has a mass of 78.9183 u and an abundance of 50.69%, and bromine-81 has a mass of 80.92 u and an abundance of 49.31%. The equation above can be used to solve for the relative atomic mass of bromine:

Atomic mass of Br = (0.5069 x 78.9183 u) + (0.4931 x 80.92 u) = 79.91 u

This is the relative atomic number of bromine that is listed on the periodic table (See Chapter Four for details).

Comparing their isotopic masses of any given element to the relative atomic mass of the element reveals that the A_r is very close to the isotope that occurs most frequently. Thus, the isotope whose isotopic mass is closest to the atomic mass of the element is the isotope that occurs in the greatest abundance.

Allotropes

Some chemical elements are known to exist in two or more different forms, because the atoms are bounded together in different manners. Most common example is carbon, which exists in diamond, graphite, fullerenes, etc. allotropy is for elements and not for compounds. For example, water and ice are not allotropes. The changes in states of matter are not allotropy. Allotropes should not be confused with isomers. Isomers are compounds with different structural formulas, but the same molecular formula.

Allotropes of Carbon

1. Diamond – extremely hard, transparent crystal in which atoms are arranged in a tetrahedral lattice.
2. Lonsdaleite – also known as hexagonal diamond. It has a hexagonal lattice in comparison to the diamond, which has tetrahedral crystal structure. It is less hard than diamond. It is a brown coloured substance.
3. Graphite – soft, black and flaky and a moderate electrical conductor. In graphite, the C atoms are bonded in flat hexagonal lattices layered in sheets. Each lattice is called a Graphene.
4. Amorphous Carbon – it has no crystalline structure.
5. Fullerenes – they exist in various shapes such as hollow sphere, ellipsoid, or tubes. Accordingly, they have been named buckyball (for spherical) and buckytubes for tube fullerenes. Tube fullerenes are the carbon nanotubes. The first fullerene was discovered as C_{60} in 1985 and it was called buckminsterfullerene. Carbon nanotubes display extra-

ordinary properties that make them potentially useful in many applications, including nanotechnology, electronics, optics and other fields of material science. They exhibit extraordinary strength and unique electrical properties, and are efficient thermal conductors. They are either single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs).

Allotropes of Phosphorus

1. The crystalline solid phosphorus is P_4, which is called white phosphorus.
2. The red phosphorus is polymeric
3. There are scarlet phosphorus, violet phosphorus, black phosphorus and diphosphorus.
4. Black phosphorus is a semiconductor, which is very much equivalent to graphite

Allotropes of Oxygen

1. Dioxygen, O_2, which is colourless.
2. Ozone, O_3, which is blue.
3. Tetraoxygen, O_4, which is also called oxozone and it is metastable.
4. The solid oxygen is octaoxygen, which exists in 6 phaes under various pressures and temperatures, it is also called red oxygen.

Allotropes of Nitrogen

1. N_2 (dinitrogen) is a stable allotrope
2. N_4 (polynitrogen) is an unstable molecule

Allotropes of Sulphur

1. Amorphous sulphur is called plastic sulphur.
2. Large crystalline structures are called rhombic sulphur (S_8 molecules).
3. Fine needle like structures are called monoclinic sulphur (S_8 molecules)
4. Ring molecules such as S_7 and S_{12}

CHAPTER THREE

Quantum Theory

The quantum theory, named perhaps from the discrete nature of energy levels in microscopic systems, gives good interpretations of the phenomena of the atomic and subatomic world. In this microscopic world, distances are measured in nanometers (10^{-9} or $1e^{-9}$ meter) and fantometers ($1e^{-15}$ meter, also called fermi, in honour of Fermi who built the first nuclear reactor).

The quantum theory has many mathematical approaches, but the philosophy is essentially the same. Quantum mechanics is the foundation of chemistry, because it deals with subatomic particles, as well as atoms, molecules, elements, compounds, and much larger systems.

At the sub-atomic scale, there is no boundary between particles and waves. In fact, both particles and wave properties must be considered simultaneously for a system. The study of quantum mechanics lead us to understand the material and the universe beyond the general perception of matter by our ordinary senses of tasting, seeing, hearing, feeling, and sensing.

Furthermore, when coupled with the theory of relativity developed by Einstein, there is no boundary between material and energy. Energy and mass are equivalent, and they can convert into each other.

The quantum theory does much more than explaining the structure of the simplest atom, that is, hydrogen, but rationalizes the existence of the chemical elements also. The most widely used periodic table of chemical elements today is based on the results of quantum theory.

A hydrogen atom is the simplest atom. It consists of a proton in the nucleus and an electron around it. This type of atom is also the most abundant atom in the solar system, as well as the universe. Closer to home, hydrogen is also very abundant on the surface of the planet of Earth. Most hydrogen atoms are combined with oxygen to form the water molecule. In organic substances, hydrogen atoms are mostly attached to carbon, nitrogen, and oxygen atoms. In terms of number, hydrogen is the most abundant atom in our body.

Electromagnetic Waves

Transmission of energy through a vacuum or using no medium is accomplished by electromagnetic waves, caused by the oscillation of electric and magnetic fields. They move at a constant speed of 3×10^8 m/s. Often, they are called electromagnetic radiation, light, or photons. Electromagnetic radiation is caused by the disturbance of an electromagnetic field.

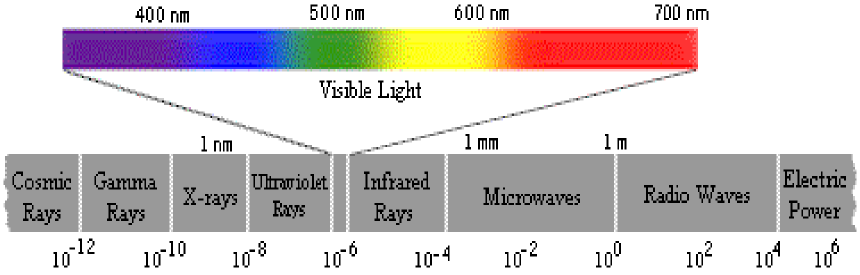


***Figure 3.1**: Electromagnetic spectrum*

Electromagnetic waves are used to transmit long/short/FM wavelength radio waves, and TV/telephone/wireless signals or energies. They are also responsible for transmitting energy in the form of microwaves, infrared radiation (IR), visible light (VIS), ultraviolet light (UV), X-rays, and gamma rays. Each region of this spectrum plays an important part in our lives, and in the business involving communication technology. The list given above are in increasing frequency (or decreasing wavelength) order.

Electromagnetic radiations are usually treated as wave motions. The electronic and magnetic fields oscillate in directions perpendicular to each other and to the direction of motion of the wave.

The wavelength, the frequency, and the speed of light obey the following relationship:

wavelength * frequency = speed of light.

The speed of light is usually represented by c, the wavelength by the lower case Greek letter lambda, l and the frequency by lower case Greek letter nu n. In these symbols, the above formula is:

$$\lambda v = c$$

Note:
Wavelengths of the visible region of the spectrum range from 700 nm for red light to 400 nm for violet light (red, 700 *n*m; orange, 630 *n*m; yellow, 550 *n*m; green, 500 *n*m; blue, 450 *n*m; violet, 400 *n*m).

Photons: Bundles of Electromagnetic Energy

In his research on the radiation from a hot (black) body, Max Planck made a simple proposal. He suggested that light consists of photons. The energy, E, of each individual photon of a monochromatic light wave, is proportional to the frequency, v, of the light:

$$E = hv$$

where, h, Planck constant $= 6.626 \times 10^{-34}$ Js

Note:

1 Hz = 1, hertz: cycle per second, for frequency
1 nm = 1×10^{-9}m, nanometer: for wavelength of IR, visible, UV and X-rays
1 pm = 1×10^{-12}m, picometer: for X-rays and gamma rays

The Photoelectric Effect

The basic idea behind the photoelectric effect is that under certain conditions, when light is shined on a sample, electrons are ejected from that sample. Experimentation showed that frequency of the light has to be above a certain threshold value for electrons to be emitted.

After studying the photoelectric effect under several conditions, three observations were made:

1. A certain minimum frequency is required for electrons to be emitted.
2. Kinetic energy is directly proportional to frequency.
3. The number of electrons emitted from the surface was not dependent on intensity.

Albert Einstein proposed that electromagnetic radiation also had particle-like qualities. Each of these particles of light was called a photon. Einstein suggested that each photon has an energy equal to *hv*, which is called a quantum of energy. This quantum of energy is the energy that that is required of each electron in order to leave the metal surface.

The above-mentioned threshold value for the frequency comes from the work function

$$h\nu=\frac{1}{2}mu^2 + \omega$$

where,

ω is the potential energy that is required to remove the electron from the surface and

$\frac{1}{2}mu^2$ is the kinetic energy of the electron once it has left the surface of the solid.

The threshold frequency, v_0, is the energy that is just sufficient to remove one electron and is denoted by

$$\nu_o= \frac{\omega}{h}$$

$$h\nu=\frac{1}{2}mu^2 + \omega$$

where,

ω is the potential energy that is required to remove the electron from the surface and

$\frac{1}{2}mu^2$ is the kinetic energy of the electron once it has left the surface of the solid.

The threshold frequency, v_o, is the energy that is just sufficient to remove one electron and is denoted by

$$\nu_o= \frac{\omega}{h}$$

A light of smaller frequency cannot eject an electron no matter how long it falls on the metal surface. The reason the photoelectric effect was so significant was because the relationship between radiation and a particle of matter caused scientists to understand that the wave theory of radiation was not going to be enough to explain a lot of phenomena. This led to the development of a new way of thinking: wave-particle duality.

Wave-Particle Duality

One important idea that is the basis of quantum theory is wave-particle duality, first shown through the photoelectric effect. In order to prove that the electron was a wave G.P. Thomson designed an experiment – the double slit experiment. When a steam of electrons was directed at metal foil through one slit, a thin band was formed on the foil as expected. Likewise, when the electrons were directed through two slits, two bands would be expected to form. However, the experiment showed that an interference pattern, like would be expected of a wave, was formed instead. This experiment was one of several that gave rise to.

This is an example of another separate rule for quantum mechanics. In the macroscopic world of classical theory, a wave is a wave and a particle is a particle. One cannot and will not ever be the other. However in the microscopic quantum world, this is not true. Electrons of atoms and photons of light are not necessarily particles or waves.

Another important idea in the field of quantum mechanics is the **Heisenberg uncertainty principle**. In a broad perspective, the uncertainty principle states that the position and momentum of a particle can never be precisely measured simultaneously. If one is known, the other cannot be determined accurately. This principle is a consequence of wave-particle duality and therefore leads physicists to embrace a modern description of atoms.

Light Spectra

The intensity of light as a function of wavelength is a spectrum. To see a spectrum, a beam of electromagnetic radiation is spread according to wavelength or colour so that the intensity as a function of wavelength is represented. A visible spectrum has many colours, and a rainbow is a typical spectrum.

Visible light is only in a small range of the total electromagnetic radiation spectrum and a partial spectrum may be in regions that are not visible. Classified according to region of radiation, we have infrared-, ultraviolet-, X-ray-, and gamma-ray-spectra.

Kinds of Spectra

Light beams (radiations) from (hot) solids may be spread (by a prism) into a continuous display of colour, and such beams give continuous spectra or white spectra.

Emission Spectrum

When an electron falls from one energy level in an atom to a lower energy level, it emits a photon of a particular wavelength and energy. When many electrons emit the same wavelength of photons it will result in a spike in the spectrum at this particular wavelength, resulting in the banding pattern seen in atomic emission spectra. Light beams from a gaseous sample usually show coloured lines called line spectra or discontinued spectra. These continuous and line spectra are called **emission spectra**. The spectra of H, Hg, and Ne are line spectra.

Absorption Spectrum

When a white light beam passes through a medium, light of some colours will be absorbed. As a result, the spectrum shows dark (absent) lines. Such a spectrum is called an **absorption spectrum**. When an electron jumps from a low energy level to a higher level, the electron will absorb a photon of a particular wavelength. This will show up as a drop in the number of photons of this wavelength and as a black band in this part of the spectrum. A white light is shone through a sample. The atoms in the sample absorb some of the light, exciting their electrons. Since the electrons only absorb light of certain frequencies, the absorption spectrum will show up as a series of black bands on an otherwise continuous spectrum.

The dark lines in the absorption spectrum of a gas correspond exactly to some of the bright lines in the emission spectrum of that gas.

Spectra of the H Atom

Since the invention of the spectrometer to analyze light, the light source from hydrogen gas has been intensely studied. Lines were observed in the infrared, visible, and ultraviolet regions. The wavelengths or frequencies of these lines had been known for a long time.

Table 3.1: The frequency, wave number and wavelength of some of the lines in the visible region

Frequency (10^{14} Hz)	**Wavelength (*n*m)**	**Wave number (number/m)**	**Energy (10^{-19} J)**
4.57	656.3	1523	3.028
6.17	486.1	2056	4.088
6.91	434.0	2303	4.578
7.32	410.2	2437	4.845
7.56	397.0	2518	5.006
7.71	388.9	2571	5.110
7.82	383.5	2606	5.181

Electrons can only exist in certain areas around the nucleus called shells. Each shell corresponds to a specific energy level which is designated by a quantum number n. Since electrons cannot exist between energy levels, the quantum number n is always an integer value (n=1,2,3,4…). The electron with the lowest energy level (n=1) is the closest to the nucleus. An electron occupying its lowest energy level is said to be in the ground state.

The energy of an electron in a certain energy level can be found by the equation:

$$\frac{R_H}{n^2} = E$$

where, R_H is the Rydberg constant, *n* an integer, and *K* some constant

According to Bohr's derivation, the energy of the photons of these lines vary according to:

$$E = -R_H\left(\frac{1}{n^2} - \frac{1}{4}\right)$$

and $R_H = 2.179 \times 10^{-18} J$, is the Rydberg constant.

Depending on the units used for R_H, the energy *E* of this formula can be wavenumbers or frequencies.

Furthermore, the formula also applies to lines of the hydrogen spectrum in the infrared and ultraviolet regions, if the 4 is replaced by the square of some other integer, n'. Thus, the formula has a general form of:

$$E = -R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right)$$

Depending on the value of n', we have the following series:

n' = 1, Lyman series (ultraviolet)

n' = 2, Balmer series (visible) Wavelength vary from 400 to 700 nm
n' = 3, Ritz-Paschen series (short wave infrared)
n' = 4, Pfund series (long wave infrared)

Thus, this formula agrees with all observed lines in the hydrogen spectrum. The above formula has been employed to calculate the spectra of the hydrogen atom.

Worked Example

A photon with a wavelength of 397nm is emitted from an electron in energy level 7 of a Hydrogen atom. What is the new energy level of the electron?

Solution

$$E_n = -\frac{R_H}{n^2}$$

$$E_7 = -\frac{2.179 \times 10^{-18}}{7^2}$$

$$E_n = -4.447 \times 10^{-20}\, J$$

Then,

$$E_{photon} = \frac{hc}{\lambda}$$

$$E_{photon} = \frac{(6.62607 \times 10^{-34}) \times (3.0 \times 10^{8})}{3.97 \times 10^{-7}}$$

$$E_{photon} = 5.0036 \times 10^{-19} \text{ J}$$

Then,

$$E_{n\,final} = E_{n\,initial} - E_{photon}$$

$$E_{n\,final} = (-4.447 \times 10^{-20}) - (5.0036 \times 10^{-19})\,J$$

$$E_{n\,final} = (-5.4483 \times 10^{-19})\,J$$

To figure out the energy level *(n)*,

$$E_n = -\frac{R_H}{n^2}$$

$$E_n = -\frac{R_H}{n^2}$$

$$-5.4483 \times 10^{-19} = \frac{-2.179 \times 10^{-18}}{n^2}$$

Therefore, $n = 2$

Quantum Numbers

A total of four quantum numbers were developed to better understand the movement and pathway of electrons in its designated orbital within an atom. Each quantum number indicates an electron's trait within an atom, which satisfies to explain the movement of electrons as a wave function, described by the Schrödinger equation. Each electron in an atom has a unique set of quantum numbers; no two electrons can share the same combination of four quantum numbers. Quantum numbers are very significant, because they can determine the electron configuration of an atom and a probable location of the atom's electrons. They can also aid in graphing orbitals. Quantum numbers can help determine other characteristics of atoms, such as ionization energy and the atomic radius.

The solution of the 3-dimensional wave equation leads to three quantum numbers: n, l and m.

The principle quantum number n most affects the energy of the state of the electron. For hydrogen-like atoms, the energy is related to n by the equation:

$$E = \frac{2\pi^2 m Z^2 e^2}{h^2 n^2}$$

where, $\pi^2 = 3.1416$, m is the mass of the electron, Z is the atomic number or number of protons in the nucleus, e is the charge of the electron, h is the Planck's constant, and n is the principle quantum number.

The Four Quantum Numbers

Quantum numbers designate specific levels, subshells, orbitals, and spins of electrons. This means that they are describing in detail the characteristics of the electrons in the atoms. They describe each unique solution to the Schrödinger equation, or the wave function, of electrons in an atom. There are a total of four quantum numbers: the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s).

Principal Quantum Number

The principal quantum number, n, designates the principal electron shell. Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electrons are from the nucleus, the larger the size of the orbital, and the larger the atom is. n can be any positive integer starting at 1, as *n*=1 designates the first principal shell (the innermost shell). The first principal shell is also called the ground state, or lowest energy state. This explains why n cannot be 0 or any negative integer, because there exists no atoms with zero or a negative amount of energy levels/principal shells. When an electron is in an excited state or it gains energy, it may jump to the second principle shell, where *n*=2. This is called absorption because the electron is "absorbing" photons, or energy. Known as emission, electrons can also "emit" energy as they jump to lower principle shells, where n decreases by whole numbers. As energy of the electron increases, so does the principal quantum number. *n*=3 designates the third principal shell, *n*=4 designates the fourth principal shell, and so on. Thus, *n*=1,2,3,4…

Orbital Angular Momentum Quantum Number

The orbital angular momentum quantum number l determines the shape of an orbital, and therefore the angular distribution. The number of angular nodes is equal to the value of the angular momentum quantum number *l*. Each value of *l* indicates a specific s, p, d, f subshell (each unique in shape.) The value of *l* is dependent on the principal quantum number n. Unlike n, the value of *l* can be zero. It can also be a positive integer, but it cannot be larger than one less than the principal quantum number (n-1):

$$l=0, 1, 2, 3, 4\ldots, (n-1)$$

Example 1

If n=7, what are the possible values of *l*?

Answer

Since *l* can be zero or a positive integer less than (n-1), it can have a value of 0, 1, 2, 3, 4, 5 or 6.

Example 2

If *l*=4, how many angular nodes does the atom have?

Answer

The number of angular nodes is equal to the value of *l*, so the number of nodes is also 4.

Magnetic Quantum Number

The magnetic quantum number m_l determines the number of orbitals and their orientation within a subshell. Consequently, its value depends on the orbital angular momentum quantum number *l*. Given a certain *l*, m_l is an interval ranging from –l to +l, so it can be zero, a negative integer, or a positive integer.

$$m_l = -l, (-l+1), (-l+2), \ldots, -2, -1, 0, 1, 2, \ldots (l-1), (l-2), +l$$

Example

If *n*=3, and *l*=2, then what are the possible values of m_l?

Answer

Since m_l must range from –l to +l, then m_l can be: -2, -1, 0, 1, or 2.

Electron Spin Quantum Number

Unlike *n*, *l*, and m_l, the electron spin quantum number m_s does not depend on another quantum number. It designates the direction of the electron spin and may have a spin of + ½, represented by↑, or –½, represented by↓. This means that when m_s is positive the electron has an upward spin, which can be referred to as "spin up." When it is negative, the electron has a downward spin, so it is "spin down." The significance of the electron spin quantum number is its determination of an atom's ability to generate a magnetic field or not.

Example 1

List the possible combinations of all four quantum numbers when n=2, l=1, and m_l=0.

Answer

The fourth quantum number is independent of the first three, allowing the first three quantum numbers of two electrons to be the same. Since the spin can be +½ or = –½.

There are two combinations: n=2, l=1, m_l =0, m_s= +½ and n=2, l=1, m_l=0 m_s= –½

Example 2

Can an electron with m_s=+½ have a downward spin?

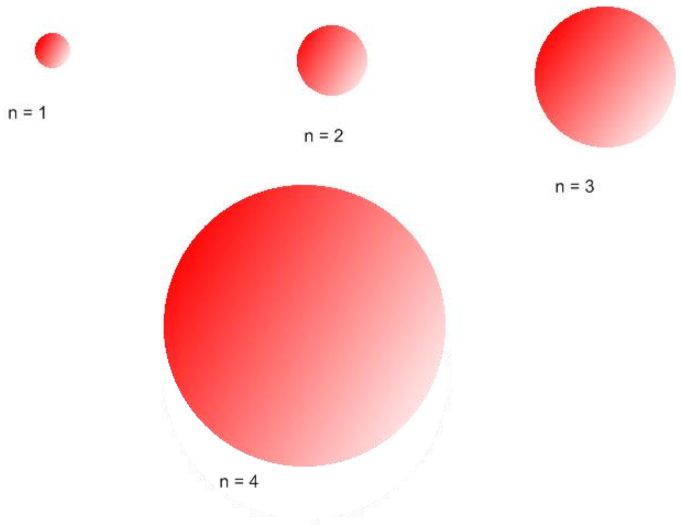
Answer

No, if the value of ms is positive, the electron is "spin up."

Shells, Subshells, and Orbitals

Principal Shells

The value of the principal quantum number n is the level of the principal electronic shell (principal level). All orbitals that have the same n value are in the same principal level. For example, all orbitals on the second principal level have a principal quantum number of n=2. When the value of n is higher, the number of principal electronic shells is greater. This causes a greater distance between the farthest electron and the nucleus. As a result, the size of the atom and its atomic radius increases.



Subshells

The number of values of the orbital angular number, *l* can also be used to identify the number of subshells in a principal electron shell:

When *n* = 1, *l*= 0 (*l* takes on one value and thus there can only be one subshell)

When *n* = 2, l= 0, 1 (*l* takes on two values and thus there are two possible subshells)

When *n* = 3, *l*= 0, 1, 2 (*l* takes on three values and thus there are three possible subshells)

Thus,
Principal shell with n = 1 has one subshell
Principal shell with n = 2 has two subshells
Principal shell with n = 3 has three subshells

Table 3.2: Relationship between subshell and orbital angular number

Name of Subshell	**Value of *l***
s subshell	0
p subshell	1
d subshell	2
f subshell	3

Therefore,
Principal shell with *n* = 1 has one s subshell (*l* = 0)
Principal shell with n = 2 has one s subshell and one p subshell (*l* = 0, 1)
Principal shell with n = 3 has one s subshell, one p subshell, and one d subshell (*l* = 0, 1, 2)

We can designate a principal quantum number, *n*, and a certain subshell by combining the value of *n* and the name of the subshell (which can be found using *l*). For example, 3p refers to the third principal quantum number (*n* =3) and the p subshell (*l*=1).

Example
What is the name of the orbital with quantum numbers n=4 and *l*=1?

Answer
Knowing that the principal quantum number *n* is 4 and using the Table 3.2 above, we can conclude that it is 4p.

Orbitals

The number of orbitals in a subshell is equivalent to the number of values the magnetic quantum number *ml* takes on. A helpful equation to determine the number of orbitals in a subshell is 2*l* +1. This equation will not give you the value of ml, but the number of possible values that ml can take on in a particular orbital.

For example, if *l*=1 and *ml* can have values -1, 0, or +1, the value of 2*l*+1 will be three and there will be three different orbitals.

Table 3.3: Relationship between orbitals and subshells

	s orbitals	p orbitals	d orbitals	f orbitals
L	0	1	2	3
m_l	0	-1, 0, +1	-2, -1, 0, +1, +2	-3, -2, -1, 0, +1, +2, +3
Number of orbitals in designated subshell	1	3	5	7

To visualize and organize the first three quantum numbers, we can think of them as constituents of a house. The roof represents the principal quantum number n, each level represents a subshell *l*, and each room represents the different orbitals ml in each subshell. The s orbital, because the value of ml can only be 0, can only exist in one plane. The p orbital, however, has three possible values of ml and so it has three possible orientations of the orbitals, shown by P_x, P_y, and P_z. The pattern continues, with the d orbital containing 5 possible orbital orientations, and f has 7:

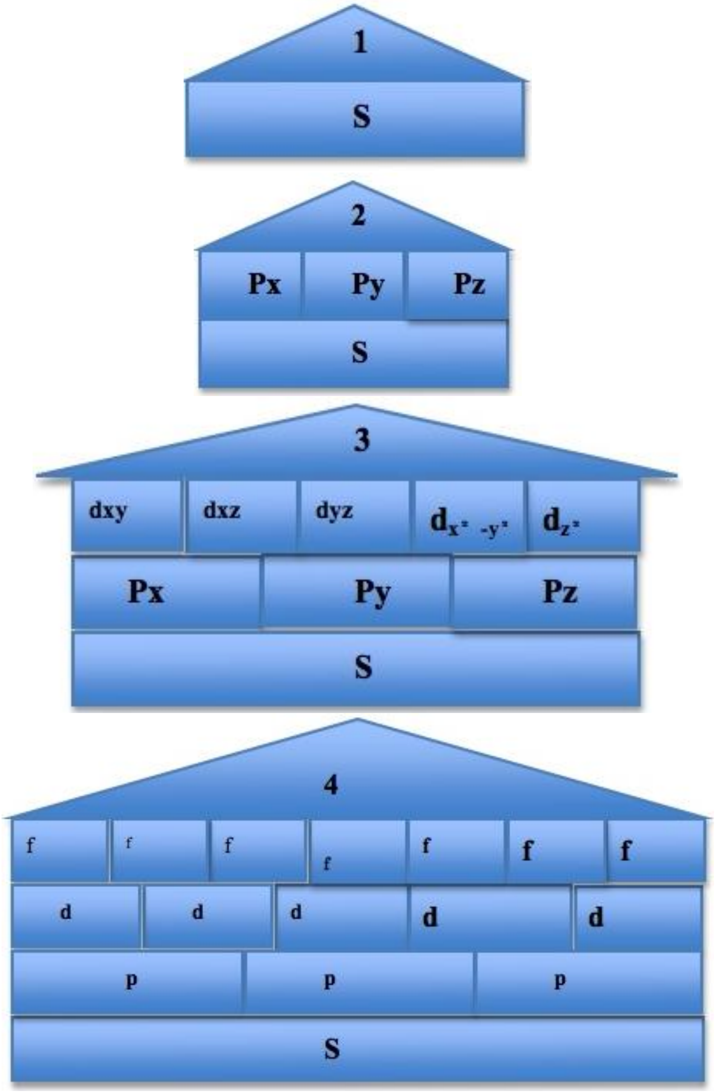
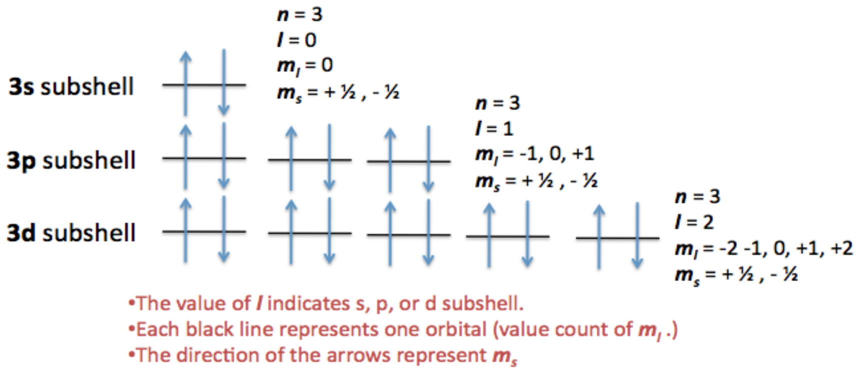


Figure 3.2*: Diagrammatic representation of quantum numbers*

Another helpful visual in looking at the possible orbitals and subshells with a set of quantum numbers would be the electron orbital diagram. The characteristics of each quantum number are depicted in different areas of this diagram.



- The value of *l* indicates s, p, or d subshell.
- Each black line represents one orbital (value count of m_l .)
- The direction of the arrows represent m_s

Figure 3.3*: Electron orbital diagram of subshell/orbital combination when n=3*

The Aufbau Principle

The Aufbau principle (from the German Aufbau meaning "building up, construction": also Aufbau rule or building-up principle) is used to determine the electron configuration of an atom, molecule or ion. The principle postulates a hypothetical process in which an atom is "built up" by progressively adding electrons. As they are added, they assume their most stable conditions (electron orbitals) with respect to the nucleus and those electrons already there.

According to the principle, electrons fill orbitals starting at the lowest available (possible) energy levels before filling higher levels (e.g. 1s before 2s). The number of electrons that can occupy each orbital is limited by the Pauli Exclusion Principle. If multiple orbitals of the same energy are available, Hund's rule states that unoccupied orbitals will be filled before occupied orbitals are reused (by electrons having different spins).

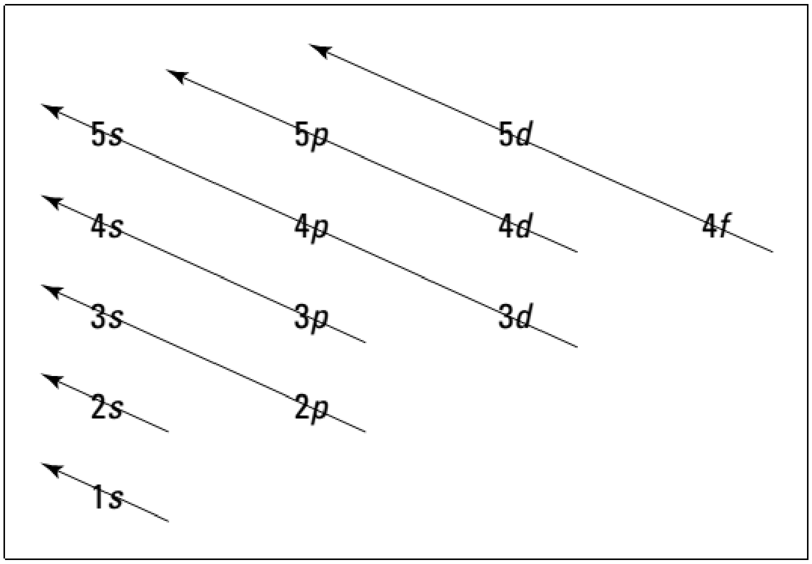


Figure 3.4*: The Aufbau filling chart*

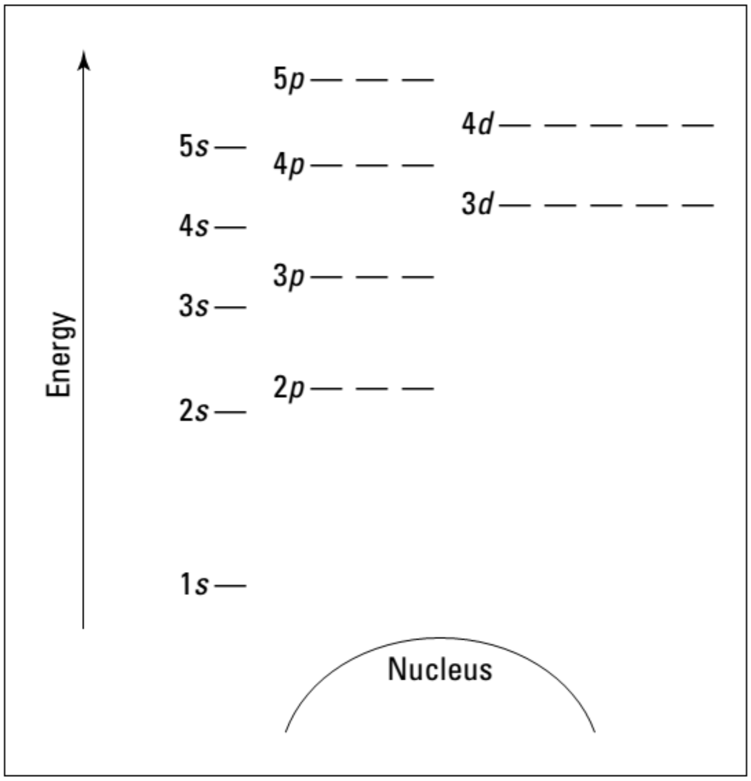


Figure 3.5: *Energy level diagram*

Pauli Exclusion Principle

In 1926, Wolfgang Pauli discovered that a set of quantum numbers is specific to a certain electron. That is, no two electrons can have the same values for n, l, m_l, and m_s. Although the first three quantum numbers identify a specific orbital and may have the same values, the fourth is significant and must have opposite spins.

Hund’s Rule

Orbitals may have identical energy levels when they are of the same principal shell. These orbitals are called degenerate, or “equal energy”. According to Hund's Rule, electrons fill orbitals one at a time. This means that when drawing electron configurations using the model with the arrows, you must fill each shell with one electron each before starting to pair them up. Remember that the charge of an electron is negative and electrons repel each other. Electrons will try to create distance between it and other electrons by staying unpaired. This further explains why the spins of electrons in an orbital are opposite (i.e. +½ and –½).

Heisenberg Uncertainty Principle

According to the Heisenberg Uncertainty Principle, we cannot precisely measure the momentum and position of an electron at the same time. As the momentum of the electron is more and more certain, the position of the electron becomes less certain, and vice versa. This helps explain integral quantum numbers and why n=2.5 cannot exist as a principal quantum number. There must be an integral number of wavelengths (n) in order for an electron to maintain a standing wave. If there were to be partial waves, the whole and partial waves would cancel each other out and the particle would not move. If the particle was at rest, then its position and momentum would be certain. Because this is not so, n must have an integral value. It is not that the principal quantum number can only be measured in integral numbers, it is because the crest of one wave will overlap with the trough of another, and the wave will cancel out.

Bohr Model

Niels Bohr proposed the Bohr Model of the Atom in 1915. Because the Bohr Model is a modification of the earlier Rutherford Model, some people call Bohr's Model the Rutherford-Bohr Model. The modern model of the atom is based on quantum mechanics. The Bohr Model contains some errors, but it is important because it describes most of the accepted features of atomic theory without all of the high-level math of the modern version. Unlike earlier models, the Bohr Model explains the Rydberg formula for the spectral emission lines of atomic hydrogen.

The Bohr Model is a planetary model in which the negatively-charged electrons orbit a small, positively-charged nucleus similar to the planets orbiting the Sun (except that the orbits are not planar). The gravitational force of the solar system is mathematically akin to the Coulomb (electrical) force between the positively-charged nucleus and the negatively-charged electrons.

Main Points of the Bohr Model

1. Electrons orbit the nucleus in orbits that have a set size and energy.
2. The energy of the orbit is related to its size. The lowest energy is found in the smallest orbit.
3. Radiation is absorbed or emitted when an electron moves from one orbit to another.

Bohr Model of Hydrogen

The simplest example of the Bohr Model is for the hydrogen atom (Z=1) or for a hydrogen-like ion (Z>1), in which a negatively-charged electron orbits a small positively-charged nucleus. Electromagnetic energy will be absorbed or emitted if an electron moves from one orbit to another. Only certain electron orbits are permitted. The radius of the possible orbits increases as n^2, where n is the principal quantum number. The 3→2 transition produces the first line of the Balmer series. For hydrogen (Z=1) this produces a photon having wavelength 656 nm (red light).

Limitations of Bohr Model

1. It violates the Heisenberg Uncertainty Principle because it considers electrons to have both a known radius and orbit.
2. The Bohr Model provides an incorrect value for the ground state orbital angular momentum.
3. It makes poor predictions regarding the spectra of larger atoms.
4. It does not predict the relative intensities of spectral lines.
5. The Bohr Model does not explain fine structure and hyperfine structure in spectral lines.
6. It does not explain the Zeeman Effect.

Study Questions

1. What is a quantum of energy?
2. Explain the significance of the photoelectric effect.
3. If an atom has a frequency of $5.357 \times 10^{14}\ s^{-1}$, using Planck's equation, what is the energy of a single photon? (Ans. 3.550×10^{-19} J)
4. Using the answer from number 3, calculate the energy of a mole of photons. Assume you have light at a wavelength of 640*n*m. (Ans. 3.106×10^{-19} J)
5. Using the Balmer equation, find the frequency of the radiation corresponding to n=3. (Ans. **ν=4.5668 s^{-1})**
6. What is the frequency of the spectral line produced when an electron moves from n=5 to n=2 in a Hydrogen atom? (Ans. **ν= 6.905x$10^{14}s^{-1}$)**

7. What value of n does the line at 656.3 nm in the Balmer series correspond to? (Ans. **n=3**)
8. Find the frequency in Hertz of radiation with energy of $2.179\text{x } 10^{-18}$ J per photon. (Ans. **$v = 3.289 \text{ x } 10^{15} \text{ s}^{-1}$)**
9. What frequency of light would be needed to make an electron in a Hydrogen atom jump from n=1 to n=3? (Ans. **$\nu_{photon} = 2.923301 \text{ x } 10^{15} \text{s}^{-1}$)**
10. A spectral line is measured to have a wavelength of 1000nm. Is this within the Balmer series?

CHAPTER FOUR

The Periodic Table

Let us start our journey into the world of the periodic table by echoing the statement by late American astronomer Harlow Shapley that says, ‘The periodic table is probably the most compact and meaningful compilation of knowledge that man has yet devised. The periodic table does for matter what the geological age table does for cosmic time. Its history is the story of man's great conquests in the micro-cosmos.’ The periodic table is one of the indispensable learning aids in chemistry. Its predictive power is so amazing and affords chemists (both old and young) to understand the properties and chemical reactions of elements. Dimtri Mendeleev is often considered the father of the periodic table but it must be stated that the periodic table in its present form was the efforts of many notable scientists.

Starting from the 19th century, chemists began to categorize the elements according to similarities in their physical and chemical properties. Johann Dobereiner (1780-1849) in 1829 classified some elements into groups of three, which he called Triads. These elements had similar chemical properties and orderly physical properties. Examples include Cl, Br, I and Ca, Sr, Ba. Dobereiner called them Triads i.e. grouped in 3’s.

In 1863, John Newlands (1838-1898) suggested that elements be arranged in “octaves” because he noticed (after arranging the elements in order of increasing atomic mass) that certain properties repeated every 8th element. Newlands’ idea was met with so much ridicule by scientists that his publication was rejected by Royal Chemical Society of London but a few years later it was realized that Newlands arrangement of elements into a repeating pattern was a major breakthrough and the Royal Society honoured him with Davy medal.

In the mid-1800s, Dmitri Ivanovich Mendeleev, a Russian chemist, noticed a repeating pattern of chemical properties in the elements that were known at the time. Mendeleev arranged the elements in order of increasing atomic mass to form something that fairly closely resembles the modern periodic table. He was even able to predict the properties of some of the then unknown elements. Later, the elements were rearranged in order of increasing atomic number, i.e. the number of protons in the nucleus of the atom. It is important to note that Lothar Meyer at the same time as Mendeleev independently published his own table of elements organized by increasing atomic mass. Why then is Mendeleev credited as the father of the periodic table? Mendeleev's table became available to the scientific community through publication in 1869 before Meyer's was available in 1870.

Besides this, Mendeleev's periodic table had the following attributes that made it acceptable to the then community of scientists:

1. It has gaps in it such that similar elements would fall in the same vertical column
2. It suggested that in due course elements would be discovered to fill these gaps
3. It predicted properties of the missing elements. Interestingly, during Mendeleev's life time some of the missing elements were discovered and their properties coincided very closely with his prediction.

Modern Periodic Table

In 1913, Henry Moseley published the results of his measurements of the wavelengths of the X-ray spectral lines of a number of elements which showed that the ordering of the wavelengths of the

X-ray emissions of the elements coincided with the ordering of the elements by atomic number. With the discovery of isotopes of the elements, it became apparent that atomic weight was not the significant player in the periodic law as Mendeleev, Meyers and others had proposed, but rather, the properties of the elements varied periodically with atomic number.

Henry Moseley in 1913 through his work with X-rays determined the actual nuclear charge (atomic number) of the elements. He rearranged the elements in order of increasing atomic number and came to this conclusion:

> *"There is in the atom a fundamental quantity which increases by regular steps as we pass from each element to the next. This quantity can only be the charge on the central positive nucleus."*

Unfortunately, the world lost the great scientist during World War I when he was shot and killed by a sniper in Turkey in 1915.

The last major changes to the periodic table resulted from Glenn Seaborg's work in the middle of the 20th Century. Starting with his discovery of plutonium in 1940, he discovered all the transuranic elements from 94 to 102. He reconfigured the periodic table by placing the actinide series below the lanthanide series. In 1951, Seaborg was awarded the Nobel Prize in chemistry for his work. Element 106 has been named seaborgium (Sg) in his honour. He was the only person to have an element named after him while still alive.

Periodic Law

Mendeleev stated that the physical and chemical properties of elements vary periodically with increasing atomic mass. This has been replaced by the modern periodic law which says that when elements are arranged in order of increasing atomic number, there is a periodic pattern (repeating pattern) in their physical and chemical properties. Put in another way, the physical and chemical properties of elements are periodic functions of their atomic numbers.

> *"A tabular arrangement of elements in rows and columns, highlighting the regular repetition of properties of the elements, is called a periodic table."*

Divisions of Periodic Table

The elements in periodic table may be subdivided in multiple ways as discussed below:

Periods and Groups

The basic structure of the periodic table is its division into rows and columns, or periods and groups. A period consists of the elements in any one horizontal row of the periodic table. A group consists of the elements in any one column of the periodic table.

There are three distinct areas of the periodic table – the main group elements, the transition group elements, and the inner transition group elements.

The periods and the groups are identified differently. The periods are labelled from 1 to 7. The groups are referred to extensively by number. The groups have been labelled in three different ways:

1. **Classical:** Main groups are labelled IA through VIIA plus 0. Transition groups are labelled IB through VIII (although not in that order).
2. **Amended:** Main groups and transition groups are labelled IA through VIII and then IB through VIIB plus 0.

3. **Modern:** Groups are labelled with Arabic numerals from 1 through 18. In this book, we will stick to the modern method of labelling groups in the periodic table.

Let us expand further on what is said earlier, the elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called periods, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called groups, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the main group elements, listed as *A*in older tables. Groups 3–12 are in the middle of the periodic table and are the transition elements, listed as *B* in older tables. The two rows of 14 elements at the bottom of the periodic table are the lanthanides and the actinides, whose positions in the periodic table are indicated in group 3.

Metals, Non-metals, and Metalloids

The elements of the periodic table in Figure 4.1 are divided by a heavy “staircase” line into metals on the left and non-metals on the right. A **metal** is a substance or mixture that has a characteristic luster, or shine, and is generally a good conductor of heat and electricity. Except for mercury, the metallic elements are solids at room temperature (about 20^o). They are more or less malleable (can be hammered into sheets) and ductile (can be drawn into wire).

A **non-metal** is an element that does not exhibit the characteristics of a metal. Most of the non-metals are gases (for example, chlorine and oxygen) or solids (for example, phosphorus and sulphur). The solid non-metals are usually hard, brittle substances.

Bromine is the only liquid non-metal. Most of the elements bordering the staircase line in the periodic table (Figure 4.1) are metalloids, or semimetals. A **metalloid,** or **semimetal,** is an element having both metallic and non-metallic properties. These elements, such as silicon (Si) and germanium (Ge), are usually good semiconductors – elements that, when pure, are poor conductors of electricity at room temperature but become moderately good conductors at higher temperatures.

Division in Blocks

As shown in fig, group 1 and 2 elements have their valence electrons in s orbitals, and hence these elements are called s-block elements. Groups 13 to 18 of the periodic table constitute the p-block elements. The s- and p-block elements are collectively referred to as representative elements or main group elements. The elements from Group 3 to group 12 are called transition elements. The properties of these elements are transitional or intermediate between those of s block elements on their left and p-block elements on their right. They have partially filled d orbitals in the valence shell and are, therefore, also called d-block elements.

The elements from Group 3 to group 12 are called transition elements. The properties of these elements are transitional or intermediate between those of s block elements on their left and p-block elements on their right. They have partially filled d orbitals in the valence shell and are, therefore, also called d-block elements.

As shown in Figure 4.1, there are 3 series of transition elements:

(i) 3d or the 1 series, from scandium (Sc) to zinc (Zn), with valence shell electronic configuration $3d^n 4s^2$.

(ii) 4d or the 2 series, from yttrium (Y) to cadmium (Cd), with valence shell electronic configuration $4d^n 5s^2$.

(iii) 5d or the 3 series, from lutetium (Lu) to mercury (Hg), with valence shell electronic configuration $5d^n\ 6s^2$.

The lanthanides and the actinides are together called f-block elements or inner transition elements. The lanthanoids have partially filled 4f orbitals, while the actinoids have partially filled 5f orbitals.

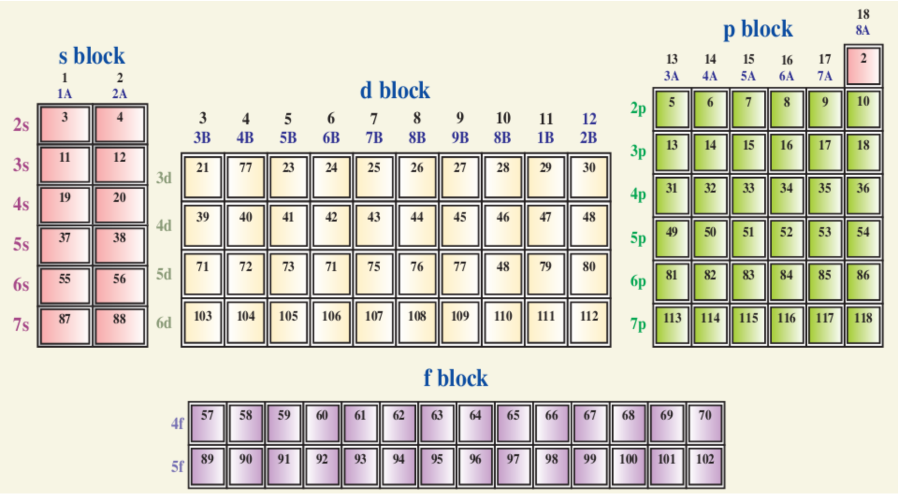


Figure 4.1*: Division of elements in the periodic table into blocks*

Periodicity in the Main-Group Elements

The chemical and physical properties of the main-group elements clearly display periodic character. For instance, the metallic elements lie to the left of the “staircase” line in the periodic table, non-metals lie to the right, and the metalloids (with intermediate characteristics) lie along this line. So, as you move left to right in any row of the periodic table, the metallic character of the elements decreases. As you progress down a column, however, the elements tend to increase in metallic character.

These variations of metallic-nonmetallic character can be attributed in part to variations in the ionization energies of the corresponding atoms. Elements with low ionization energy tend to be metallic, whereas those with high ionization energy tend to be non-metallic. As earlier mentioned, ionization energy is a periodic property, so it is not surprising that the metallic-non-metallic character of an element is similarly periodic.

The basic–acidic behaviour of the oxides of the elements is a good indicator of the metallic-non-metallic character of the elements. Oxides are classified as basic or acidic depending on their reactions with acids and bases. A **basic oxide** is *an oxide that reacts with acids.* Most metal oxides are basic. An **acidic oxide** is *an oxide that reacts with bases.* Most non-metal oxides are acidic oxides. An **amphoteric oxide** is *an oxide that has both basic and acidic properties.*

In the following brief descriptions of the main-group elements, we will note the metallic-non-metallic behaviour of the elements, as well as the basic-acidic character of the oxides. Although elements in a given group are expected to be similar, the degree of similarity does vary among the groups. The alkali metals (Group 1) show marked similarities, as do the halogens (Group 17). On the other hand, the Group IVA elements range from a non-metal (carbon) at the top of the column to a metal (lead) at the bottom. In either case, however, the changes from one element in a column to the next lower one are systematic, and the periodic table helps us to correlate these systematic changes.

Hydrogen ($1s^1$)

Although the electron configuration of hydrogen would seem to place the element in Group 1, its properties are quite different, and it seems best to consider this element as belonging in a group by itself. The element is a colourless gas composed of H_2 molecules.

Group 1(IA) Elements, the Alkali Metals (ns^1)

The *alkali metals* are soft and reactive, with the reactivities increasing as you move down the column of elements. All of the metals react with water to produce hydrogen.

$$2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2LiOH_{(aq)} + H_{2(g)}$$

The vigour of the reaction increases from lithium (moderate) to rubidium (violent). All of the alkali metals form basic oxides with the general formula R_2O.The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behaviour.

Reactions and Compounds of the Alkali Metals

All alkali metals are electropositive elements with an *ns*1 valence electron configuration, forming the monocation (M^+) by losing the single valence electron. Because removing a second electron would require breaking into the (n−1) closed shell, which is energetically prohibitive, the chemistry of the alkali metals is largely that of ionic compounds that contain M^+ ions. The lighter group 1 elements also form a series of organometallic compounds that contain polar covalent M–C bonds.

All the alkali metals react vigorously with the halogens (group 17) to form the corresponding ionic halides, where X is a halogen:

$$2M_{(s)} + X_{2(s,\,l,\,g)} \rightarrow 2M^+X^-_{(s)}$$

Similarly, the alkali metals react with the heavier chalcogens (sulphur, selenium, and tellurium in group 16) to produce metal chalcogenides, where Y is S, Se, or Te:

$$2M_{(s)} + Y_{(s)} \rightarrow M_2Y_{(s)}$$

When excess chalcogen is used, however, a variety of products can be obtained that contain chains of chalcogen atoms, such as the sodium polysulphides ($Na_2S\textit{n}$, where n = 2–6). For example, Na_2S_3 contains the S_3^{2-} ion, which is V shaped with an S–S–S angle of about 103°. The one-electron oxidation product of the trisulphide ion (S_3^{-}) is responsible for the intense blue colour of the gemstones lapis lazuli and blue ultramarine.

Uses of the Alkali Metals

Because sodium remains liquid over a wide temperature range (97.8–883 °C), it is used as a coolant in specialized high-temperature applications, such as nuclear reactors and the exhaust valves in high-performance sports car engines. Caesium, because of its low ionization energy, is used in photosensors in automatic doors, toilets, burglar alarms, and other electronic devices. In these devices, caesium is ionized by a beam of visible light, thereby producing a small electric current; blocking the light interrupts the electric current and triggers a response.

Compounds of sodium and potassium are produced on a huge scale in industry. Each year, the top 50 industrial compounds include NaOH, used in a wide variety of industrial processes; Na_2CO_3, used in the manufacture of glass; K_2O, used in porcelain glazes; and Na_4SiO_4, used in detergents.

Several other alkali metal compounds are also important. For example, Li_2CO_3 is one of the most effective treatments available for manic depression or bipolar disorder. It appears to modulate or dampen the effect on the brain of changes in the level of neurotransmitters, which are biochemical substances responsible for transmitting nerve impulses between neurons. Consequently, patients who take “lithium” do not exhibit the extreme mood swings that characterize this disorder.

Group 2(IIA) Elements, the Alkaline Earth Metals (ns^2)

The *alkaline earth metals* are also chemically reactive but much less so than the alkali metals. Reactivities increase going down the group. The alkaline earth metals form basic oxides with the general formula RO.

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rather rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Reactions and Compounds of the Alkaline Earth Metals

With their low first and second ionization energies, the group 2 elements almost exclusively form ionic compounds that contain M^{2+} ions. As expected, however, the lightest element (Be), with its higher ionization energy and small size, forms compounds that are largely covalent. Some compounds of Mg^{2+} also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2. All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides (MX_2). Except for the beryllium halides, these compounds are all primarily ionic in nature, containing the M^{2+}cation and two X^- anions. The beryllium halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid state. As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which the central beryllium is surrounded by an octet of electrons:

$$BeCl_{2(s)} + 2(CH_3CH_2)_2O_{(l)} \rightarrow BeCl_2[O(CH_2CH_3)_2]_{2(aq)}$$

Uses of the Alkaline Earth Metals

Elemental magnesium is the only alkaline earth metal that is produced on a large scale (about 5 × 10^5 ton per year). Its low density (1.74 g/cm^3 compared with 7.87 g/cm^3 for iron and 2.70 g/cm^3 for aluminium) makes it an important component of the lightweight metal alloys used in aircraft frames and aircraft and automobile engine parts. Most commercial aluminium actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reducing agent for the production of a number of metals, including titanium, zirconium, uranium, and even beryllium, as shown in the following equation:

$$TiCl_{4(l)} + 2Mg_{(s)} \rightarrow Ti_{(s)} + 2MgCl_{2(s)}$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. Ingestion of beryllium or exposure to beryllium-containing dust causes a syndrome called berylliosis, characterized by severe inflammation of the respiratory tract or other tissues. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys, which are used in nonmagnetic, non-sparking tools (such as wrenches and screwdrivers), camera springs, and electrical contacts. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity. Both elemental Be and BeO, which is a high-temperature ceramic, are used in nuclear reactors, and the windows on all x-ray tubes and sources are made of beryllium foil.

Millions of tons of calcium compounds are used every year. $CaCl_2$ is used as “road salt” to lower the freezing point of water on roads in cold temperatures. In addition, $CaCO_3$ is a major component of cement and an ingredient in many commercial antacids. “Quicklime” (CaO), produced by heating $CaCO_3$, is used in the steel industry to remove oxide impurities, make many kinds of glass, and neutralizes acidic soil. Other applications of group 2 compounds include the medical use of $BaSO_4$ in “barium milkshakes” for identifying digestive problems by x-rays and the use of various alkaline earth compounds to produce the brilliant colours seen in fireworks.

Group 13 (IIIA) Elements (ns^2np^1)

Groups 1(IA) and 2 (IIA) exhibit only slight increases in metallic character down a column, but with Group 3(IIIA) we see a significant increase. The first Group 3 (IIIA) element, boron, is a metalloid. Other elements in this group – aluminium, gallium, indium, and thallium – are metals. (Gallium is a curious metal; it melts readily in the palm of the hand. The oxides in this group have the general formula R_2O_3. Boron oxide, B_2O_3, is an acidic oxide; aluminium oxide, Al_2O_3, and gallium oxide, Ga_2O_3, are amphoteric oxides. The change in the oxides from acidic to amphoteric to basic is indicative of an increase in metallic character of the elements.

Reactions and Compounds of Group 13 Elements

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity.

All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalized, metallic bonding. With its high ionization energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalized valence electrons. Instead, boron forms unique and intricate structures that contain *multicenter bonds*, in which a pair of electrons holds together three or more atoms. Elemental boron forms multicenter bonds, whereas the other group 13 elements exhibit metallic bonding.

The basic building block of elemental boron is not the individual boron atom, as would be the case in a metal, but rather the B_{12}icosahedron. Because these icosahedra do not pack together very well, the structure of solid boron contains voids, resulting in its low density Elemental boron can be induced to react with many non-metallic elements to give binary compounds that have a variety of applications. For example, plates of boron carbide (B_4C) can stop a 30-caliber, armour-piercing bullet, yet they weigh 10%-30% less than conventional armour. Other important compounds of boron with non-metals include boron nitride (BN), which is produced by heating boron with excess nitrogen (Equation 1); boron oxide (B_2O_3), which is formed when boron is heated with excess oxygen (Equation 2); and the boron trihalides (BX_3), which are formed by heating boron with excess halogen (Equation 3).

$$2B + N_2 \rightarrow 2BN \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$4B + 3O_2 \rightarrow 2B_2O_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$2B + 3Cl_2 \rightarrow 2BCl_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

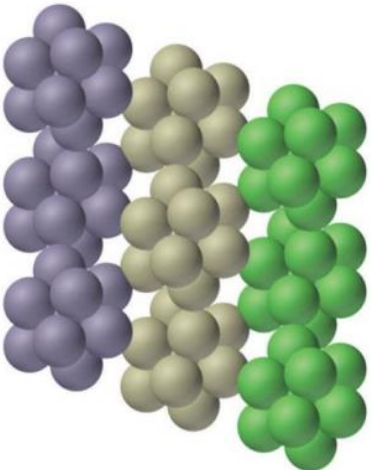


***Figure 4.2**: A side view of icosahedrons of solid boron*

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_{6(s)}$$

The reaction of Tl with iodine is an exception: although the product has the stoichiometry TlI_3, it is *not* thallium(III) iodide, but rather a thallium(I) compound, the Tl^+ salt of the triiodide ion (I^{3-}). This compound forms because iodine is not a powerful enough oxidant to oxidize thallium to the +3 oxidation state of the halides, only the fluorides exhibit behaviour typical of an ionic compound: they have high melting points (>950 °C) and low solubility in nonpolar solvents. In contrast, the trichorides, tribromides, and triiodides of aluminium, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers. Bridging halides are poor electron-pair donors, so the group 13 trihalides are potent Lewis acids that react readily with Lewis bases, such as amines, to form a Lewis acid–base adduct:

$$Al_2Cl_{6(aq)} + 2(CH_3)_3N_{(aq)} \rightarrow 2(CH_3)_3N{:}AlCl_{3(aq)}$$

In water, the halides of the group 13 metals hydrolyze to produce the metal hydroxide [$M(OH)_3$]:

$$MX_3 + 3H_2O \rightarrow M(OH)_3 + 3HX$$

In a related reaction, $Al_2(SO_4)_3$ is used to clarify drinking water by the precipitation of hydrated $Al(OH)_3$, which traps particulates. The halides of the heavier metals (In and Tl) are less reactive with water because of their lower charge-to-radius ratio. Instead of forming hydroxides, they dissolve to form the hydrated metal complex ions: $[M(H_2O)_6]^{3+}$. Group 13 trihalides are potent Lewis acids that react with Lewis bases to form a Lewis acid-base adduct.

Like boron, all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide (M_2O_3), although Tl_2O_3 is unstable:

$$4M + 3O_2 \rightarrow 2M_2O_3$$

Group 14 (IVA) Elements (ns^2np^2)

This group shows the most distinct change in metallic character. It begins with the non-metal carbon, C, followed by the metalloids silicon, Si, and germanium, Ge, and then the metals tin, Sn, and lead, Pb. Both tin and lead were known to the ancients.

All the elements in this group form oxides with the general formula RO_2, which progress from acidic to amphoteric. Carbon dioxide, CO_2, an acidic oxide, is a gas. (Carbon also forms the monoxide, CO.) Silicon dioxide, SiO_2, an acidic oxide, exists as quartz and white sand (particles of quartz). Germanium dioxide,

GeO_2, is acidic, though less so than silicon dioxide. Tin dioxide, SnO_2, an amphoteric oxide, is found as the mineral cassiterite, the principal ore of tin. Lead dioxide, PbO_2, is amphoteric. Lead has a more stable monoxide, PbO.

Reactions and Compounds of Group 14 Elements

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon – diamond, graphite, fullerenes, and nanotubes – are distinct, but they all contain simple electron-pair bonds. Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(\text{–C≡C–C≡C–})_n$. Carbon nanotubes (“buckytubes”) are being studied as potential building blocks for ultra-micro scale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Although all the carbon tetrahalides (CX_4) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)}$$

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2 °C, and the non-metallic α form is stable below 13.2 °C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behaviour than silicon. For example, it dissolves in hot oxidizing acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above −150 °C, and $GeCl_2$ is relatively stable at temperatures below 20 °C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

Group 15 (VA) Elements (ns^2np^3)

The Group 5 (VA) elements also show the distinct transition from non-metal (nitrogen, N, and phosphorus, P) to metalloid (arsenic, As, and antimony, Sb) to metal (bismuth, Bi). Nitrogen occurs as a colourless, odourless, relatively unreactive gas with N_2 molecules; white phosphorus is a white, waxy solid with P_4 molecules. Gray arsenic is a brittle solid with metallic lustre; antimony is a brittle solid with a silvery, metallic lustre. Bismuth is a hard, lustrous metal with a pinkish tinge.

The Group 5 (VA) elements form oxides with empirical formulas R_2O_3 and R_2O_5. In some cases, the molecular formulas are twice these formulas – that is, R_4O_6 and R_4O_{10}. Nitrogen has the acidic oxides N_2O_3 and N_2O_5, although it also has other, better known oxides, such as NO. Phosphorus has the acidic oxides P_4O_6 and P_4O_{10}.

Arsenic has the acidic oxides As_2O_3 and As_2O_5; antimony has the amphoteric oxides Sb_2O_3 and Sb_2O_5; and bismuth has the basic oxide Bi_2O_3.

Group 16 (VIA) Elements, the Chalcogens (ns^2np^4)

These elements, the *chalcogens* (pronounced kal_-ke-jens), show the transition from non-metal (oxygen, O, sulphur, S, and selenium, Se) to metalloid (tellurium, Te) to metal (polonium, Po). Oxygen occurs as a colourless, odourless gas with O_2 molecules.

It also has an allotrope, ozone, with molecular formula O_3. Sulphur is a brittle, yellow solid with molecular formula S_8. Tellurium is a shiny gray, brittle solid; polonium is a silvery metal. Sulphur, selenium, and tellurium form oxides with the formulas RO_2 and RO_3. (Sulphur burns in air to form sulphur dioxide. These oxides, except for TeO_2, are acidic; TeO_2 is amphoteric. Polonium has an oxide PoO_2, which is amphoteric, though more basic in character than TeO_2.

Reactions and Compounds of Oxygen

As in groups 14 and 15, the lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. As with nitrogen, electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from forming stable catenated compounds. In fact, except for O_2, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form. Ozone (O_3), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide (H_2O_2) is so thermodynamically unstable that it has a tendency to undergo explosive decomposition when impure.

Because most of the heavier chalcogens (group 16) and group 15 are non-metals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulphur) form catenated compounds and form multiple allotropes. The tendency to catenate decreases as we go down the group.

Sulphur and selenium both form a fairly extensive series of catenated species. For example, elemental sulphur forms S_8 rings packed together in a complex “crankshaft” arrangement, and molten sulphur contains long chains of sulphur atoms connected by S–S bonds. Moreover, both sulphur and selenium form polysulfides (Sn^{2-}) and polyselenides (Sen^{2-}), with $n \leq 6$. The only stable allotrope of tellurium is a silvery white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulphur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

As in group 15, the reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulphur does. As expected for non-metals, sulphur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidizing acids such as HNO_3 to form oxoacids such as H_2SO_4. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain the Po^{2+} ion

Group 17 (VIIA) Elements, the Halogens (ns^2np^5)

The name *halogen* is derived from the Greek for “salt forming,” which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt). Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth’s ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

The *halogens* are reactive non-metals with the general molecular formula X_2, where X symbolizes a halogen. Fluorine, F_2, is a pale yellow gas; chlorine, Cl_2, a pale greenish yellow gas; bromine, Br_2, a reddish brown liquid; and iodine, I_2, a bluish black solid that has a violet vapour. Little is known about the chemistry of astatine, At, because all isotopes are radioactive with very short half-lives. (The half-life of a radioactive isotope is the time it takes for half of the isotope to decay, or break down, to another element.) It might be expected to be a metalloid.

Each halogen forms several compounds with oxygen; these are generally unstable, acidic oxides.

Reactions and Compounds of the Halogens

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only O_2, N_2, and Kr react slowly. There are three reasons for the high reactivity of fluorine:

1. Because fluorine is so electronegative, it is able to remove or at least share the valence electrons of virtually any other element.
2. Because of its small size, fluorine tends to form very strong bonds with other elements, making its compounds thermodynamically stable.
3. The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell F^- ion. In contrast, with less electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as SF_6. Because of its high electronegativity and $2s^2 2p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as AlF_3, can share a lone pair of electrons with a fluoride ion, forming AlF_6^{3-}.

The halogens (X_2) react with metals (M) according to the general equation

$$M(s,l) + nX_2(s,l,g) \rightarrow MXn(s,l)$$

For elements that exhibit multiple oxidation states fluorine tends to produce the highest possible oxidation state and iodine the lowest. For example, vanadium reacts with the halogens to give VF_5, VCl_4, VBr_4, and VI_3.

Metal halides in the +1 or +2 oxidation state, such as CaF_2, are typically ionic halides, which have high melting points and are often soluble in water. As the oxidation state of the metal increases, so does the covalent character of the halide due to polarization of the M–X bond. With its high electronegativity, fluoride is the least polarisable, and iodide, with the lowest electronegativity, is the most polarizable of the halogens. Halides of small trivalent metal ions such as Al^{3+} tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged Al_2Br_6 molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

Group 18 (VIIIA) Elements, the Noble Gases (ns^2np^6)

The Group 8 (VIIIA) elements exist as gases consisting of uncombined atoms. For many years, it was thought that the only compounds the noble gases could form were *clathrates*. Clathrates are solid compounds in which a gas, the guest, occupies holes in a lattice formed by a less volatile, chemically dissimilar substance, the host. Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved. In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans. It is estimated that the amount of methane in such deposits could have a major impact on the world's energy needs later in this century.

Reactions and Compounds of the Noble Gases

The widely held belief in the intrinsic lack of reactivity of the noble gases was challenged when Neil Bartlett, a British professor of chemistry at the University of British Columbia, showed that PtF_6, a compound used in the Manhattan Project, could oxidize O_2. Because the ionization energy of xenon (1170 kJ/mol) is actually lower than that of O_2, Bartlett recognized that PtF_6should also be able to oxidize xenon. When he mixed colourless xenon gas with deep red PtF_6vapour, yellow-orange crystals immediately formed. Although Bartlett initially postulated that they were $Xe^+PtF_6^-$, it is now generally agreed that the reaction also involves the transfer of a fluorine atom to xenon to give the XeF^+ ion:

$$Xe_{(g)} + PtF_{6(g)} \rightarrow [XeF^+][PtF_5^-]_{(s)}$$

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(s)}$$

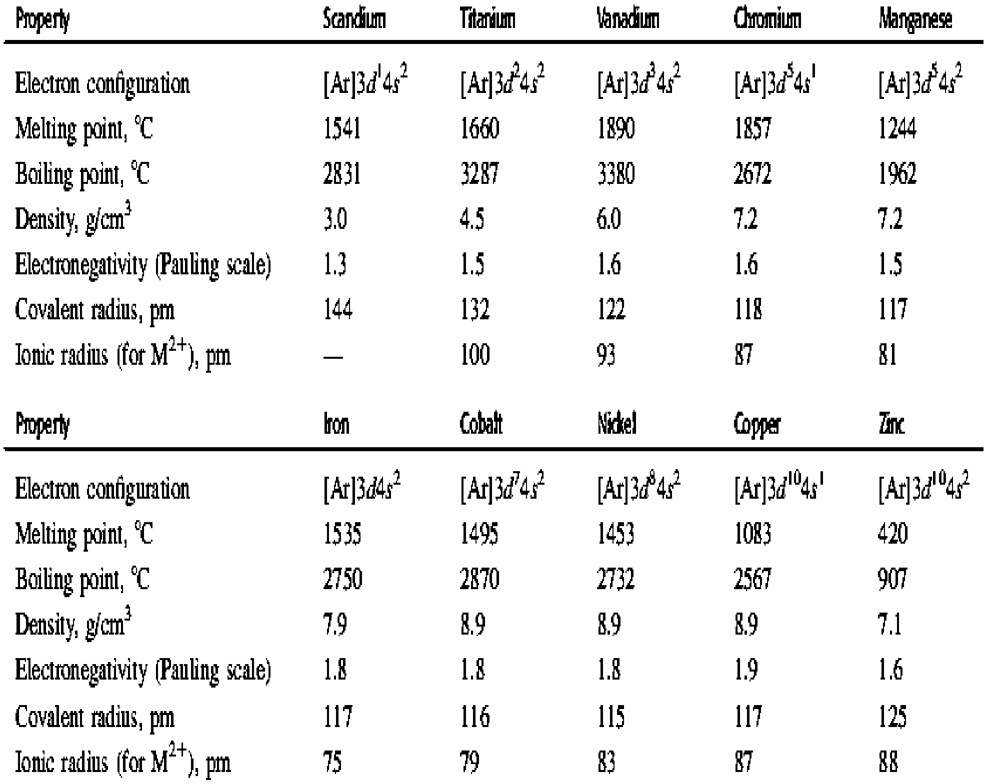
The ionization energies of helium, neon, and argon are so high that no stable compounds of these elements are known. The ionization energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidized themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $XeCl_2$ and KrF_2 can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

Transition Metals

IUPAC defines the transition metals as any element with an incomplete *d* subshell or that may form stable ions only with an incomplete *d* subshell. By this definition, zinc, cadmium, and mercury are excluded from the transition metals, as they have a d^{10} configuration. Only a few transient species of these elements that leave ions with a partly filled *d* subshell have been formed, and mercury (I) only occurs as Hg_2^{2+}, which does not strictly form a lone ion with a partly filled subshell, and hence these three elements are inconsistent with the latter definition. They do form ions with a +2 oxidation state, but these retain the $4d^{10}$ configuration. Element 112 may also be excluded although its oxidation properties are unlikely to be observed due to its radioactive nature. This definition includes groups 3 to 11 on the periodic table.

The transition metals are the forty chemical elements 21 to 30, 39 to 48, 71 to 80, and 103 to 112. The name *transition* comes from their position in the periodic table of elements. In each of the four periods in which they occur, these elements represent the successive addition of electrons to the *d* atomic orbital of the atoms.

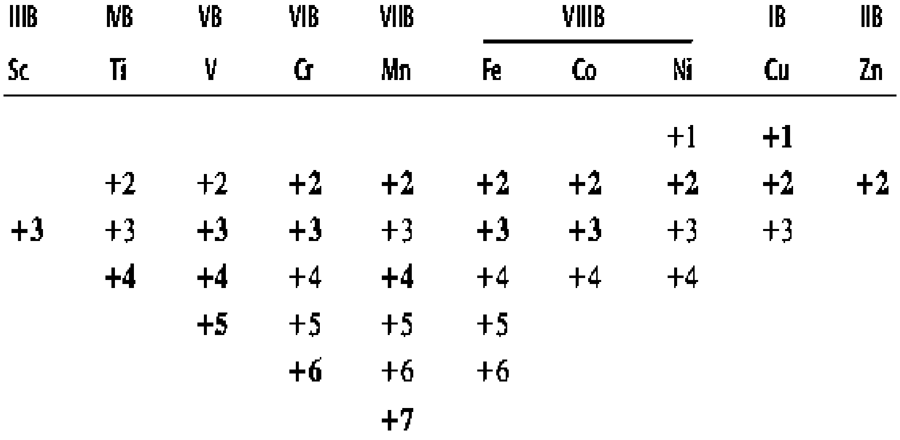
In this way, the **transition metals** represent the *transition* between group 2elements and group 13 elements.



Property	Scandium	Titanium	Vanadium	Chromium	Manganese
Electron configuration	$[Ar]3d^1 4s^2$	$[Ar]3d^2 4s^2$	$[Ar]3d^3 4s^2$	$[Ar]3d^5 4s^1$	$[Ar]3d^5 4s^2$
Melting point, °C	1541	1660	1890	1857	1244
Boiling point, °C	2831	3287	3380	2672	1962
Density, g/cm^3	3.0	4.5	6.0	7.2	7.2
Electronegativity (Pauling scale)	1.3	1.5	1.6	1.6	1.5
Covalent radius, pm	144	132	122	118	117
Ionic radius (for M^{2+}), pm	—	100	93	87	81

Property	Iron	Cobalt	Nickel	Copper	Zinc
Electron configuration	$[Ar]3d4s^2$	$[Ar]3d^7 4s^2$	$[Ar]3d^8 4s^2$	$[Ar]3d^{10} 4s^1$	$[Ar]3d^{10} 4s^2$
Melting point, °C	1535	1495	1453	1083	420
Boiling point, °C	2750	2870	2732	2567	907
Density, g/cm^3	7.9	8.9	8.9	8.9	7.1
Electronegativity (Pauling scale)	1.8	1.8	1.8	1.9	1.6
Covalent radius, pm	117	116	115	117	125
Ionic radius (for M^{2+}), pm	75	79	83	87	88

***Figure 4.3**: Properties of the fourth-period transition metals*



IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	**+1**	
	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**	**+2**
+3	+3	**+3**	**+3**	+3	**+3**	**+3**	+3	+3	
	+4	**+4**	+4	**+4**	+4	+4	+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

***Figure 4.3**: Oxidation state of the fourth-period transition metals*

Properties of Transition Metals

Transition elements tend to have high tensile strength, density and melting and boiling points. As with many properties of transition metals, this is due to *d* orbital electrons' ability to delocalise within the metal lattice. In metallic substances, the more electrons shared between nuclei, the stronger the metal.

There are several common characteristic properties of transition elements:

- They often form coloured compounds.
- They can have a variety of different oxidation states.
- They are often good catalysts.
- They are silvery-blue at room temperature (except copper and gold).
- They are solids at room temperature (except mercury).
- They form complexes.

Variable Oxidation States

As opposed to group 1 and group 2 metals, ions of the transition elements may have multiple, stable oxidation states, since they can lose *d* electrons without a high energetic penalty. Manganese, for example has two 4*s* electrons and five 3*d* electrons, which can be removed. Loss of all of these electrons leads to a 7+ oxidation state. Certain patterns in oxidation state emerge across the period of transition elements:

- The number of oxidation states of each ion increases up to Mn, after which they decrease. Later transition metals have a stronger attraction between protons and electrons (since there are more of each present), which then would require more energy to remove the electrons.
- When the elements are in lower oxidation states, they can be found as simple ions. However elements in higher oxidation states are usually bonded covalently to electronegative compounds such as O or F, often as a polyatomic ion such as chromate, vanadate and permangante ions.

Other properties with respect to the stability of oxidation states:

- Ions in higher oxidation states tend to make good oxidising agents, whereas elements in low oxidation states become reducing agents.
- The 2+ ions across the period start as strong reducing agents, and become more stable.
- The 3+ ions start stable and become more oxidizing across the period.

Catalytic Activity

Transition metals form good homogeneous or heterogeneous catalysts, for example iron is the catalyst for the Haber process. Nickel or platinum is used in the hydrogenation of alkenes.

Coloured compounds

We observe colour as varying frequencies of electromagnetic radiation in the visible region of the electromagnetic spectrum. Different colours result from the changed composition of light after it has been reflected, transmitted or absorbed after hitting a substance. Because of their structure, transition metals form many different coloured ions and complexes. Colour even varies between the different ions of a single element

- MnO_4
- (Mn in oxidation state +7) is a purple compound, whereas Mn^{2+} is pale-pink.

Coordination by ligands can play a part in determining colour in a transition compound, due to changes in energy of the *d* orbitals. Ligands remove degeneracy of the orbitals and split them in to higher and lower energy groups. The energy gap between the lower and higher energy orbitals will determine the colour of light that is absorbed, as electromagnetic radiation is only absorbed if it has energy corresponding to that gap. When a ligated ion absorbs light, some of the electrons are promoted to a higher energy orbital. Since, different frequency light is absorbed, different colours are observed.

The colour of a complex depends on:

- the nature of the metal ion, specifically the number of electrons in the *d* orbitals
- the arrangement of the ligands around the metal ion (for example geometric isomers can display different colours)

- the nature of the ligands surrounding the metal ion. The stronger the ligands then the greater the energy difference between the split high and low 3*d* groups.

The complex formed by the d block element zinc (though not strictly a transition element) is colourless, because the 3d orbitals are full – no electrons are able to move up to the higher group

Coordination

Transition metals differ from main group metals in several key properties as earlier mentioned. One of the more interesting aspects of transition metals is their ability to form **coordination compounds**. Coordination compounds are formed between a metal ion and a molecule with one or more unshared electron pairs, called a **ligand**. Ligands may be classified according to the number of donor atoms they contain. A **monodentate** ligand donates a single electron pair to the metal or metal ion. Common examples of monodentate ligands include NH_3, H_2O, NO_2^-, and CN^-. A **bidentate** ligand, as the name suggests, donates twoe lectron pairs to the metal or metal ion. A good example is ethylenediamine, $H_2CH_2CH_2NH_2$.

Anions as well as neutral molecules may act as ligands. If one or more neutral molecules coordinate to metal ion, the resulting species retains the charge of the transition metal ion and is called a **complex ion**. For example, most transition metal ions form complex ions with water molecules when in aqueous solution. Examples include $[Co(H_2O)]_6]_3^+$ and$[Ni(H_2O)_6]_2^+$. If one or more anions coordinate to a metal ion, a complex ion with an overall negative charge may result. Examples include $[Co(NO_2)6]_3^-$ and $[Fe(CN)_6]_4^-$.

In writing formulas for complex ions and coordination compounds, the molecules inside the brackets represent ligands physically coordinated to the metal ion. Anything outside of the brackets is present for charge balance. Therefore the compounds $[Co(H_2O)_6]Cl_3$ and $[Ni(H_2O)_6]Cl_3$ contain positively charged complex ions in which the chloride ions are present for charge balance. The compounds $K_3[Co(NO_2)_6]$ and $K_4[Fe(CN)_6]$ containnegatively charged complex ions with potassium ions present for charge balance.

Naming Coordination Compounds

The coordination compounds are named in the following way:

1. When naming coordination compounds, **always name the cation before the anion.** This rule holds regardless of (ethylenediamine)). **Important exceptions**: water iscalled 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl', and the N_2 and O_2 molecules are called 'dinitrogen' and 'dioxygen'. whether the complex ion is the cation or the anion.

2. In naming the complex ion:
   - Name the ligands first, in alphabetical order, and then name the metal atom or ion. Note: The metal atom or ion is written before the ligands in the chemical formula.
   - *Anionic ligands end in "-o."* For anions that end in "-ide" (e.g. chloride, hydroxide), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nirite), change the endings as follows:

     -ide → -o; e.g., chloride → chloro and hydroxide → hydroxo

     -ate → -ato; e.g., sulfate→ sulfato and nitrate → nitrato

     -ite→ - ito; e.g., nitrite → nitrito
   - For neutral ligands, the common name of the molecule is used (e.g. $H_2NCH_2CH_2NH_2$)

3. The Greek prefixes di-, tri-, tetra-, etc. are used to designate the number of each type of ligand in the complex ion. If the ligand already contains a Greek prefix (e.g. ethylene diamine) or if it is a polydentate ligand (i.e. it can attach at more than one coordination site), the prefixes bis-, tris-, tetrakis-, and pentakis- are used instead

4. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate.

   For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions (e.g. Fe is called ferrate and not ironate).

Table 4.1: Metal and its name in anionic complex

Name of Metal	**Name in Anionic Complex**
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

5. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

To name a neutral complex molecule, follow the rules of naming a complex cation. **Remember:** Name the (possibly complex) cation **BEFORE** the (possibly complex) anion.

For historic reasons, some coordination compounds are called by their common names. For example, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are named ferricyanide and ferrocyanide respectively, and $Fe(CO)_5$ is called iron carbonyl.

Examples

Give the systematic names for the following coordination compounds:

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$
Answer: triamminetriaquachromium(III) chloride

Solution

- The complex ion is found inside the parentheses. In this case, the complexion is a cation.
- The ammine ligands are named first because alphabetically, "ammine" comes before "aqua."
- The compound is electrically neutral and thus has an overall charge of zero.
- Since there are three chlorides associated with one complex ion and each chloride has a –1 charge, the charge on the complex ion must be +3.
- From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $[Pt(NH_3)_5Cl]Br_3$

*Answer***:** pentaamminechloroplatinum(IV) bromide

Solution

- The complex ion is a cation, and the counter anions are the 3 bromides.
- The charge of the complex ion must be +3 since it is associated with 3 bromides.
- The NH_3 molecules are neutral while the chloride carries a -1 charge.
- Therefore, the oxidation number of platinum must be +4.
- Therefore, the oxidation number of platinum must be +4.

Table 4.2: Anionic ligands and names

Anionic Ligands	**Names**
Br^-	Bromo
F^-	Fluoro
O^{2-}	Oxo
OH^-	Hydroxo
CN^-	Cyano
$C_2O_4^{2-}$	Oxalate
CO_3^{2-}	Carbonato
CH_3COO^-	Acetate

Valence or Oxidation States of Elements

The valence of an element represents its combining power for other elements. For example, normally one atom of hydrogen combines with no more than one atom of any other element. Therefore, hydrogen has a valence of 1. An oxygen atom combines with two atoms of hydrogen to yield water molecule, H_2O. The valence of oxygen is 2. Two (2) nitrogen atom combines with three hydrogen atoms to give ammonia molecule, NH_3, while a carbon atom combines with four hydrogen atoms to give methane molecule, CH_4. Thus nitrogen and carbon are said to have valences of 3 and 4 respectively.

The valence of an element is related to its position in the periodic table. All elements within a group have same valence. For example, all the alkali metals, the elements of Group 1, have a valence of 1. Likewise, the Group 2 elements or the alkaline earth metals have a valence of 2. Valences of elements in period 2 and 3 are shown in Table 4.3. Neon and Argon have not been given since these have complete octet and therefore no tenderness to attract electrons.

Knowing the valences, it is possible to predict the compositions of the compounds formed by the concerned element. For example, all the second and third period elements form binary compounds of hydrogen, called hydrides. The empirical formulas of the hydrides of these elements are presented in Table 4.3.

Table 4.3: Empirical formulas of hydrides

Group	**1**	**2**	**13**	**14**	**15**	**16**	**17**	**18**
Period 2	Li	Be	B	C	N	O	F	Ne
Period 3	Na	Mg	Al	Si	P	S	Cl	Ar
Valency	1	2	3	4	3	2	1	0

Table 4.4: Valencies of elements in periods 2 and 5

Period 2	LiH	BeH_2	BH_3	CH_4	NH_3	H_2O	HF
Period 3	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl

In Table 4.4, the values of neon and argon have not been given since these have completed octet and therefore no tendency to attract electrons.

Like hydrogen, chlorine too has a valence of 1. Oxygen, with a valence of 2, combines with two atoms of an element with a valence of 1, such as hydrogen, to form H_2O, and with one atom of an element with a valence of 2, such as beryllium, to form BeO. In a compound of the type, A_pB_q , the values of p and q are such that – p× valence of A = q × valence of B

On this basis, the compositions of the oxides of Group 1, 2 and 13 will have thecompositions, M_2O, MO and M_2O_3, respectively.

Some of the s- and p-block elements have one or more valences in addition to those given in Table 4.4. For example, phosphorus shows valence of 5 in addition to 3. It forms chlorides having compositions PCl_5 and PCl_3.

Nitrogen forms oxides in valences ranging from 1 to 5. In group 13, thallium shows two valence states, 1 and 3. The latter corresponds to the group valence. The former arises because in the valence shell electronic configuration of thallium, $6s^2$ $6p^1$, and the two electrons in the 6s shell remains inert and do not participate in bonding. Only the 6p electron enters into compound formation, implying that the combining capacity of thallium is 1. The inability of the 6s electrons to enter into chemical reactions is called inert pair effect. Due to inert pair effect, the predominant valence state for lead is 2, although the valence shell electronic configuration, $6s^2$ $6p^2$ suggests that valence state 4 should also be possible. However, the compounds of lead in valence state 4 are largely unstable.

All the transition elements show more than one valence. For example, iron forms most of its compounds in valence state 2 and 3, and a few in valence state 6 as well. Manganese is known to have valences ranging from 2 to 7. The transition elements have the configuration ns (n-1) d^p (p = 1-10) in their valence shell. The energies of ns and (n-1)d shells are comparable, and electrons may be lost from both the shells with almost equal ease. The loss of two electrons from ns shell gives rise to valence 2. Subsequently, electrons may ionize successively from the (n-1) d shell, giving rise to more valence states. The existence of more than one valence for a particular element is referred to as variable valence concept.

Trends in the Periodic Table

Ionization Energy

The ionization energy of the elements is another important property with periodic characteristics. Remove one or more electrons from an atom and you get an ion. **The energy required to remove electrons from an atom in the gaseous state is called the ionization energy.** First ionization energy is the energy required to remove one electron from an atom, specifically the highest energy electron, the one bound least tightly to the nucleus. Second ionization energy is the energy needed to remove the most energetic electron remaining in the atom after the first one is gone – and so on.

First ionization energies generally increase as one moves from left to right along a row in the periodic table. They tend to decrease from the top to the bottom of a group. This is the same pattern exhibited by atomic radii. It gets harder to remove an electron as you move from left to right because the increasing nuclear charge tends to hold them more tightly. Within vertical groups, though, the increased nuclear charge is offset by electron repulsion and higher principal energy levels; it gets easier to remove an electron as one goes down the group.

Ionization energies are important indicators of how atoms behave in chemical reactions. Atoms with low first ionization energies, such as sodium, give up an electron easily. This means they form ions readily. Carbon, on the other hand, has a first ionization energy that is twice as large as that of sodium; it does not give up electrons as willingly. This difference in first ionization energies has a dramatic impact on the chemical properties of the two elements.

Sodium reacts with chlorine to form sodium chloride, table salt, a white crystalline material that dissolves in water.

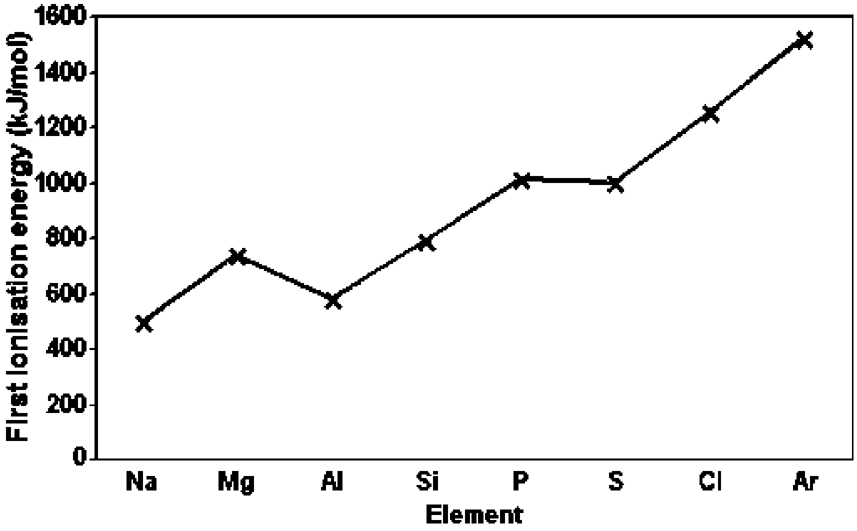


Figure 4.4*: First ionization energies of period 3 elements*

Carbon combines with chlorine to form carbon tetrachloride, a colourless liquid once used in fire extinguishers. It does not dissolve in water, and it is toxic – do not sprinkle this chloride on your food. In other words, carbon tetrachloride is about as different from table salt as day is from night. One reason is the big difference in the ionization energies of sodium and carbon. This difference determines the type of the bond between the two elements, which strongly affects the properties of the resulting compound.

The group whose elements have the lowest ionization energies is the alkali metals, which easily lose an electron. The group with the highest ionization energies is the noble gases, which have filled energy shells and strongly resist losing or gaining electrons.

After the noble gases, the elements that cling most tightly to their electrons are their next-door neighbours in Group 17 of the periodic table. The elements in this group are called the **halogens**. The two elements most eager to react and exchange an electron are francium at the bottom left of the periodic table and fluorine at the top of the halogen group. Francium is highly radioactive and quite rare.

Less than a kilogram of francium exists at any given instant in all of the Earth's crust. The element with the next lowest first ionization energy is cesium. Cesium wants to give up an electron and fluorine wants one badly. Consequently, when cesium and fluorine are brought together, the result is what chemists like to call a "vigorous reaction." Others might call it an explosion.

Electronegativity

The last periodic characteristic of the elements considered here is **electronegativity**. Electronegativity is almost the exact reverse of ionization energy. Ionization energy is a measure of how hard it is to remove an electron from an atom. Electronegativity measures the tendency of an atom to attract electrons. The two numbers are arrived at differently, however. Ionization energy is a property of an atom in the gaseous state. Electronegativity is a property of an atom when it is joined to another atom in a chemical bond.

The periodic nature of the electronegativity of the elements is shown in Figure 4.5. Electronegativity generally decreases going down a group and generally increases going from left to right in a row.

Francium is the least electronegative element; fluorine is the most. Like valency, the concept of electronegativity has been around a long time. However, it was not an especially useful idea until 1932 when the two-time Nobel Prize – winning chemist Linus Pauling developed a method to quantify the electronegativity of the elements.

Pauling's approach was to assign a value of 3.98 to fluorine, the most electronegative element. Most tables of electronegativity round this number off to 4.0. Pauling then calculated the electronegativity of the other elements based on this value for fluorine. The electronegativity scale ranges from a low of 0.7 to a high of 4.0.

The difference in the electronegativity of two elements chemically joined in a compound determines the nature of the bond between them. When two elements with similar electronegativity combine, they tend to share an electron. In a carbon-carbon bond, for example, the two atoms would share valence electrons equally.

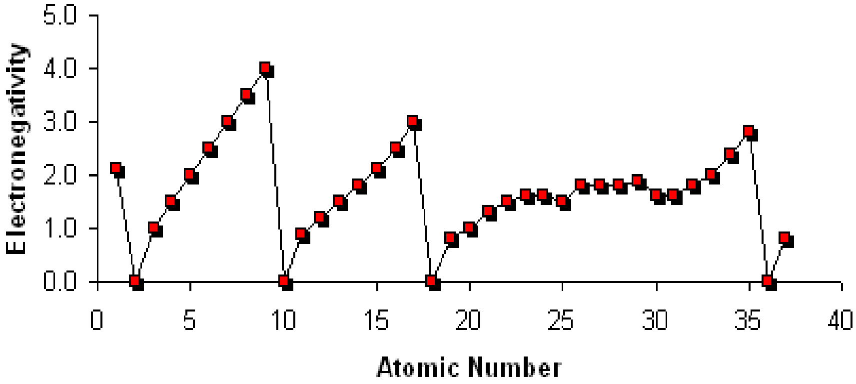


Figure 4.5: *Periodic nature of electronegativity of elements*

Bonds of this sort are called **covalent** bonds. Two elements with similar electronegativities, such as carbon and chlorine, would form covalent-like bonds. But elements with greatly different electronegativities would tend to have an electron closer to one atom than the other. In the caesium fluoride example, fluorine wants to grab an electron to fill its outermost orbital, and caesium is barely holding on to one in its outermost orbital. When the two combine, the electron migrates from caesium to fluorine. The resulting bond is called an **ionic bond**. As was the case in comparing table salt with carbon tetrachloride, the nature of the bond between two atoms – ionic or covalent – plays a big role in determining the properties of the resulting compound.

Electron Affinity

When a neutral atom in the gaseous state picks up an electron to form a stable negative ion, energy is released. For example, a chlorine atom can pick up an electron to give a chloride ion, Cl^-, and 349 kJ/mol of energy is released. You write the process as follows, with electron configurations noted in parentheses:

$$\mathrm{Cl([Ne]3}s^2\mathrm{3}p^5\mathrm{)+ e^- \rightarrow Cl^-([Ne]3}s^2\mathrm{3}p\mathrm{6)}$$

The **electron affinity** is

the energy change for the process of adding an electron to a neutral atom in the gaseous state to form a negative ion.

If the negative ion is stable (does not spontaneously disintegrate into the neutral atom and free electron), the energy change for its formation is a negative number. Thus, the electron affinity of Cl is -349 kJ/mol. Large negative numbers such as this indicate that a very stable negative ion is formed. Small negative numbers indicate that a less stable ion is formed.

Electron affinities, *E.A.*, have a periodic variation, just as atomic radii and ionization energies do, though somewhat more complicated. To see this variation, consider each of the main groups of elements beginning with Group 1(IA). All of the Group 1(IA) elements have small negative electron affinities. When you add an electron to a lithium atom, for example, it goes into the 2*s* orbital to form a moderately stable negative ion, releasing energy.

$$\mathrm{Li}(1s^22s^1) + e\text{-} \rightarrow \mathrm{Li}^-(1s^22s^2);\ E.A. = -60\ \mathrm{kJ/mol}$$

None of the Group 2 (IIA) elements form stable negative ions; that is, the electron affinities of these elements are positive. Each of the atoms has a filled *ns* subshell, so that if you were to add an electron, it would have to go into the next higher energy subshell (*np*). Instead of releasing energy, the atom would absorb energy.

For example:

$$\mathrm{Be}(1s^22s^2) + e^- \rightarrow \mathrm{Be}^-(1s22s^22p1);\ E.A. >0$$

(For a similar reason, the Group VIIIA elements also do not form stable negative ions.) From Group 13(IIIA) to Group 17 (VIIA), the added electron goes into the *np* subshell of the valence shell. With the exception of the Group VA elements, the electron affinities tend toward more negative values as you progress to the right through these elements in any period (more energy is released and stabler negative ions are formed). The electron affinity of a Group VA element is generally less negative than the preceding Group IVA element. Note the trend in electron affinities in the following:

$$\mathrm{B}(1s22s22p1) + e^- \rightarrow \mathrm{B}^-(1s^22s^22p^2);\ E.A. =-27\ \mathrm{kJ/mol}$$
$$\mathrm{C}(1s22s22p2) + e^- \rightarrow \mathrm{C}^-(1s^22s^22p^3);\ E.A. =-122\ \mathrm{kJ/mol}$$
$$\mathrm{N}(1s22s22p3) + e^- \rightarrow \mathrm{N}^-(1s^22s^22p^4);\ E.A.=0\ \mathrm{kJ/mol}$$
$$\mathrm{O}(1s22s22p4) + e^- \rightarrow \mathrm{O}^-(1s^22s^22p^5);\ E.A.=-141\ \mathrm{kJ/mol}$$
$$\mathrm{F}(1s22s22p5) + e^- \rightarrow \mathrm{F}^-(1s^22s^22p^6);\ E.A.=-328\ \mathrm{kJ/mol}$$

Broadly speaking, the general trend is toward more negative electron affinities from left to right in any period. Note especially that the Group 16 (VIA) and Group 17 (VIIA) elements have the largest negative electron affinities of any of the main-group elements.

Atomic Radius

An atom does not have a definite size, because the statistical distribution of electrons does not abruptly end but merely decreases to very small values as the distance from the nucleus increases. Consequently, atomic size must be defined in a somewhat arbitrary manner, so various measures of atomic size exist.

It is a measure of the distance from the centre of the nucleus to the outermost shell of the atom.

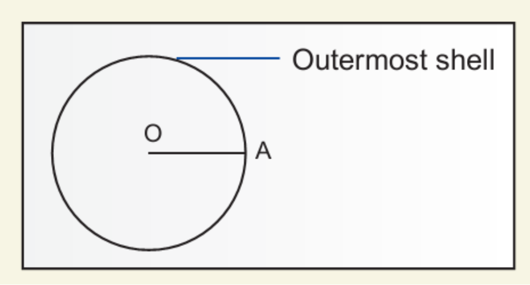
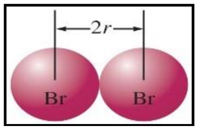


Figure 4.6*: Atomic radius*

In Figure 4.6, O is the centre of the nucleus and OA is the atomic radius. However, since the Heisenberg uncertainty principle states that it is impossible to precisely locate the outermost electron, the distance OA cannot be measured. Yet, the internuclear distance or the bond length between two adjacent atoms in a metallic crystal or in a covalent molecule can be elucidated. If it is assumed that the atoms behave as spheres which are barely in contact with each other, the distance between the centres of the two nuclei gives the sum of atomic radii of the two atoms.

For example, to calculate the atomic radius of bromine, the internuclear distance in a gaseous bromine molecule is measured. Assuming that the two bromine atoms in the molecule touch each other (fig), the atomic radius is half theinternuclear distance. The internuclear or the bond distance in fluorine is 228 pm and therefore, the atomic radius of a bromine atom is 114 pm.



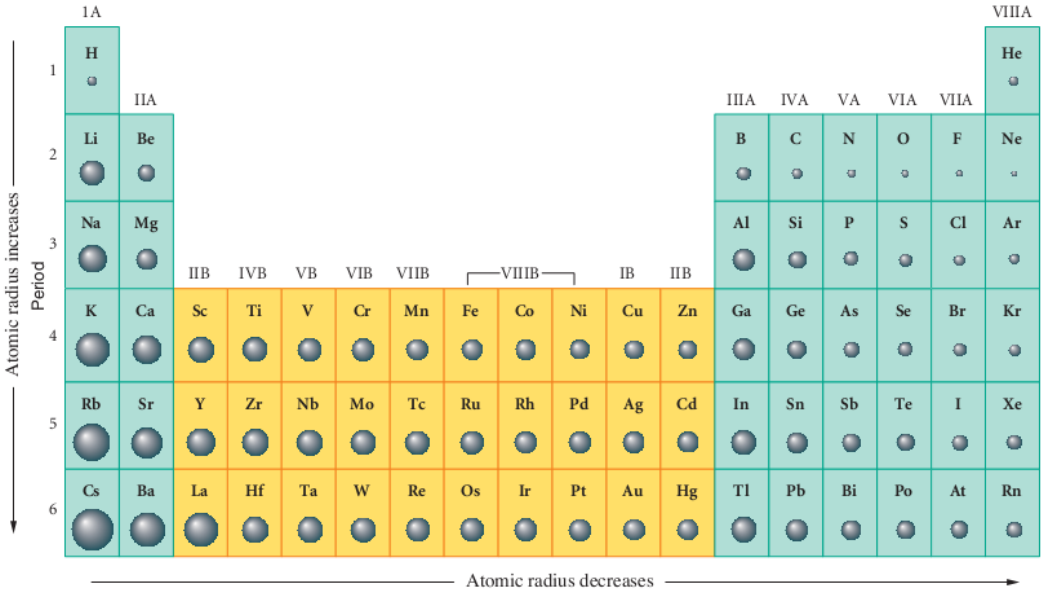


Figure 4.7: *Trends in atomic radii within each period and each group of the periodic table*

Ionic radius, r_{ion}, is the radius ascribed to an atom's ion. Although neither atoms nor ions have sharp boundaries, it is useful to treat them as if they are hard spheres with radii such that the sum of ionic radii of the cation and aniongives the distance between the ions in a crystal lattice. Ionic radii are typically given in units of either picometers (pm) or Angstroms (Ä), with 1Å= 100Åpm. Typical values range from 30Åpm (0.3Å) to over 200Åpm (2Å).

Ions may be larger or smaller than the neutral atom, depending on the ion's charge. When an atom loses an electron to form a cation, the lost electron no longer contributes to shielding the other electrons from the charge of the nucleus; consequently, the other electrons are more strongly attracted to the nucleus, and the radius of the atom gets smaller. Likewise, when an electron is added to an atom, forming an anion, the added electron shields the other electrons from the nucleus, with the result that the size of the atom increases.

The ionic radius is not a fixed property of a given ion, but varies with coordination number, spin state and other parameters.

Nevertheless, ionic radius values are sufficiently transferable to allow periodic trends to be recognized. As with other types of atomic radius, ionic radii increase on descending a group. Ionic size (for the same ion) also increases with increasing coordination number, and an ion in a high-spin state will be larger than the same ion in a low-spin state. In general, ionic radius decreases with increasing positive charge and increases with increasing negative charge.

Diagonal Relationship

Another trend in chemical behaviour of the main group elements is the *diagonal relationship*. This refers to similarity between the first member of one group and the second member of the succeeding group. Specifically, the first three members of the second period, that is, lithium, beryllium and boron, exhibit closeness to those elements that occupy a diagonal position below them in the periodic table. As shown in Figure 4.8, diagonal relationship holds for lithium and magnesium; beryllium and aluminium; and boron and silicon.

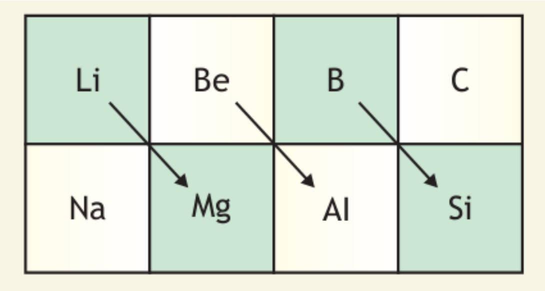


***Figure 4.8**: Diagonal relationships in the periodic table*

Predicting Properties of the Periodic Table

Predicting properties of the periodic table are highlighted below:

- Valence electrons are the outermost electrons and are involved in bonding.
- Similarity of valence electron configurations helps predict chemical properties.
- Group 1, 2 and 18 all have similar properties to other members of their respective group.
- Group 13-17 show considerable variation among properties from metallic to non-metallic.
- Transition metals do not always exhibit regular patterns in their electron configurations but have some similarities as a whole such as coloured compounds and multiple oxidation states.

Representing Free Elements in Chemical Equations

- metals are always represented by their empirical formulas (same as symbol for element)
- non-metals may be written as empirical formula (C) or as polyatomic molecules (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2 and P_4)
- Sulphur usually S instead of S_8
- Noble gases all exist as isolated atoms, so use symbols (Xe, He, Ar, etc.)
- Metalloids or semimetals are represented with empirical formula (B, Si, Ge, etc.).

The metals are on the bottom left in the periodic table, and the non-metals are at the top right. The semimetals lie along a diagonal line separating the metals and non-metals.

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties (such as radium (Ra) for its radioactivity), for the native country of the scientist(s) who discovered them (polonium (Po) for Poland), for eminent scientists (curium (Cm) for the Curies), for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to remind us of their origin. Examples are Fe for iron, from the Latin ferrum; Na for sodium, from the Latin natrium; and W for tungsten, from the German wolfram.

Did you know?

The elements of Group 17 may be remembered with the aid of the following mnemonics:

Frank **Cl**everly **Br**ought **I**ndian **At**tire
The elements of the 2nd Period may be remembered as follows:
Little **B**en **B**ecame **C**harlie's **N**umber **O**ne **F**ighting **N**emesis

The elements of the 3rd Period may be remembered as follows:
Native **M**agpies **A**lways **S**it **P**eacefully **S**earching **C**lear **A**reas

CHAPTER FIVE

Oxygen

Oxygen is the most abundant element in the earth's crust. It exists in the free state as O_2molecule and makes up 20.9% by the volume and 23% by weight of the atmosphere. Most of the oxygen is produced by the process of photosynthesis. Oxygen makes up 46.6% by weight of the earth's crust, where it is the major constituent of silicate minerals. Oceans cover about 71% of the earth's surface, and oxygen makes up 89% by weight of the water in the oceans.

Properties and Preparation of Oxygen

Oxygen is a colourless, odourless gas under standard conditions. Oxygen exists as the allotrope ozone.

The critical temperature is -118°C. Therefore, you can liquefy oxygen if you first cool the gas below this temperature and then compress it. Both liquid and solid O_2 have a pale blue colour. The melting point of the solid is -218°C, and the boiling point at 1 atmosphere is -183°C.

Oxygen is produced in enormous quantity from air. Air is first liquefied, and then distilled. Nitrogen and argon are more volatile components of air and distil off, leaving liquid oxygen behind.

Oxygen can be prepared in small quantities by decomposing certain oxygen containing compounds. Both the Swedish chemist Karl Wilhelm Scheele and the British chemist Joseph Priestley are credited with the discovery of oxygen. Priestley obtained the gas in 1774 by heating mercury (II) oxide.

$$2HgO \rightarrow 2Hg + O_2$$

In laboratory preparation, potassium trioxochlorate (V), $KClO_3$, is heated with pure manganese(IV) oxide, MnO_2, as a catalyst.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

Reactions of Oxygen

Molecular oxygen is a very reactive gas and combines directly with many substances. The products are usually oxides. An **oxide** is *a binary compound with oxygen in the -2 oxidation state.*

Most metals react readily with oxygen to form oxides, especially if the metal is in a form that exposes sufficient surface area. For example, magnesium wire and iron wool burn brightly in air to yield the oxides.

$$2Mg + O_2 \rightarrow 2MgO$$
$$3Fe + 2O_2 \rightarrow Fe_3O_4$$

The resulting oxides MgO and Fe_3O_4 are basic oxides, as is true of most metal oxides. If the metal is in a high oxidation state, however, the oxide may be acidic. For example, chromium (III) oxide, Cr_2O_3, is a basic oxide, but chromium (VI) oxide, CrO_3, is an acidic oxide.

The alkali metals form an interesting series of binary compounds with oxygen. When an alkali metal burns in air, the principal product with oxygen depends on the metal. With lithium, the product is the basic oxide, Li_2O. With the other alkali metals, the product is predominantly the peroxide and superoxide. A **peroxide** is a compound with oxygen in the -1 oxidation state. (Peroxides contain either the O_2^{2-} ion or the covalently bonded group –O-O-.) A **superoxide** is a binary compound with oxygen in the -1/2oxidation state;superoxides contain the superoxide ion, O_2^{-}. Sodium metal burns in air to give mainly the peroxide.

$$2Na + O_2 \rightarrow Na_2O_2$$

Potassium and the other alkali metals form mainly the superoxides.

$$K + O_2 \rightarrow KO_2$$

Non-metals react with oxygen to form covalent oxides, most of which are acidic. For example, carbon burns in an excess of oxygen to give carbon dioxide, which is the acid anhydride of carbonic acid (that is, carbon dioxide produces carbonic acid when it reacts with water). Sulphur, S, burns in oxygen to give sulphur dioxide, SO_2, the acid anhydride of trioxosulphate (IV) acid.

$$S + O_2 \rightarrow SO_2$$

Sulphur forms another oxide, sulphur trioxide, SO_3, but only small amounts are obtained during the burning of sulphur in air. Sulphur trioxide is the acid anhydride of tetraoxosulphate (VI) acid.

Compounds in which at least one element is in a reduced state are oxidized by oxygen, giving compounds that would be expected to form when the individual elements are burned in oxygen. For example, a hydrocarbon such as octane, C_8H_{18}, burns to give carbon dioxide and water.

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

Some other examples are given in the following equations:

$$\begin{aligned} &2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \\ &CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2 \\ &2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \end{aligned}$$

Note the products that are formed; sulphur compounds usually form SO_2.

CHAPTER SIX

Hydrogen

Hydrogen is the most abundant element in the universe, comprising nearly 90% of all atoms, and is the third most abundant element on the surface of the earth. (Oxygen and silicon are the most abundant.) Most stars, including our sun, consist primarily of hydrogen. The hydrogen in our sun is the fuel for the fusion reactions that produce the life-sustaining energy that reaches our planet. On earth, the majority of hydrogen is found in oceans combined with oxygen as water.

Properties and Preparation of Hydrogen

The first known preparation of elemental hydrogen was in 1671, when Robert Boyle dissolved iron in dilute acid and obtained a colourless, odourless, gaseous product. Hydrogen was finally identified as an element in 1766, when Henry Cavendish showed that water was the sole product of the reaction of the gas with oxygen. Hydrogen gas can easily be produced in the laboratory according to the reaction:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

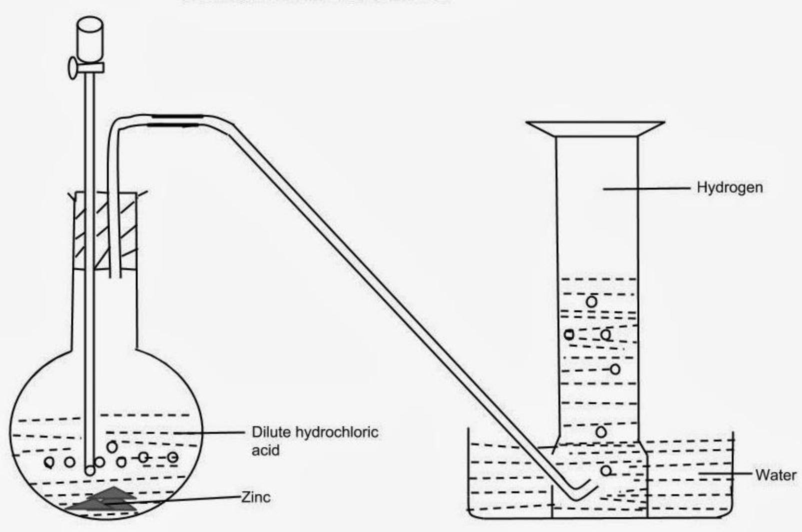


***Figure 6.1**: Laboratory preparation of hydrogen*

There are three isotopes of hydrogen: *protium*, $^{1}_{1}H$ or H, which is the most abundant; *deuterium*, $^{2}_{1}H$ or D; and *tritium*, $^{3}_{1}H$ or T. All three isotopes are naturally occurring; however, only 0.0156% is D and a trace is T. Because an atom of D has about twice the mass of protium, compounds that contain deuterium often have different properties than those that contain only protium. For example, the normal boiling point of D_2O is 101.42 ^{o}C versus 100.00^{o}C for H_2O. Tritium is produced naturally in the upper atmosphere by nuclear reactions that are induced by cosmic rays or in a nuclear reactor by bombarding lithium-6 with neutrons. Tritium is radioactive with a half-life of 12.3 years, hence very little of what is naturally produced in the upper atmosphere reaches the surface of the earth.

The isotopes of hydrogen find many applications. They are used as markers or labels that can be followed during chemical reactions. For example, a chemist who was interested in determining whether hydrogen atoms move between water molecules could make a solution that contains DOD and HOH. If hydrogen atom transfer takes place (which is the case in this example), then the solution, after a period of time, would be expected to contain DOD, HOH, and the new compound DOH. Information about the exchange rate of H with D can also be obtained from the experiment by measuring the rate at which the DOH forms. Because so many compounds contain hydrogen, the hydrogen isotopes are widely used in this manner.

The elemental form of hydrogen is a diatomic molecule having bond dissociation energy of 432 kJ/mol. This is a large value when compared with chlorine at 240 kJ/mol. This relatively high bond dissociation energy indicates why hydrogen is less reactive than its halogen counterparts. However, with the addition of heat or light, or in the presence of a suitable catalyst, hydrogen can be induced to react.

Industrially, hydrogen is prepared using the **steam-reforming process** where steam and hydrocarbons from natural gas or petroleum react at high temperature and pressure in the presence of a catalyst (e.g. Nickel) to form carbon monoxide and hydrogen. For example:

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$$

Another route for hydrogen production is the water–gas reaction, which is no longer used commercially but may become important in the future as natural gas and petroleum become more expensive and scarce. In this reaction, steam is passed over red-hot coke or coal.

$$C + H_2O \rightarrow CO + H_2$$

Both of these reactions produce a mixture of hydrogen and carbon monoxide. Such mixtures are used to produce various organic compounds, but to obtain pure hydrogen the carbon monoxide must be removed. First the carbon monoxide is reacted with steam in the presence of a catalyst to give carbon dioxide and more hydrogen.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is then removed by passing the mixture of gases through a basic aqueous solution.

Hydrogen Reactions and Compounds

In addition to the preparation of ammonia, the other major use of hydrogen is in the petrochemical industry. In many cases the reaction is one where hydrogen is added to hydrocarbon compounds containing carbon-carbon double bonds to produce compounds that contain carbon-carbon single bonds. For example, 1-butene can be reacted with hydrogen using a platinum or palladium catalyst to produce butane.

$$CH_3CH_2CH = CH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$$

This process, called *hydrogenation*, is used in the food processing industry where oils (liquids) that contain many carbon-carbon double bonds are converted to fats (solids) that contain few or no carbon-carbon double bonds. Another important process that requires hydrogen is the cobalt-catalyzed *synthesis gas* reaction with carbon monoxide to produce methanol (vapour).

$$CO + 2H_2 \rightarrow CH_3OH$$

Hydrogen is also used to reduce metal oxides to extract pure metals. For example, tungsten (VI) oxide can be reduced at high temperatures via the reaction

$$WO_3 + 3H_2 \rightarrow W + 3H_2O$$

When hydrogen combines with another element it forms a **binary hydride** – that is, *a compound that contains hydrogen and one other element.* There are three categories of binary hydrides: ionic hydrides, covalent hydrides, and metallic hydrides.

Ionic hydrides, which contain the hydride ion, H^-, can be directly formed via the reaction of an alkali metal or the larger Group 2 metals (Ca, Sr, and Ba) with hydrogen gas near 400°C.

$$2Li + H_2 \rightarrow 2LiH$$
$$Ba + H_2 \rightarrow BaH_2$$

These hydrides are white crystalline compounds in which the H atoms have an oxidation state of -1. Ionic hydrides can undergo an oxidation–reduction reaction with water to produce hydrogen and a basic solution. For example:

$$LiH + H_2O \rightarrow H_2 + LiOH$$

Because of this, hydrides can be used as a source of hydrogen gas where transportation of $H_{2(g)}$ is impractical, such as for inflating weather balloons. Ionic hydrides are also used as reducing agents (a source of electrons) during chemical reactions.

Covalent hydrides are molecular compounds in which hydrogen is covalently bonded to another element. Examples of these compounds are NH_3, H_2O, H_2O_2, and HF. Some of these compounds often can be formed from the direct reaction of the elements. If the non-metal reacting with hydrogen is reactive, the reaction will readily occur without the need for elevated temperatures or a catalyst:

$$F_2 + H_2 \rightarrow 2HF$$

The reaction of hydrogen with oxygen to form water is an example of a reaction that requires the input of energy to get started; however, once it does, the reaction is rapid and exothermic.

$$2H_2 + O_2 \rightarrow 2H_2O \text{ -484 kJ}$$

Because it is such an exothermic reaction and the product is a gas, it is an ideal rocket fuel. The combustion of hydrogen produces more heat per gram than any other fuel (120 kJ/g). Unlike hydrocarbons, it is a "clean fuel" because the product (water) is environmentally benign. Because of these features, hydrogen may become the favourite fuel of the twenty-first century.

Metallic hydrides are compounds containing a transition metal and hydrogen. Generally, the formula of these compounds is MH*x*, where *x* is often not an integer. These compounds contain hydrogen atoms that are spread throughout a metal crystal occupying the holes in the crystal lattice. Often, hydrogen atoms enter the holes in nonstoichiometric amounts. The result is that the composition of the metallic hydride is variable. For example, under one pressure of H2 the composition of the metallic hydride MH*x*might be $MH_{0.4}$, whereas at a higher pressure of H_2 it might be $MH_{0.5}$.Examples of these compounds are $TiH_{1.7}$ and $ZrH_{1.9}$.

CHAPTER SEVEN

Chemical Bonds

In nature, achieving a filled (complete) valence energy level is a driving force of chemical reactions, because when that energy level is full, elements become stable, or “satisfied” – stable elements don’t lose, gain, or share electrons. The *noble gases* – the VIIIA elements on the periodic table are extremely non-reactive because their valence energy level (outermost energy level) is filled. However, the other elements in the A families on the periodic table do gain, lose, or share valence electrons to fill their valence energy level and become satisfied.

Because filling the valence energy level usually involves filling the outermost s and p orbitals, it’s sometimes called the *octet rule* – elements gain, lose, or share electrons to reach a full octet (eight valence electrons: two in the s orbital and six in the p orbital). There are exceptions to the octet rule. Hydrogen and lithium, for instance, require only two electrons to fill their outer orbital. But the octet rule works well for most elements. We shall now discuss different types of chemical bonds.

Ionic Bonds

Atoms in a molecule are joined by bonds. Bonds are formed when the valence or outermost electrons of two or more atoms interact. The nature of the bond between atoms goes a long way toward determining the properties of the molecule. Elements with similar electronegativities share electrons and form covalent bonds. But elements with greatly different electronegativities exchange one or more electrons. This is called an ionic bond.

The transfer of electrons from one atom to another produces charged species called **ions**. Positively charged ions are called **cations** and negatively charged ions are called **anions**. Ions that have a positive charge due to the loss of electrons are called *cations*. In general, a cation is smaller than its corresponding atom.

Consider sodium, an alkali metal and a member of the I family on the periodic table. Sodium has one valence electron and 11 total electrons, because its atomic number is 11. It has an electron configuration of $1s^2 2s^2 2p^6 3s^1$. By the octet rule, sodium becomes stable when it has eight valence electrons. Two possibilities exist for sodium to become stable: It can gain seven more electrons to fill energy level 3, or it can lose the one 3s electron so that energy level 2 (which is already filled at eight electrons) becomes the valence energy level.

So to gain stability, sodium loses its 3s electron. At this point, it has 11 protons (11 positive charges) and 10 electrons (10negative charges). The once-neutral sodium atom now has a single positive charge [11 (+) plus 10 (–) equals 1+]. It's now an *ion,* an atom that has a charge due to the loss or gain of electrons. Ionic bonds are **non-directional** (ions may be attracted to one another in any direction)

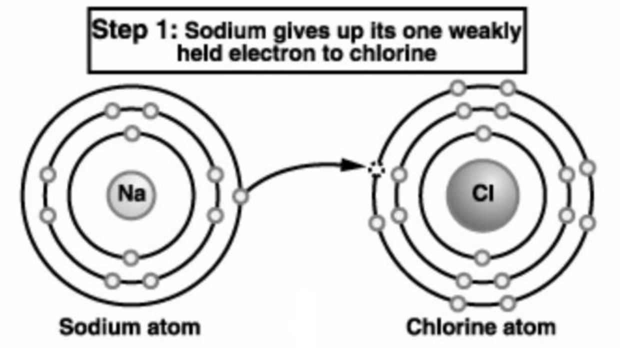
You can write an electron configuration for the sodium cation:

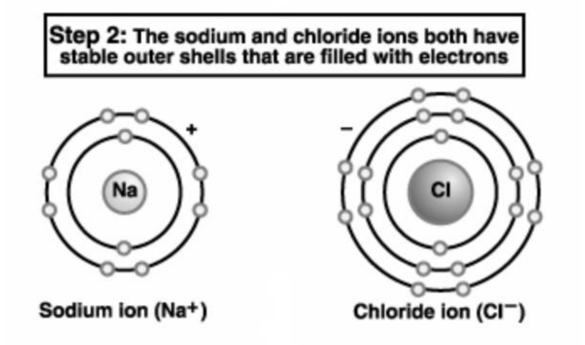
Na+: $1s^2 2s^2 2p^6 3s^1$

Note that if an ion simply has 1 unit of charge, positive or negative, you normally don't write the 1; you just use the plus or minus symbol, with the 1 being understood.

Atoms that have matching electron configurations are *isoelectronic* with each other. The positively charged sodium ion (cation) has the same electron configuration as neon, so it's isoelectronic with neon. So does sodium become neon by losing an electron? No. Sodium still has 11 protons, and the number of protons determines the identity of the element.

We will study the reaction between sodium and chlorine to illustrate ionic bonding:





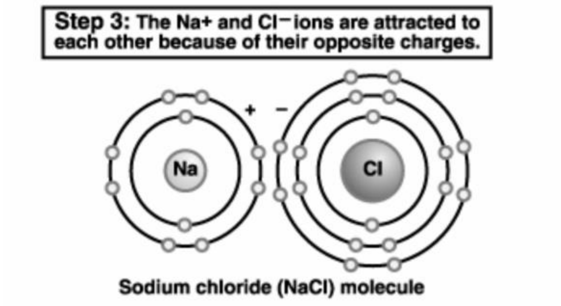


Table 7.1: Typical Properties of Ionic Compounds

Property	**Example**
High melting point	We need a blast furnace to melt metals
High boiling point	A lightning strike is needed to volatilize some substances
Physically hard	Ceramics (e.g. plates) can bear heavy weights
Often physically brittle	Table salt can be crushed to form a powder
High electrical conductivity in solution	Using a hair dryer in the bath risks electrocution
Dissolve in polar solvents	Table salt dissolves in water
Insoluble in non-polar solvents	We dry an organic solvent by adding solid $CaCl_2$

Covalent Bonding

Atoms form compounds to achieve a filled valence energy level. But instead of achieving it by gaining or losing electrons, as in ionic bonding, *covalent bond* is formed by sharing of one or more electron pairs between two atoms.

Elements that tend to form covalent bonds are those that are:

1. strongly electronegative,
2. not strongly electropositive, or
3. have similar electronegativities

Covalent bonds can be formed not only between identical atoms but also between different atoms. By sharing electrons, the atoms completely fill their valence shell and achieve a stable-octet arrangement of electrons. It forms a strong localized and directional bond (in the direction of the greatest orbital overlap). If the atoms in a covalent bond are different from one another, the electron pair may not be shared equally between them. The atoms that are linked will carry a partial negative or positive charge. Such a bond is called **a *polar covalent bond***.

Example 1

Let us consider the covalent bond formed between hydrogen (H) and fluorine (F), because the electrons spend more time around F, they spend less time around H. F gets a partial negative charge (indicated with a δ–), and H gets partial positive charge (indicated with a δ+):

$$\overset{\delta+}{\mathbf{H}}\text{—}\overset{\delta-}{\mathbf{F}}$$

Polar molecules will have an **overall dipole** which can be represented with a dipole arrow (pointing to the more electronegative end of the molecule). The quantitative measure of a molecule's polarity is called its **dipole moment**.

Delta (δ) Notation for polar bonds:

– *Electrons concentrate around the more electronegative atom in a molecule*

→ *Atom gains a partial negative charge, indicated with δ–.*

– *Since electrons spend less time around the other atom*

→ *Other atom gains a partial positive charge, indicated with δ+.*

Exercise

Use delta notation to indicate which atom in each bond is more electronegative. Then, use a dipole arrow that points towards the negative pole.

C—F N—O H—B O—C

Non-polar Covalent Bond

In some covalent bonds, both atoms have equal electronegativity values. The two atoms share the bonding electrons equally. Most common example is between two identical atoms: H_2, O_2, N_2, Cl_2, F_2, I_2, Br_2

H—H

Non-polar covalent bonds can also occur between **different** atoms which have identical electronegativity values.

Example

Cl_2 molecule. $Z_{Cl}=17$ ($1s^2 2s^2 2p^6 3s^2 3p^5$) N'= 7, 8 -N'= 1 →can form only one covalent bond−•

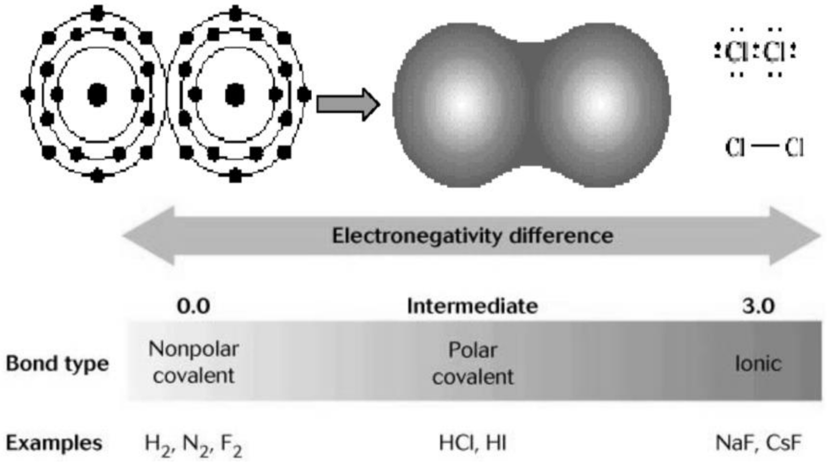


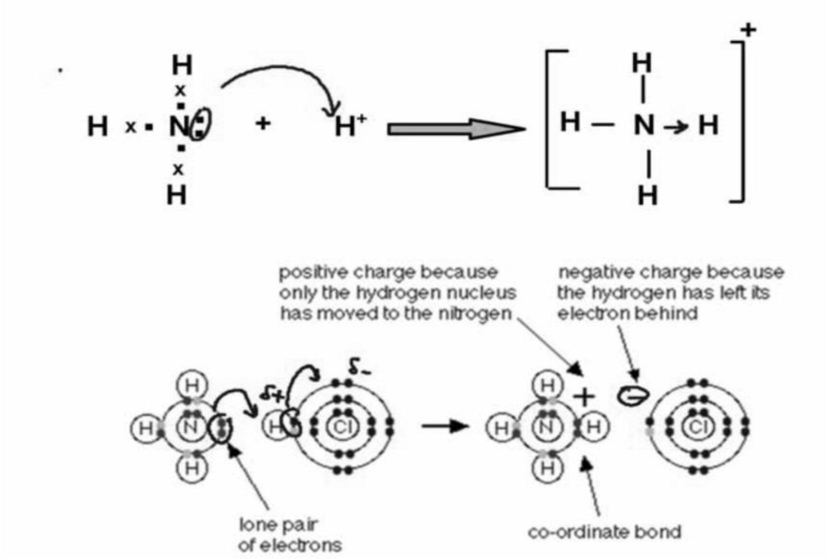
Table 7.1: Typical Properties of Covalent Compounds

Property	Example
Low melting point	Ice melts in the mouth
Low boiling point	Molecular nitrogen is a gas at room temperature
Physically soft	We use petroleum jelly as a lubricant
Malleable, not brittle	Butter is easily spread on a piece of bread
Low electrical conductivity	We insulate electrical cables with plastic
Dissolve in non-polar solvents	We remove grease with methylated spirit
Insoluble in polar solvents	Polyurethane paint protects the window frame from rain

Coordinate Covalent Bonds

The covalent bonds examined so far have consisted of electrons contributed equally from both of the atoms involved in the bond. It is possible to have covalent bonds in which only 1 of the 2 atoms that are joined together contributes both of the electrons in the bond. The bond so formed is called a **coordinate covalent bond** or a **dative bond**. A typical coordinate covalent bond forms when ammonia gas and hydrogen chloride gas react. This sometimes happens accidentally in the laboratory when these gases are evolved from beakers of concentrated ammonia solution and concentrated hydrochloric acid (a solution of HCl gas) that are accidentally left uncovered. When these two gases meet, a white chemical fog is formed. It is ammonium chloride, NH_4Cl, a salt that is produced by the reaction in which the unshared pair of electrons from NH3 forms a coordinate covalent bond with an H^+ ion released from HCl. The product is an ion of NH_4. After the coordinate covalent bond has formed, the ammonium ion has four equivalent N-H bonds; the one formed by coordinate covalent bonding is indistinguishable from the other three bonds.

Example 1
Formation of ammonium chloride



Example 2
Formation of hydroxonium ion

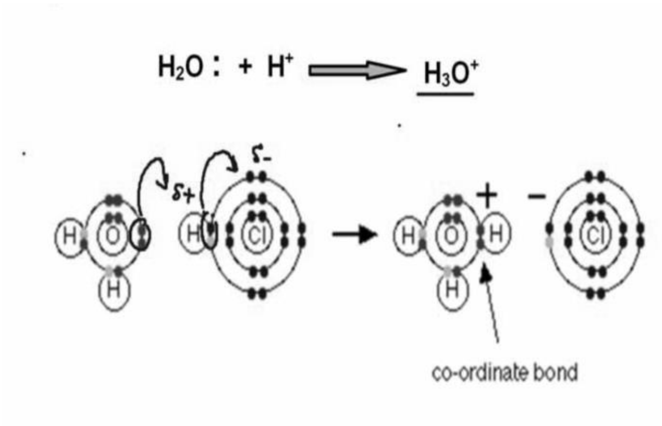


Table 7.2: Comparison between covalent and co-ordinate covalent bonds

Covalent Bond	**Co-ordinate Covalent**
Formed by mutual sharing of electrons	Formed by one sided sharing of electron pair
Formed between similar or dissimilar atoms	Formed between two unlike atoms
May be polar or non-polar	Always polar, because it is formed between unlike atoms
Shared pair of electrons are denoted by short lines	Shared pair of electrons are denoted by an arrow
Compounds are usually insoluble in water	Compounds are sparingly soluble in water

Metallic Bonds

Metals exist as nuclei surrounded by a sea of electrons

- The electrons in a metal are shared among all the nuclei, so the electrons are ***delocalized*** (i.e., they are not fixed to a specific atom)
- The electrons can shift throughout the entire metal.
- Electrons are free to move throughout the solid
- Metals' unique properties e.g. metals conduct heat and electrical because electrons flow through the metal; metals are malleable and ductile because electrons act as a glue, holding the positively charged nuclei together.

Compounds that do not Conform to the Octet Rule

By now a number of examples of bonding have been shown that are explained very well by the octet rule. There are numerous exceptions to the octet rule, however. These fall into the three following major categories:

1. Molecules with an uneven number of valence electrons. A typical example is nitric oxide, NO. Recall that the nitrogen atom has 5 valence electrons and the oxygen atom 6, so that NO must have 11, an uneven number.
2. Molecules in which an atom capable of forming an octet has fewer than 8outer electrons. A typical example is highly reactive, toxic boron trichloride, BCl_3.
3. Molecules in which an atom has more than 8 outer electrons. This can occur with elements in the third and higher periods of the periodic table because of their underlying *d* orbitals capable of accepting electron pairs, so that the valence shell is no longer confined to one *s* orbital and three *p* (orbitals that make up an octet of electrons). An example of a compound with more than 8 outer electrons is chlorine trifluoride, composed of 4 halide atoms (Cl and F), each of which has 7 valence electrons for a total of 28. These are accommodated by placing 5 electron pairs – 2 of them non-bonding – around the central Cl atom.

Intermolecular Forces

London force (dispersion force): This very weak type of attraction generally occurs between nonpolar covalent molecules, such as nitrogen (N_2), hydrogen (H_2), or methane (CH_4). It results from the ebb and flow of the electron orbitals, giving a very weak and very brief charge separation around the bond.

Dipole-dipole interaction: This intermolecular force occurs when the positive end of one dipole molecule is attracted to the negative end of another dipole molecule. It is much stronger than a London force, but it's still pretty weak.

Hydrogen bond: The third type of interaction is really just an extremely strong dipole-dipole interaction that occurs when a hydrogen atom is bonded to one of three extremely electronegative elements: O, N, or F. These three elements have a very strong attraction for the bonding pair of electrons, so the atoms involved in the bond take on a large amount of partial charge. This bond turns out to be highly polar – and the higher the polarity, the more effective the bond.

When the O, N, or F on one molecule attracts the hydrogen of another molecule, the dipole-dipole interaction is very strong. This strong interaction (only about 5 percent of the strength of an ordinary covalent bond but still very strong for an intermolecular force) is called a *hydrogen bond*. Water is a good example of hydrogen bonding. Because of their small positive charge, the hydrogen atoms tend to associate with the oxygen atoms in nearby molecules. Because of the electric interaction, hydrogen-bonded molecules hold on to each other more tightly than those in substances with pure covalent bonds. This cohesiveness is why water is a liquid at room temperature, whereas heavier covalent-bonded molecules such as chlorine, in the form of Cl_2, are gases.

Study Questions

1. Define covalent bond.
2. List the typical physical properties of ionic and covalent compounds?

3. Classify as ionic, covalent, or polar covalent: H_2, CH_4, LiF, H_2O. Order these from low to high boiling points.

4. Example: Identify the bonds in the following by circling one for each:
   a. The bonds in HF.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   b. The bond in F_2.
      (a) ionic b) polar covalent (c) nonpolar covalent
      (d) metallic
   c. The bonds in K_2O
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   d. The bonds in Cu.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   e. The bonds in CO.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   f. The bonds in O_2.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   g. The bond in $MgCl_2$.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   h. The bonds in NO.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   i. The bonds in Br_2.
      (a) ionic (b) polar covalent (c) nonpolar covalent
      (d) metallic
   k. The bonds in NiO.
      (a) ionic (b) polar covalent (c) nonpolar covalent

(d) metallic

The atom which supplies the pair of electrons for co-ordinate covalent bond formation is known as:

A. acceptor B. donor C. neutral D. metalloid

5. Which of the following pairs of compounds can form co-ordinate covalent bonds

A. PH_3/BF_3 B. CH_4/H_2O C. H_2S/CCl_4 D. NH_3/H_2O

CHAPTER EIGHT

Chemical Stoichiometry

Chemistry is a practical science. Imagine how useful it could be to determine the formula of a compound from the masses of its elements or to predict the amounts of substance consumed and produced in reaction.

Stoichiometry in Greek word: stoicheion "element or part" + metron, "measure"; is the study of the quantitative aspect of chemical formulae and reactions. It can also be defined as the science of measuring how much of one thing can be produced from certain amounts of others.

The Mole

In daily life, we typically measure things out by counting or by weighing, with the choice based on convenience. It is more convenient to weigh beans or rice than to count individual pieces, and it is more convenient to count eggs or pencils than to weigh them. To measure such things, we use mass units (a kilogram of rice) or counting units (a dozen pencils). Similarly, daily life in the laboratory involves measuring substances. However, an obvious problem arises when we try to do this. The atoms, ions, molecules, or formula units are the entities that react with one another, so we would like to know the numbers of them that we mix together. But, how can we possibly count entities that are so small? To do this, chemists have devised a unit called the mole to count chemical entities by weighing them.

The mole is the SI unit for amount of substance. It is defined as the amount of a substance that contains the same number of entities as there are atoms in exactly 12g of carbon = 12. Entities may be atoms, molecules, electrons, ions, etc.

One mole contains 6.022×10^{23} entities. This number is called Avogadro's number in honour of Amedeo Avogadro who laid the groundwork for the mole concept.

Thus:

1mol of carbon contains 6.022×10^{23} carbon-12 atoms
1mol of H_2O contains 6.022×10^{23} H_2O molecules
1mol of NaCl contains 6.022×10^{23}NaCl formula units

Molar Mass

The molar mass (M) of a substance is the mass per mole its entities (atoms, molecules, or formula units). The unit of molar mass is grams per mole (g/mol).

For elements, the molar mass is its atomic mass in the periodic table. The molar mass of monoatomic elements is the numerical value from the periodic table and is expressed in grams/mole. For example, iron has a molar mass of 55.85 g/mol, gold is 197.0g/mole, neon is 20.18 g/mol, etc.

Some element also occurs naturally as molecules for example oxygen (O_2). The molecule formula is used to determine the molar mass. The molar mass of O_2 molecules is twice that of oxygen (O) atom.

Molar mass of O_2 = 2 x molar mass of oxygen atoms = 2x16.00 g/mol = 32.00 g/mol.

Another example is sulphur which consists of octatomic molecules, S_8.

M of S_8 =8 x M of sulphur = 8 x32.07g/mol.
= 256.6 g/mol

The molecular mass of any compound is the sum of the molar masses of the atoms of the element in the formula. For example, sulphur dioxide (SO_2).

Molar mass of sulphur = 32.07g/mol
molar mass of oxygen = 2x16.00g/mol = 32.00g/mole.
(32.07 + 32.00)g/mole = 64.07g/mole

Inter-converting moles, mass, and number of chemical Entities (Ions, electrons, molecules, atoms)
mass(g) = no of moles x molar mass

moles = $\frac{\text{mass (g)}}{\text{molar mass}}$

number of entities = no of moles x6.022×10^{23} entities

no of moles = $\frac{\text{no of entities}}{6.022 \times 10^{23}\text{entities}}$

Example

i) How many grams of silver (Ag) are in 0.0342mol of Ag?
Molar mass = 107 g/mol

Mass of Ag = 0.0342×107 g Ag
= 3.69 g Ag

ii) How many iron (Fe) atoms are in 95.8g of Fe?
molar mass of iron = 55.85 g/mol.
no of Fe atoms = 6.022×10^{23} x 1.72 mol Fe
= 1.04×10^{24} atoms Fe

Mass Percent from the Chemical Formula

Each element in a compound constitutes its own particular portions of the compounds mass. The molecular mass and chemical formulas are used to calculate the mass percent of any element in a compound.

Example

i) What is the mass percent of each element in glucose $C_6H_{12}O_6$?

ii) How many grams of carbon are in 16.55g of glucose?

(C = 12.01, H= 1.008, 0 = 16.00)

Molar mass C_6H_{12} O_6=

Mass of carbon = 6 x 12.01 = 72.06 g/mol

Mass of hydrogen = 12 x 1.008 =12.096 g/mol

Mass of oxygen = 6 x 16.00 g/mol

Molar mass of $C_6H_{12}O_6$ = 180.16 g/mol

Mass percent of carbon = $\frac{72.06}{180.16}$ x 100

= 40.00 mass % C

iii) Mass % of Hydrogen = $\frac{12.096}{180.16}$ X 100

= 6.71 mass % H

iv) Mass % of Oxygen = $\frac{96.00 \times 100}{180.16}$

= 53.29 mass % O

v) Mass of carbon in C_6H_{12}O6

= $\frac{72.06}{180.16}$ = 0.400 g of carbon

vi) Mass of C= mass of glucose x mass of fraction of C

= 16.55g glucose x 0.4000gC

= 6.620gC.

Determining the Formula of an Unknown Compound

An analytical chemist investigating a compound decomposes it into simpler substances, finds the mass of each component element, converts these masses to numbers of moles, and then arithmetically converts the moles to whole-number (integer) subscripts. This procedure yields the empirical formula, the simplest whole-number ratio of moles of each element in the compound.

Empirical formula shows the relative number of atoms of each element in the compound. It is the simplest types of formula and is derived from the masses of the component elements.

Example

Elemental analysis of a sample of an ionic compound gave the following results:

2:82g of Na, 4.35g of Cl, and 7.83g of O.

What is the empirical formula and name of the compound? Na = 23.00, Cl = 35.5,O = 16.00

Solution

1) Finding moles of elements.

Mole of Na= $\frac{2.82}{23.0}$ = 0.123 mol Na

Moles of Cl= $\frac{4.35}{35.5}$ = 0.123 mol CL

Moles of O = $\frac{7.83}{16.00}$ = 0.489 mol O

Dividing by the smallest

Na $=\frac{0.123}{0.123}$, Cl $=\frac{0.123}{0.123}$ = O = $\frac{0.4898}{0.123}$

1 1 3.98 ($\simeq$ 4)
Na =1, Cl =1 O =4

The empirical formula is $NaClO_4$. The name is sodium tetraoxochlorate (vii).

Molecular Formula

Through the knowledge of the molar mass of a compound, empirical formula can be used to obtain the molecular formula.

The molecular formula shows the actual number of atoms of each element in a molecule of the compound.

Example

Elemental analysis of lactic acid (molecular mass of 90.08g/mol) shows that is contains 40.0 mass percent C, 6.71 mass percent H, and 53.3 mass percent O.

a) Determine the empirical formula of lactic acid.
b) Determine the molecular formula.

Solution

C$=\frac{40.0}{12.01}$ = 3.33mol of C

H $=\frac{6.71}{1.008}$ = 6.66 mol of H

O = $\frac{53.3}{16.00}$ = 3.33mol of O

Divide each of the moles by the smallest

C = = 1.00

$H = \frac{6.66}{3.33} = 2.00$

$O = \frac{3.33}{3.33} = 1.00$

The empirical formula = CH_2O

c) Determining the molecular formula

$$(CH_2O)_x = 90.08$$
$$((1 \times 12) + (2 \times 1) + (16 \times 1))x = 90.08$$
$$(12 + 2 + 16)x = 90.08$$
$$30x = 90.08$$
$$x = \frac{90.08}{30} = 3$$

The molecular formula is $C_3H_6O_3$.

Combustion Analysis

Another method of determining a chemical formula is combustion analysis, a method that is used to measure the amounts of carbon and hydrogen in a combustible organic compound.

In a quantitative combustion, a weighed sample of the organic compound is passed through a combustion tube, a tube filled with copper oxide heated to 600-800^oC joined to a tube containing a drying agent usually **magnesium perchlorate and another tube containing a strong base usually ascarite, sodium hydrogen on asbestos.** The drying agent absorbs, the water formed during the process while the base absorbs the carbon dioxide formed. The increase in weight of each tube gives the weight of product formed.

Example

When a 1.00g sample of vitamin C (molecular mass 176.12g/mole) is placed in a combustion chamber and burned, the following data are obtained.

Initial mass of CO_2 = 83.85g
Final mass of CO_2 = 85.35g
Initial mass H_2O = 37.55g
Final mass of H_2O = 37.96g

What is the molecular formula of vitamin C?

Solution

Mass of CO_2 = 85.35g -83.85g
= 1.50g of CO_2
Mass of C = mass of H_2O = 37.96g-37.55g
= 0.41g H_2O

$$\text{Mass of C} = \frac{\text{mass of } CO_2 \times 1 \text{ mole } \times \text{molar mass of carbon}}{\text{Molear mass of } CO_2}$$

$$= \frac{1.50\text{g x } 12.01\text{g}}{44.012} = 0.409\text{gC}$$

$$\text{Mass of H} = \text{mass of } H_2O \text{ Mass of } H_2O \times \frac{2 \text{ molH} \times \text{Molar mass of H}}{\text{Molear mass of } H_2O}$$

$$= 0.41\text{g} \times \frac{2.016}{18.02\text{g}} 0.046\text{gH}$$

Mass of oxygen = mass of sample – (mass of C + mass of H)
= 1.000g – (0.409g+0.046g) = 0.54gO

Finding the amounts (mol) of elements

$$C = \frac{0.409}{12} = 0.0341 \text{ mol}$$

$H = \frac{0.046}{1.008} = 0.0461$ mol

$O = \frac{0.545}{16.00} = 0.0341$ mol

Dividing each mole by the smallest

$C = \frac{0.0341}{0.0341} = 1.00$

$H = \frac{0.046}{0.0341} = 1.3$

$O = \frac{0.0341}{0.0341} = 1.00$

The values are multiplied by 3 to make them approximately into integers: then:

$C = 1.00 \text{ x } 3 = 3.00$
$H = 1.3 \text{ x } 3 = 3.9 \simeq 4$
$O = 1.00 \text{ x } 3 = 3.00$

The empirical formula = $C_3H_4O_3$
To determine the molecular formula:

$$(C_3H_4O_3)_x = 176.12$$
$$((3 \times 12) + (4 \times 1) + (16 \times 3))x = 176.12$$
$$(36 + 4 + 48)x = 176.12$$
$$88x = 176.12$$
$$x = \frac{176.12}{88} = 2$$

The molecular formula is $C_6H_8O_6$

Writing and Balancing Chemical Equations

A chemical equation is a statement in formula that expresses the identities and quantities of the substance involved in a chemical or physical change.

Equations are the "sentences" of chemistry. The left-hand side (LHS) of an equation is the amounts of each substance present before the change whiles the right-hand side (RHS) indicate the amounts present after the change. The reactants are always written at the left-hand side, and the products at the right-hand side.

Balancing Chemical Equations

Some reactions that are simple can be balanced at a glance, others need more work. Take for example the reaction of hydrogen and oxygen to form water. We start by writing by the skeletal equations:

$$H_2 + O_2 \rightarrow H_2O$$

We find the stoichiometry coefficients that balance all the elements:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Once the equation is balanced, we add the state symbols:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

You must never balance an equation by changing the subscripts in the chemical formulae.

To balance a chemical equation, consider one element at a time. Balance first the element that occurs in the fewest. Balance last the element that is found in the greatest number.

For example,

$$CH_4 + O_2 \rightarrow CO_2 + H_2O \text{ unbalanced}$$

Because C and H are present in two formulae and O occurs in three, we start with C and H, note that the C atoms are already balanced. We balance the H atoms by adding 2 as coefficient to H_2O to give four H atoms on each side:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O \text{ balanced}$$

We verify that the equation is balanced by counting the numbers of atoms of each element on each side of the arrow.

At this stage we specify the states.

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Calculations from Equations

A balanced equation is essential for all calculations involving amount of reactants and products; if you know the number of moles of one substance the balanced equation tells you the number of moles of all the others in the reaction.

For example,

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

1mol + 5mol → 3 mol + 4 mol

44.09 (amu) + 160.00 (amu) → 132.03 (amu) + 72.06 (amu)

Mass (g) 44.09 g + 160.00g → 132.03 + 72.06g

Total (g) 204.09g → 204.099

Example

Copper is obtained from sulphide ores by roasting the ore with oxygen to form powdered copper (1) oxide and gaseous sulphur dioxide.

(a) How many moles of oxygen are required to roast 10.0 mol of copper (i) sulphide?

(b) How many grams of sulphur dioxide are formed when 10.0 of copper (I) sulphide is roasted?
(c) How many kilograms of oxygen are required to form 2.86kg of copper (I) oxide?

Solution

(a) Determining the moles of O_2
$2Cu_2S_{(s)} + 3O_{2(g)} \rightarrow 2Cu_2O_{(s)} + 2SO_{2(g)}$.
From the equation:
2mol of Cu_2S react with 3mol O_2
10.0mol of Cu_2S will produce;
5.0 x 3mol O_2
2mol = 15.0mol O_2

(b) To calculate the mass of SO_2
The first step is to determine the number of moles of SO_2 produce by 10mol of Cu_2S.

From the equation;
2mol Cu_2S → 2mol SO_2
10.0mol Cu_2S → 10.0mol Cu_2S x 2mol SO_2
2mol Cu_2S
= 10.0mol SO_2
Mass of SO_2 = mole SO_2 x molar mass SO_2
= 10.0mol x 64.07g/molSO_2
= 641gSO_2

Limiting Reactants

During chemical reactions, it is quite likely that one of reactants will be completely used up before the others are used up. The reactant that disappears first i.e. the reactant that is consumed completely is called the limiting reactant. Any other reactant is present in excess. For example, if 5mol of H_2 and 1mol of O_2 are mixed and allowed to react according to the equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

Only 2 moles of H_2 will react completely consuming the 1mol of O_2. Immediately the O_2 is used up, no further reaction will take place and no amount of product is formed. Therefore, the amount of product formed is limited by the reactant that disappears first. In this case O_2 is the limiting reactant.

Example

The equation for the reaction is:

$$Zn + S \rightarrow ZnS$$

If 12.0g of Zn are mixed with 6.50g of S and allowed to react.

(a) Which is the limiting reactant?
(b) How many grams of Zn can be formed from the particular reaction mixture?
(c) How many grams of which element will remain unreacted in this experiment?

Solution

(a) From the equation, we have
1mol Zn → 1 mol S.
To determine the limiting reactant, we need to convert our reactant quantities to moles.

(i) For Zn we have;
12.0g Zn/65.4g Zn x 1mol Zn = 0.183mol Zn

(ii) 6.50g S/32.1g S x 1molS = 0.202 mol S

Since the elements combine in a 1 to 1 ratio, it means that 0.183mol Zn requires 0.183 mol S. We see that there is more S than is required for the Zn to react with. Zn is therefore the limiting reactant.

(b) The amount of product formed depends only on the amount of limiting reactant.
From the equation, we write 1mol Zn → 1 molZnS.
∴ 0.183mol Zn/molZnS x 97.5gZnS = 1.78gZnS

(c) To calculate the weight of unreacted sulphur the number of moles of sulphur that is subtracted from the number of moles of sulphur initially available.
Moles S unreacted = (0.202mol – 0.183mol) = 0.019mol S
Therefore, 0.019mol S x 32.1g S = 0.61gS (the leftover) 1molS.

Theoretical Yield and Percentage Yield

Theoretical yield of a given product is the maximum yield that could be obtained if the reactants gave only that product, that is, the maximum mass product that can be obtained from a given mass of reactant.

The percent yield (% yield) is the actual yield expressed as a percentage of the theoretical yield:

Percentage yield = actual yield/theoretical yield x 100%

Example

When a large volume of water poured on 100g of calcium carbide, 28.3g of ethyne (C_2H_2) was produced. Calculate the percentage yield of ethyne for the reaction.

$$CaC_{2(s)} + 2H_2O_{(1)} \rightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$$

Solution

Mole of CaC_2 100/64.10 = 1.56mol CaC_2

But 1mol $CaC_2 \rightarrow$ 1 mol C_2H_2

$\therefore$ 1.56mol $CaC_2 \rightarrow$ 1.56mol C_2H_2

Mass of ethyne = 1.56 x 26.04 =40.6g C_2H_2

The actual yield of ethyne is 28.3g

Percentage yield of ethyne = actual yield/theoretical yield x 100%

28.3g/40.65 x 100% = 69.7%

Study Questions

1. Calculate the number of moles of CO_2 produced when 1.5mol hexane molecules, C_6H_{14} burn in air by the reaction.
   $2C_6H_{14(1)} + 19O_{2(g)} \rightarrow 12CO_{2(g)} + 14\ H_2O_{(g)}$
2. Calculate the weight of hydrogen in 12.0g of $NH_{3.}$
3. Ammonium nitrate is used as a fertilizer and to manufacture explosives. Agronomists base the effectiveness of fertilizers on their nitrogen content. (a) Calculate the mass percent of nitrogen in ammonium trioxonitrate (V). (b) How many grams of nitrogen are in 35.81kg of ammonium trioxonitrate (V)?
4. An unknown metal M reacts with sulphur to form a compound with formula M_2S_3. If 3.12g of M reacts with 2.88g of S. what are the names of M and M_2S_3?
5. A dry cleaning solvent (molar mass = 146.99g 1mol) that contains C_xH_y, and Cl is suspected to be a cancer-causing agent. When a 0.250g sample was studied by combustion analysis, 0.451g of CO_2 and 0.0617g of H_2O formed. Calculate the molecular formula.
6. How many grams of solid aluminium sulphide can be prepared by the reaction of 10.0g of aluminium and 15.0g of sulphur? How much of the non-limiting reactant is in excess?

CHAPTER NINE

Acids, Bases and Salts

Arrhenius Concept of an Acid and a Base

The term *acid* was first used in the seventeenth century; it comes from the Latin root *ac*-, meaning “sharp:, as in *acetum*, vinegar.

Acids have long been recognized as a distinctive class of compounds whose aqueous solutions exhibit the following properties:

1. A characteristic sour taste;
2. ability to change the colour of litmus from blue to red;
3. react with certain metals to produce gaseous H_2;
4. react with *bases* to form a salt and water.

In 1890 the Swedish chemist Svante Arrhenius (1859-1927) was able to formulate the first useful theory of acids:

Arrhenius Acid: Substance which generate H^+ ion on dissolving in water (H^+ generator)

e.g. HNO_3, $HClO_4$, HCl, HI, HBr, H_2SO_4, H_3PO_4 etc.

If acid release only one H^+ ion is known as mono basic/monoprotic symbol - HA.
If two H+ ion releases then known as dibasic/diprotic symbol-H_2A
If triprotic/tribasic, e.g. H_3PO_4 (symbol H_3A)

$$HCl \rightarrow H^+ + Cl^-$$

$$H_2SO_4 \rightarrow H^+ + SO_4^-$$

$$HSO_4^- \rightarrow H^+ + SO_4^-$$

$$H_3CCOOH \rightarrow H^+ + H_3CCOO^-$$

Strictly speaking, an “Arrhenius acid” must contain hydrogen. However, there are substances that do not themselves contain hydrogen, but still yield hydrogen ions when dissolved in water; the hydrogen ions come from the water itself, by reaction with the substance. A more useful operational definition of an acid is therefore the following:

An acid is a substance that yields an excess of hydrogen ions when dissolved in water

There are three important points to understand about hydrogen in acids:

- Although all Arrhenius acids contain hydrogen, not all hydrogen atoms in a substance are capable of dissociating; thus the CH_3 hydrogens of ethanoic acid are “non-acidic". An important part of knowing chemistry is being able to predict which hydrogen atoms in a substance will be able to dissociate.
- Those hydrogens that do dissociate can do so to different degrees. The strong acids such as HCl and HNO_3 are effectively 100% dissociated in solution. Most organic acids, such as ethanoic acid, are weak; only a small fraction of the acid is dissociated in most solutions. HF and HCN are examples of weak inorganic acids.
- Acids that possess more than one dissociable hydrogen atom are known as polyprotic acids; H_2SO_4 and H_3PO_4 are well-known examples. Intermediate forms such as

HPO_4^{2-} , being capable of both accepting and losing protons, are called ampholytes (or amphoteric).

$$H_2SO_4 \rightarrow HSO_4^- \rightarrow SO_4^{2-}$$
$$H_2S \rightarrow HS^- \rightarrow S^{2-}$$
$$H_3PO_4 \rightarrow H_2PO_4^- \rightarrow HPO_4^{2-}$$
$$HOOC-COOH \rightarrow HOOC-COO^- \rightarrow {}^-OOC-COO^-$$

Bases (Soluble Bases are called Alkalis)

The name *base* has long been associated with a class of compounds whose aqueous solutions are characterized by:

- a bitter taste;
- a "soapy" feeling when applied to the skin;
- ability to restore the original blue colour of litmus that has been turned red by acids;
- ability to react with acids to form salts. The word "alkali" is synonymous with base. It is of Arabic origin, but the root word comes from the same Latin *kalium* (potash) that is the origin of the symbol for potassium; wood ashes have been the traditional source of the strong base KOH since ancient times.

Arrhenius Definition of bases

Arrhenius Base

Any substance which releases hydroxide ions (OH^-) ion in water (OH^- ion generator), mono acidic base: CsOH, RbOH, NH_4OH symbol BOH diacidic base : $Ba(OH)_2$, $Ca(OH)_2$ symbol $B(OH)_2$.

Tri-basic base: $Fe(OH)_3$
OH^- ion also in hydrated form of $H_3O_2^-$, $H_7O_4^-$, $H_5O_3^-$

$$NaOH \rightarrow Na^{+} + OH^{-}$$

Sodium hydroxide is an Arrhenius base because it contains hydroxide ions. However, other substances which do not contain hydroxide ions can nevertheless produce them by reaction with water, and are therefore classified as bases. Two classes of such substances are the metal oxides and the hydrogen compounds of certain *non-metals*:

$$Na_2O + H_2O \rightarrow 2NaOH \rightarrow 2Na^{+} + 2OH^{-}$$
$$NH_3 + H_2O \rightarrow NH_4{}^{+} + OH^{-}$$

Bronsted-Lowry Concept of an Acid and a Base

The ideas put forward by Arrhenius were rather limiting since they only applied to aqueous solutions. There were situations where acid-base reactions were taking place in solvents other than water or even in no solvent at all. This problem was addressed in 1923 by the Danish chemist Johannes Brønsted (1879-1947) and the English chemist Thomas Lowry (1874-1936) when they independently proposed a more general definition of acids and bases, and the study of acids and bases took a great step forward. This theory became known as the Brønsted-Lowry theory of acids and bases. Brønsted-Lowry theory defined:

An acid is a proton donor. A base is a proton acceptor.

According to the Brønsted concept, an acid HA is a substance that is able to transfer a proton to a water molecule, yielding H_3O^+ and leaving the anion A^-as the conjugate base:

$$HA + H_2O \rightarrow A^{-} + H_3O^{+}$$

Notice that because the water molecule accepts a proton, H_2O is acting as a *base* here. Thus what Arrhenius would have regarded as the simple dissociation of HA is now regarded as a reaction of an acid with a base in its own right. Although the equation above is certainly closer to describing what actually happens than $HA \rightarrow H + A^-$, this last equation is so much easier to write that chemists still use it to represent acid-base reactions in contexts in which the proton donor-acceptor mechanism does not need to be emphasized. Thus we still talk about "hydrogen ions" and use the formula "H^+" in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

These definitions carry a very important implication: a substance cannot act as an acid without the presence of a base to accept the proton, and *vice versa*.

A reaction of an acid with a base is thus a *proton exchange* reaction; if the acid is denoted by AH and the base by B, then we can write a generalized acid-base reaction as

$$AH + B \rightarrow A^- + BH^+$$

But the product BH^+ is now capable of losing its newly-acquired proton to another acceptor, and is therefore potentially another acid:

$$acid_1 + base_2 \rightarrow base_1 + acid_2$$

In this schematic reaction, $base_1$ is *conjugate* to $acid_1$, and $acid_2$ is conjugate to $base_2$. The term *conjugate* means "connected with", the implication being that any species and its conjugate species are related by the gain or loss of one proton. Table 9.1 shows the conjugate pairs of a number of typical acid-base systems

An acid and base that differ only in the presence/absence of 1 H^+ *are called a conjugate acid/base pair.*

Conjugate base is formed by removing 1 H^+ *from an acid. Conjugate acid is formed by adding 1* H^+ *to a base.*

Table 9.1: Conjugate pairs of acid-base systems

Substance	**Acid**	**Conjugate Base**
Hydrochloric acid	HCl	Cl^-
Ethanoic acid	CH_3CH_2COOH	$CH_3CH_2COO^-$
Potassium dihydrogen phosphate (V)	$H_2PO_4^-$	HPO_4^-
Trioxonitrate (V) acid	HNO_3	NO_3^-
Hydrogen tetraoxosulphate (Vi)	HSO_4^-	SO_4^-
Ammonium ion	NH_4^+	NH_3
Water	H_2O	OH^-
Hydroxonium ion	H_3O	H_2O

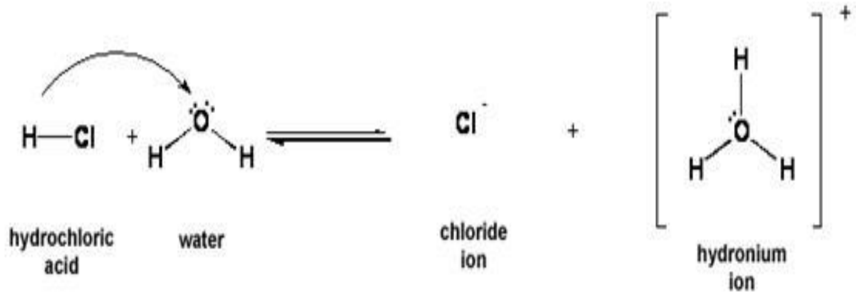


Figure 9.1*: HCl donates* H^+ *(a proton) to water. HCl is an example of a Brønsted-Lowry acid and water a base*

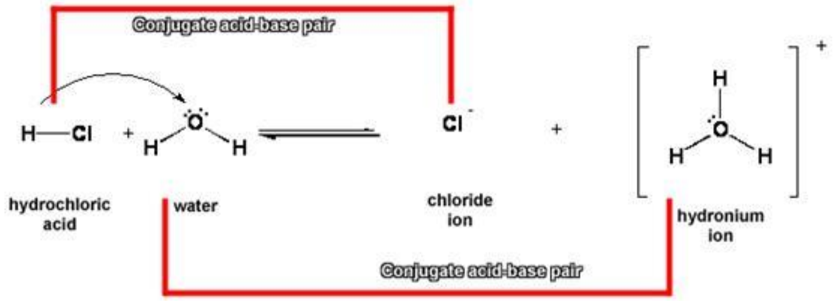


***Figure 9.2**: Conjugate acid-base pair*

Amphiprotic Species

Many substances can both donate and accept protons: examples are $H_2PO_4^-$, HCO_3^- , NH_3, and H_2O. Such substances are said to be amphiprotic; the dissolved species themselves are called ampholytes.

Acid-Base Reactions

Within the Arrhenius concept, neutralization of H^+ by $OH^-$is the only type of acid-base reaction that can occur. The Brønsted concept broadens our view, encompassing a wide variety of reactions whose common feature is the transfer of a proton from a donor to an acceptor.

Lewis Acids and Bases

Lewis proposed that:

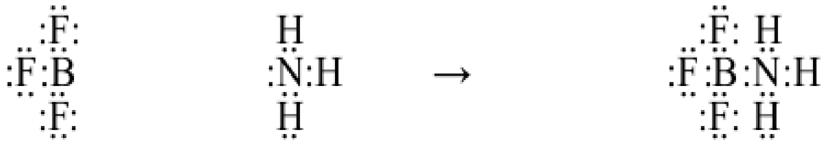
An acid is an electron-pair acceptor.
A base is an electron-pair donor.
An acid-base reaction is the sharing of an electron pair with an acid by a base.

These three simple definitions constitute the heart of what is now known as the Lewis concept of acids and bases. Experimentally and conceptually, they are an extension of the Brønsted definitions. In one broad sweep, they unleash the concept from its dependence upon hydrogen and open a broad new vista of acid-base chemistry.

The Fundamental Lewis Acid-Base Reaction

The fundamental acid-base reaction in the Lewis sense is the formation of a coordinate covalent bond between an acid and a base. The base is the electron-pair donor, the acid the acceptor. The process is called neutralization, or simply coordination. The product is a coordinated compound, coordinated complex, or adduct, made up of an acid portion and a base portion. A typical and often-cited example is the reaction of the acid boron trifluoride with the base ammonia to form the coordinated complex or adduct BF_3NH_3:

acid + base→coordinated complex



The coordinate molecule may be thought of as being made up of the acid portion BF_3 and the base portion NH_3

Classification of Lewis Acids

Bases in the Lewis system are essentially the same as those in the Brønsted system, because molecules or ions which share a pair of electrons with any other electron-pair acceptors, or Lewis acids, as a rule do also with proton.

The range of acids, however, is greatly extended by the Lewis concept; in fact, according to the Lewis definition the proton, although an important and powerful acid, is but one of many possible acids. It is apparent that for Lewis acidity there is but one requirement- at least one available unfilled orbital in a valence shell. Any species is potentially a Lewis acid which has at least one available unfilled orbital in the valence shell of one of its atoms. Lewis acids are of several types.

Simple Cations

Theoretically all simple cations are potential Lewis Acids, although their strength as acids varies within wide limits. Potassium ion (K^+) is a very weak Lewis acid, aluminium ion (Al^{3+}) a powerful Lewis acid. In general, we can expect the acid strength or coordinating ability of cations to increase with (a) an increase in positive charge on the ion, (b) an increase in nuclear charge for atoms in any horizontal period, (c) a decrease in ionic radius, and (d) a decrease in the number of shielding electron shells.

This means that Lewis acidity of simple cations tends to increase for the elements from left to right and from bottom to top in the periodic table. On the basis of the generalizations, we can predict the following representative sequences of increasing acids strength:

Order of Increasing Strength of Lewis Acids→

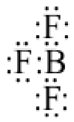
$$Fe^{2+} < Fe^{3+}$$

$$K^{+} < Na^{+} < Li^{+}$$

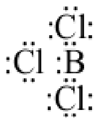
$$Li^{+} < Be^{2+} < B^{3+}$$

From the beginning to end of each of the various series of transition elements, there is a build-up of nuclear charge with simultaneous contraction of ionic radius and no increase in the number of shielding shells. As a result many of the transition element cations are strong Lewis acids and tend to form a variety of complex ions.

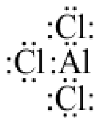
Compounds whose Central Atoms has an Incomplete Octet
Among the most important Lewis Acids are compounds whose central atom has less than a full octet of electrons. Typical examples are:



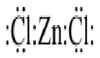
$$\begin{array}{l} \quad :\ddot{F}: \\ :\ddot{F}:\ddot{B} \\ \quad :\ddot{F}: \end{array}$$



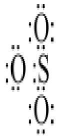
$$\begin{array}{l} \quad :\ddot{Cl}: \\ :\ddot{Cl}:\ddot{B} \\ \quad :\ddot{Cl}: \end{array}$$



$$\begin{array}{l} \quad :\ddot{Cl}: \\ :\ddot{Cl}:\ddot{Al} \\ \quad :\ddot{Cl}: \end{array}$$

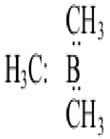


$$:\ddot{Cl}:Zn:\ddot{Cl}:$$



$$\begin{array}{l} \quad :\ddot{O}: \\ :\ddot{O}:\ddot{S} \\ \quad :\ddot{O}: \end{array}$$

$$\begin{array}{l} \quad :\ddot{Br}: \\ :\ddot{Br}:\ddot{Fe} \\ \quad :\ddot{Br}: \end{array}$$



$$\begin{array}{l} \qquad CH_3 \\ H_3C:\ \ddot{B} \\ \qquad CH_3 \end{array}$$

Strength of these Lewis Acids, in a general way increases with:

a. increase in nuclear charge of the central atom (for central atoms in the same horizontal period),
b. increase in the number and relative electronegativity of electronegative atoms attached to the central atom,

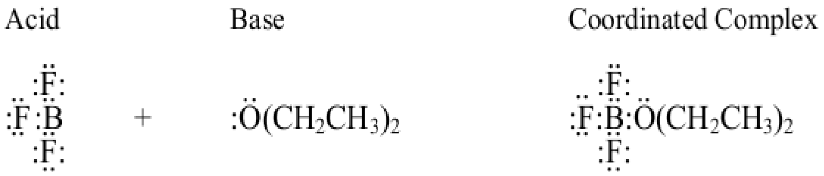
c. decrease in atomic radius of the central atom
d. decrease in number of shielding electron shells in the central atom.

These rules are by no means completely general; some anomalies, such as the increased acidity toward most bases of trimethyl boron over boron trifluoride, are difficult to explain.

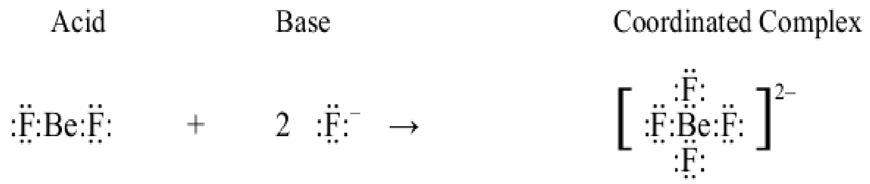
Coordination reactions of such acids are as follows:

a. Reaction of sulphur trioxide with basic oxides to form sulphate.

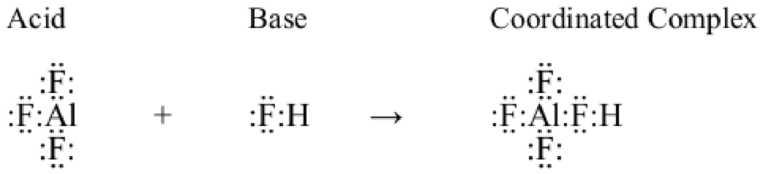
b. The formation of boron trifluorideetherate (with ethyl ether).



c. The formation of complex fluoride ions, widely used in electrolytic melts.

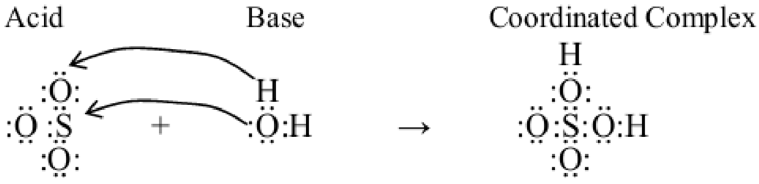


d. The formation of aluminium fluoride with hydrogen fluoride to form fluoroaluminic acid.



The fact that hydrogen fluoride acts as a base toward aluminium trifluoride suggests that the latter is an extremely strong acid.

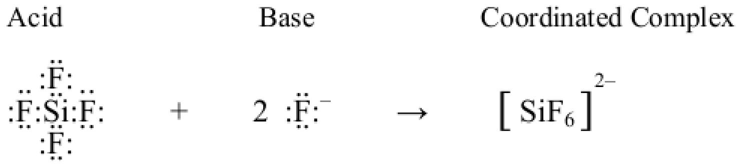
Often Lewis coordinations of this type are accompanied by a proton shift, as in the reaction of sulphur trioxide with water to form tetraoxosulphate (VI) acid:



Although the over-all reaction here is more complex, the key step is simply a Lewis acid-base reaction.

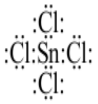
Compounds in which the Octet of the Central Atom can be Expanded

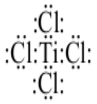
Although carbon and silicon belong to the same family of elements, silicon tetrafluoride and silicon tetrachloride are tremendously more reactive than their carbon analogues, carbon tetrafluoride and carbon tetrachloride. The explanation is straightforward- the silicon, with its vacant *d* orbitals, can act as a Lewis acid by expanding its octet. This is illustrated by the reaction of silicon tetrafluoride with fluoride ion to form fluorosilicate ion:

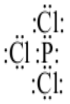


With no available *d* orbitals, carbon cannot do this, in keeping with the fact that the elements in the first period of eight in the periodic table can accommodate no more than eight electrons in their valence shell.

Actually the silicon halides typify a large group of halides which, with vacant d orbitals, can expand their octets. Some examples are:

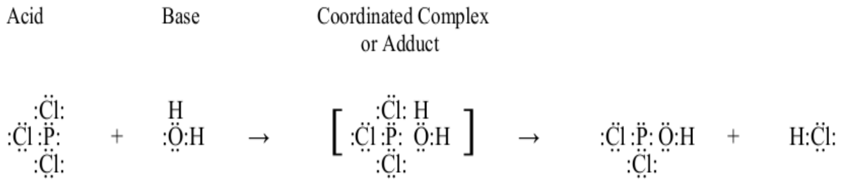




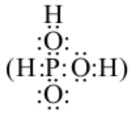


These halides tend to form adducts with halide ions and with organic bases such as ethers (R-O....-R).

Halides of this type are vigorously hydrolyzed to form an oxy-acid (or oxide) of the central atom and the appropriate hydrogen halide. This reaction depends upon the ability of the halides to act as Lewis acids. The first step in the removal of each halogen atom is undoubtedly the acid-base coordination of the acid halide with the base water. This is followed by elimination of the hydrogen halide from the adduct. The pathway or mechanism of the reaction is as follows:



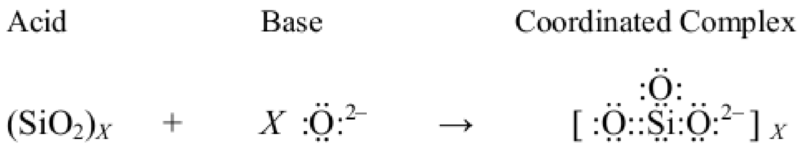
The two remaining chlorines are replaced similarly, with the ultimate formation of a total of three molecules of hydrogen chloride, and after, a proton shift, phosphorous acid. Nitrogen trichloride (NCl_3), with a central atom (nitrogen) whose octet cannot be expanded, is hydrolyzed quite differently to ammonia and hypochlorous acid:



$$\begin{array}{c} H \\ :\ddot{O}: \\ (H:\ddot{P}:\ddot{O}:H) \\ :\ddot{O}: \end{array}$$

$$NCl_3 + HOH \rightarrow NH_3 + HOCl$$

One of the most important chemical reactions in high temperature metallurgical processes is that of silica (the gangue) with basic oxide (the flux) to form silicates (the slag). This is an acid-base reaction of the acid silica (SiO_2 polymer) with the base oxide ion:

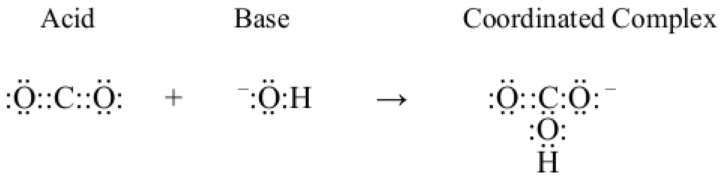


The first step in the mechanism of this reaction is undoubtedly the coordination of oxide ion with silicon in the SiO_2 polymer; this requires an expansion of the silicon octet. Similar Lewis acid-base reactions are of fundamental importance in the manufacture of glass.

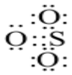
Compounds having Multiply-bonded Acid Centres

There are many compounds, particularly organic, in which a multiply-bonded atom can accept a share in an electron pair with a synchronous shift in a pair of electrons of the multiple bond. By a slight extension of the Lewis concept, we can classify such compounds as Lewis acids. Although the atom involved does not, in a strict sense, have an unfilled orbital nevertheless an orbital is made available as the incoming base forces the intramolecular electron pair shift.

A familiar example is carbon dioxide. Consider its neutralization by hydroxide ion to hydrogen carbonate ion:

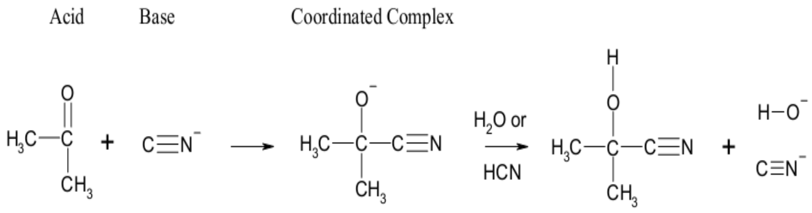


Carbon dioxide accepts a pair of electrons from the base hydroxide ion in the process of coordination. The base attacks the *less electronegative* (and therefore more positive) of the double-bonded atoms and pushes a pair of electrons to the *more* electronegative atoms. In fact, if resonance structures of the type



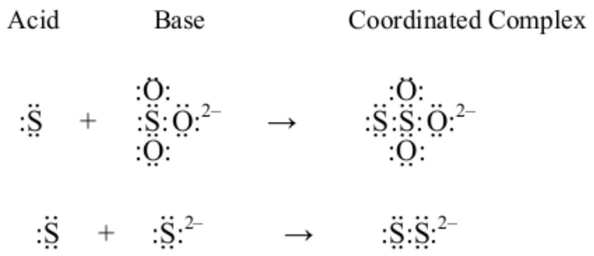
are accepted for sulphur trioxide, the acid reactions of sulphur trioxide may be regarded as being of this same type.

All the typical addition reactions of alkanals (RCOH) and alkanones (RCOR') fall into this class, In the addition of hydrogen cyanide to alkanone to form alkanone cyanohydrin, for example, the first step is the coordination of the base cyanide ion with the acid alkanone:



Elements with an Electron Sextet

To the extent that oxygen and sulphur atoms participate directly in chemical reactions, they may be regarded as Lewis acids. On this basis, the oxidation with sulphur of sulphite to thiosulphate and of sulphide to polysulfide ion can be classified as acid-base reactions:



Dissociation of water

The ability of acids to react with bases depends on the tendency of hydrogen ions to combine with hydroxide ions to form water. This tendency is very great, so the reaction below is practically complete.

$$H^{+}+ OH^{-}\rightarrow H_2O$$

No reaction, however, is really 100 percent complete; at *equilibrium* (when there is no further net change in amounts of substances) there will be at least a minute concentration of the reactants in the solution.

Another way of expressing this is to say that any reaction is at least slightly *reversible*. This means that in pure water, the reaction

$$H_2O\rightarrow H^{+}+ OH^{-}$$

will proceed to a very slight extent. Experimental evidence confirms this: the most highly purified water that chemists have been able to prepare will still conduct electricity very slightly. From this electrical conductivity it can be calculated that the equilibrium concentration of both the H+ ion and OH¡ ions is almost exactly 1.00×10^{7} at 25^{o}C. This amounts to one H_2O molecule in about 50 million being dissociated.

The degree of dissociation of water is so small that you might wonder why it is even mentioned here.

The reason it is important arises from the need to use the concentrations for H+ and OH^-in pure water to define the *equilibrium constant*

$$[H^+][OH^-] = 10^{-7} \text{ x } 10^{-7} = K_w = 10^{-14}$$

in which the square brackets [ ] refer to the concentrations of the substances they enclose.

Note: The product of the hydrogen ion and hydroxide ion concentrations in any aqueous solution will always be 1.00 $x10^{-14}$ at 25°C.

In other words,

$$[H+][OH-] = 1.00\ x10^{-14}$$

This expression is known as the *ion product* of water, and it applies to *all aqueous solutions*, not just to pure water. The consequences of this are far-reaching, because it implies that if the concentration of H+ is large, that of OH¡ will be small, and *vice versa*. This means that H^+ ions are present in *all* aqueous solutions, not just acidic ones. This leads to the following important definitions, which you must memorize:

acidic solution: $[H+] > [OH^-]$
alkaline solution: $[H+] < [OH^-]$
neutral solution: $[H+] = [OH^-]$ (=1.00 $x10^{-7}$Mat 25°C)

Acidity and pH scale

Acidic strength means the tendency of an acid to give H_3O^+ or H^+ ions in water and basic strength means the tendency of a base to give $OH^–$ ions in water. So, the more the tendency of the substance to give H^+ or OH^- ions, the more will be the acidic or basic strength of the substance.

The concentration of H^+ ions is written in a simplified scale introduced by Sorenson known as pH scale. pH is negative logarithm of activity of H^+ ions.

Therefore,

$$pH = -\log_{10}[H^+]$$

Or conversely,

$$[H^+] = 10^{-pH}$$

We can also define as

$$pOH = -\log_{10}[OH^-]$$

and

$$pK_w = -\log K_w$$

It follows then that

$$pH + pOH = pK_w \text{ (= 14.0 in pure water at 25}^{o}\text{C)}$$

In a neutral solution at 25°C, the pH will be 7.0; a higher pH corresponds to an alkaline solution, a lower pH to an acidic solution. In a solution with $[H^+] = 1M$, the pH would be 0; in a 0.00010*M* solution of H^+, it would be 4*:*0. Similarly, a 0.00010*M* solution of NaOH would have a pOH of 4.0, and thus a pH of 10.0. It is very important that you thoroughly understand the pH scale, and be able to convert between $[H^+]$ or $[OH^-]$ and pH in both directions.

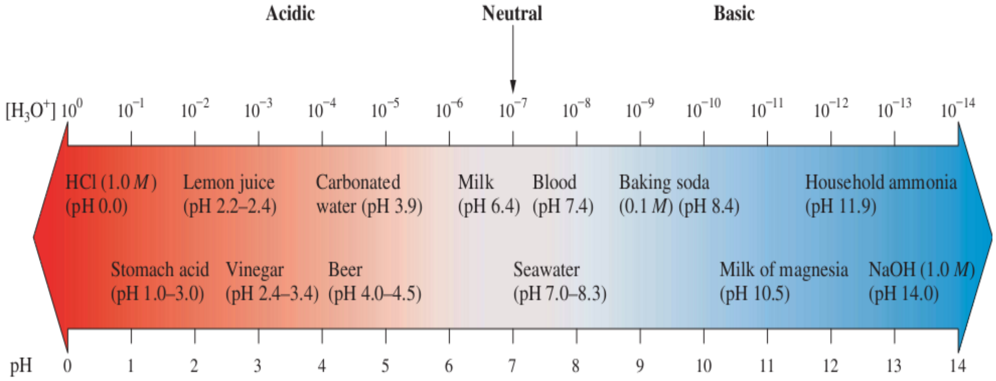


Figure 9.3: *pH scale of neutral, acidic and basic solutions*

Neutralization

Acids and bases react with one another to yield two products: water, and an ionic compound known as a *salt*. This kind of reaction is called a *neutralization* reaction.

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$KOH + HNO_3 \rightarrow KNO_3 + H_2O$$

These reactions are both exothermic; although they involve different acids and bases, it has been determined experimentally that they all liberate the same amount of heat (57.7 kJ) per mole of H^+ neutralized. This implies that all neutralization reactions are really the one net reaction:

The “salt” that is produced in a neutralization reaction consists simply of the anion and cation that were already present. The salt can be recovered as a solid by evaporating the water.

Salts

Salts are formed when an acid reacts with a base

For instance,

$$H_2SO_4 + NaOH \rightarrow Na_2SO4 + H_2O$$

Here sodium sulphate (Na2SO4) is the salt formed. Salts are ionic compounds.

The metal ion is provided by the base (in this case sodium ions, Na+).

The non-metal ion is provided by the acid (in this case sulphate ions, SO_4^{2-}).

Note: Ammonia (NH3) is an unusual base - it does not contain a metal. It forms **ammonium salts**, containing the ammonium ion, $NH4^+$. e.g.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Soluble and Insoluble Salts

Many ionic salts are soluble in (cold) water. It is useful to know whether or not a salt is soluble in water, as this will influence your choice of method for making it.

Soluble Salts

All common potassium, sodium and ammonium salts
All nitrates
All common ethanoate
All common chlorides, except lead and silver chlorides
All common sulphates, except lead, barium and calcium tetraoxosulphate (*VI*)

Soluble salts can be made in four different ways:

1) Acid + Metal →Salt + Hydrogen
2) Acid + Base →Salt + Water
3) Acid + Trioxocarbonate (IV) →Salt + Water + Carbondioxide
4) Acid + Alkali →Salt + Water

Making Insoluble Salts

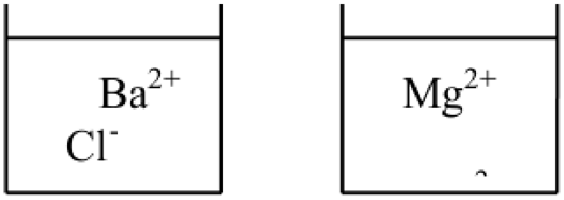
Insoluble salts cannot be prepared by acid-base reactions in the same way as soluble salts.

Insoluble salts are prepared by **precipitation**. This involves mixing solutions of two soluble salts that between them contain the ions that make up the insoluble salt. Here is an example:

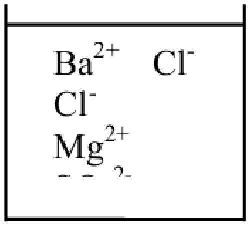
Barium Chloride + Magnesium Tetraoxosulphate (VI) → Barium tetraoxosulphate (VI) + Magnesium Chloride
(soluble salt) + (soluble salt) → (insoluble salt) + (soluble salt)

$$BaCl + MgSO_4 \rightarrow BaSO_4 + MgCl_2$$

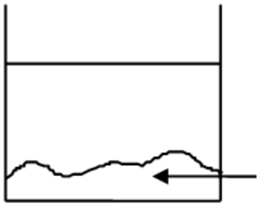
When the two solutions are mixed, a white solid **precipitate** of barium tetraoxosulphate (VI) is formed. Let us consider what happens to the ions involved in the reaction:



1. At the start, the ions of each soluble salt move about freely in solution, in their separate containers.



2. After mixing, the ions of the two solutions are free to collide with each other, so new combinations of ions are possible.



3. If one of the new combinations of ions is an insoluble salt, it will be precipitated from the solution. The other ions simply remain in solution – they are spectator ions, and play no part in the reaction.

Once the reaction is complete, the precipitate can be filtered off, washed with distilled water and dried.

This method can also be used to prepare many insoluble metal hydroxides and trixocarbonates.

All common hydroxides/carbonates are insoluble except sodium, potassium and ammonium hydroxides/carbonates.

Types of Salts

Normal Salts

Normal salts are formed when all the replaceable hydrogen ions in the acid have been completely replaced by metallic ions.

$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$H_2SO_4 + ZnO \rightarrow ZnSO_4 + H_2O$$

Normal salts are neutral to litmus paper.

Acid salts

Acid salts are formed when replaceable hydrogen ions in acids are only partially replaced by a metal. Acid salts are produced only by acids containing more than one replaceable hydrogen ion. Therefore an acid with two replaceable ions, e.g. H_2SO_4 will form only one acid salt, while acid with three replaceable hydrogen ions, e.g. H_3PO_4 will form two different acid salts.

$$H_2SO_4 + KOH \rightarrow KHSO_4 + H_2O$$
$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$$

An acid salt will turn blue litmus red. In the presence of excess metallic ions an acid salt will be converted into a normal salt as its replaceable hydrogen ions become replaced.

Basic Salts

Basic salts contain the hydroxide ion, OH^-. They are formed when there is insufficient supply of acid for the complete neutralization of the base. A basic salt will turn red litmus blue and will react with excess acid to form normal salt.

$$Zn(OH)_2 + HCl \rightarrow ZnOHCl + H_2O$$
$$Zn(OH)Cl + HCl \rightarrow ZnCl + H_2O$$
$$Mg(OH)_2 + HNO_3 \rightarrow Mg(OH)NO_3 + H_2O$$
$$Mg(OH)NO_3 + HNO_3 \rightarrow MgNO_3 + H_2O$$

Double Salts

Double salts are formed when two simple salts crystallize together in definite, simple molecular proportions. They have their own crystal form, which need not be the same as that of either of their component salts. They are a phenomenon of the solid state; in solution they are decomposed completely, or nearly so, into the ions of their component salts. In this respect double salts are distinguished from complex salts, which give complex ions of their own in solution. Double salts are extremely numerous. Typical examples include:

$CuSO_4(NH_4)_2SO_4.6H_2O$
$FeSO_4(NH_4)_2SO_4.6H_2O$
$CuCl.KCl.H_2O$

Hydrolysis of Salts

Hydrolysis refers to a reaction with water (e.g. splitting water into H^+ and OH^-). When salts are added to water, pH can change, e.g. when Na_3PO_4 is added to water, ions form

$$Na_3PO_4 \rightarrow 3Na^+ + PO_4^{3-}.$$

These ions may react with H_2O, affecting the pH

$$PO_4^{3-} + H^+ \Leftrightarrow HPO_4^{2-}$$
$$Na^+ + OH^- \Leftrightarrow NaOH$$

If the anion (negative) reacts to remove lots of H^+ but the cation (positive) removes very little OH^-, then H^+ will decrease and the solution will be basic.

The Degree of Hydrolysis

$$PO_4^{3-} + H^+ \Leftrightarrow HPO_4^{2-}$$

$$Na^+ + OH^- \Leftrightarrow NaOH$$

The problem with writing equilibriath is way is we do not know the strength of the reactions. However, if we reverse the reaction we can look up Ka and Kb values:

$HPO_4^{2-} \leftrightarrow PO_4^{3-}$ Ka = $4.5x10^{-13}$
NaOH↔Na^+ + OH^- Kb = 55

Small K_a: Few products; adding PO_4^{3-} shift left.
Large K_b: mostly products; Na^+ has little affect. Thus, adding Na_3PO_4 will cause more H^+ to be removed, resulting in a basic solution.

Theoretically, using K_a and $_{Kb}$ values you could predict the exact pH resulting from a certain salt being added to distilled water. However, you only need to be able to predict if a solution will be acidic, basic, or neutral.

Note: You cannot judge the pH change solely on the difference between K_a and K_b. Other factors are involved (e.g. the formula of the compound and its molar mass). Several variations for writing equilibriums exist. However, focusing on how the H^+/OH^-balance of water is affected is easiest.

Prediction of Whether a Salt Solution Is Acidic, Basic, or Neutral

When the CN^- ion hydrolyzes, it produces the conjugate acid, HCN. Hydrogen cyanide, HCN, is a weak acid. That means that it tends to hold on to the proton strongly (does not ionize readily). In other words, the cyanide ion, CN^-, tends to pick up a proton easily, so it acts as a base. This argument can be generalized: The anions of weak acids are basic. On the other hand, the anions of strong acids have hardly any basic character; that is, these ions do not hydrolyze. For example, the Cl^- ion, which is conjugate to the strong acid HCl, shows no appreciable reaction with water.

$$Cl^- + H_2O \rightarrow \text{no reaction}$$

Now consider a cation conjugate to a weak base. The simplest example is the NH_4^+ ion, which we just discussed. It behaves like an acid. *The cations of weak bases are acidic. On the other hand, the cations of strong bases (metal ions of Groups 1 and 2 elements – except Be) have hardly any acidic character; that is, these ions do not hydrolyze.*

For example,

$$Na^+ + H_2O \rightarrow \text{no reaction}$$

Aqueous metal ions, other than the cations of the strong bases, usually hydrolyze by acting as acids. These ions usually form hydrated metal ions. For example, the aluminium ion Al^{3+} forms the hydrated ion $Al(H_2O)_6^{3+}$. The bare Al^{3+} ion acts as a Lewis acid, forming bonds to the electron pairs on O atoms of H_2O molecules.

Because the electrons are drawn away from the O atoms by the Al atom, the O atoms in turn tend to draw electrons from the O-H bonds, making them highly polar. As a result, the H_2O molecules in $Al(H_2O)_6^{3+}$ are acidic. The $Al(H_2O)_6^{3+}$ ion hydrolyzes in aqueous solution by donating a proton (from one of the acidic

H_2O molecules on the ion) to water molecules in the solvent. After the proton leaves the hydrated metal ion, the ion charge is reduced by 1 and an H_2O molecule on the ion becomes a hydroxide ion bonded to the metal. Thus, the formula of the ion becomes $Al(H_2O)_5(OH)^{2+}$.

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+$$

To predict the acidity or basicity of a salt solution, you need to examine the acidity or basicity of the ions composing the salt. Consider potassium acetate, $KC_2H_3O_2$. The ions are K^+ and $C_2H_3O_2^-$ (ethanoate ion). Potassium is a Group 1 element, so K^+ does not hydrolyze. However, the ethanoate ion is the conjugate of acetic acid, a weak acid. Therefore, the ethanoate ion is basic.

Here are a set of rules for deciding whether a salt solution will be neutral, acidic, or basic. These rules apply to normal salts (those in which the anion has no acidic hydrogen atoms).

1. **A salt of a strong base and a strong acid.** The salt has no hydrolysable ions and so gives a neutral aqueous solution. An example is NaCl.
2. **A salt of a strong base and a weak acid.** The anion of the salt is the conjugate of the weak acid. It hydrolyzes to give a basic solution. An example is NaCN.
3. **A salt of a weak base and a strong acid.** The cation of the salt is the conjugate of the weak base. It hydrolyzes to give an acidic solution. An example is NH_4Cl.
4. **A salt of a weak base and a weak acid.** Both ions hydrolyze. Whether the solution is acidic or basic depends on the relative acid–base strengths of the two ions. To determine this, you need to compare the K_a of the cation with the K_b of the anion. If the K_a is larger, the solution is acidic. If the K_b is larger, the solution is basic. Consider solutions of ammonium formate, NH_4CHO_2. These solutions are slightly acidic, because the K_a for NH_4^+

(=5.6 x10^{-10}) is somewhat larger than the K_b for formate ion,CHO_2^-(= 5.9 x 10^{-11}).

Example

Decide whether aqueous solutions of the following salts are acidic, basic, or neutral: a) KCl; b) NaF; c) $Zn(NO_3)_2$; d**)** NH_4CN.

Solution

a. KCl is a salt of a strong base (KOH) and a strong acid (HCl), so none of the ions hydrolyze, and a solution of KCl is **neutral.**

b. NaF is a salt of a strong base (NaOH) and a weak acid (HF), so a solution of NaF is **basic** because of the hydrolysis of F^-. (You assume HF is a weak acid, because it is not one of the common strong acids).

c. $Zn(NO_3)_2$ is the salt of a weak base ($Zn(OH)_2$) and a strong acid (HNO_3), so a solution of $Zn(NO_3)_2$ is **acidic.** Note also that $Zn^{2+}$is not an ion of a Group 1 or Group 2 element, so you can expect it to form a metal hydrate ion that hydrolyzes to give an acidic solution.

d. NH_4CN is a salt of a weak base (NH_3) and a weak acid (HCN). Therefore, to answer the question, you would need the K_a for $NH_4^+$and the K_b for CN^-.

Although these are listed in some tables, more frequently they are not. However, as you will see later in this section, values are easily calculated from the molecular substances that are conjugates (NH_3 and HCN). The K_a for $NH_4^+$is 5.6 x10^{-10}, and the K_b for $CN^-$is 2.0 x10^{-5}. From these values, you conclude that a solution of NH_4CN is **basic.**

Answer Check

You can check your answers by writing hydrolysis reactions for each of the ions in solution. If either or both of these reactions produce a weak acid or base, the solution will not be neutral. You then can analyze the products of these reactions for OH^- and/or H_3O^+ to check your final answer (keep in mind you may have to look at the K_a and K_b information as well). For example, using NaF from part b, the hydrolysis reactions for the ions that make up this salt are

$$Na^+ + H_2O \rightarrow \text{no reaction}$$
$$F^- + H_2O \rightarrow HF + OH^-$$

Because there was no reaction for the Na^+, and OH^- was produced by the hydrolysis of F^-, the solution containing the NaF salt is basic.

Buffer

A **buffer** is a solution characterized by the ability to resist changes in pH when limited amounts of acid or base are added to it. If 0.01 mol of hydrochloric acid is added to 1 L of pure water, the pH changes from 7.0 to 2.0 – a pH change of 5.0 units. By contrast, the addition of this amount of hydrochloric acid to 1 L of buffered solution might change the pH by only 0.1 unit. Biological fluids, such as blood, are usually buffer solutions; the control of pH is vital to proper functioning of these fluids. The oxygen-carrying function of blood depends on its being maintained very near a pH of 7.4. If the pH were to change by a tenth of a unit, the capacity of the blood to carry oxygen would be lost.

Buffers contain either a weak acid and its conjugate base or a weak base and its conjugate acid. Thus, a buffer solution contains both an acid species and a base species in equilibrium. To understand the action of a buffer, consider one that contains approximately equal molar amounts of a weak acid HA and its conjugate base A^-. When a strong acid is added to the buffer, it supplies hydroxonium ions that react with the base A^-.

$$H_3O^+ + A^- \rightarrow HA + H_2O$$

On the other hand, when a strong base is added to the buffer, it supplies hydroxide ions. These react with the acid HA.

$$OH^- + HA \rightarrow H_2O + A^-$$

A buffer solution resists changes in pH through its ability to combine with both H_3O^- and OH^- ions.

Blood, as a buffer solution, contains H_2CO_3 and HCO_3^-, as well as other conjugate acid–base pairs. A buffer frequently used in the laboratory contains varying proportions of the conjugate acid–base pair $H_2PO_4^-$ and HPO_4^{2-}.

Buffers also have commercial applications. For example, the label on a package of artificial fruit juice mix says that it contains "citric acid to provide tartness (acidity) and sodium citrate to regulate tartness." A solution of citric acid and its conjugate base, citrate ion (provided by sodium citrate), functions as an acid–base buffer, which is what "to regulate tartness" means. The pH of the buffer is in the acid range.

Two important characteristics of a buffer are its pH and its buffer capacity, which is the amount of acid or base the buffer can react with before giving a significant pH change. Buffer capacity depends on the amount of acid and conjugate base in the solution. Figure 9.4 illustrates the change in pH of a buffer solution containing 1.0 mol of acetic acid and 1.0 mol of acetate ion to which varying amounts of H_3O^+ and OH^- are added. This buffer changes less than 0.5 pH unit as long as no more than 0.5 mol H_3O^-

or OH- ion is added. Note that this is one half (or less than one-half) the amounts of acid and conjugate base in the solution.

The ratio of amount of acid to amount of conjugate base is also important. Unless this ratio is close to 1 (between 1:10 and 10:1), the buffer capacity will be too low to be useful.

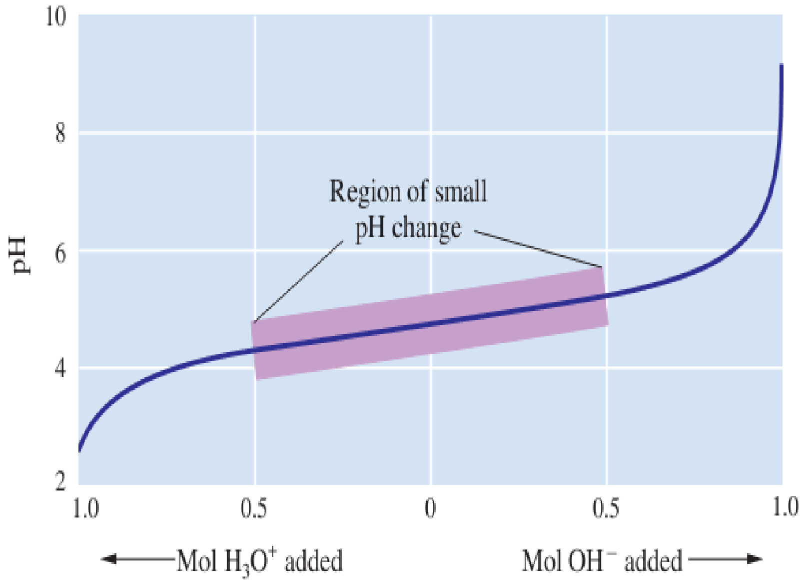


***Figure 9.4**: Effect of added acid or base on buffer solution*

Study Questions

1. Define an acid and a base according to the Brønsted-Lowry concept. Give an acid–base equation and identify each species as an acid or a base.

2. What is meant by the conjugate acid of a base?

3. Give the conjugate base to each of the following species regarded as acids.
   a. HPO_4^{2-}
   b. H2S
   c. HNO_2
   d. $H_2AsO_4^-$

4. Which of the following are strong acids? Which are weak acids? (a) $HC_2H_3O_2$; (b) HClO; (c) HCl; (d) HNO_3; (e) HNO_2; (f) HCN.

5. In the following reactions, label each reactant as a Lewis acid or a Lewis base.

$$BeF_2 + 2F^- \to BeF_4^{2-}$$
$$SnCl_4 + 2Cl^- \to SnCl_6^{2-}$$

6. Calculate the hydronium-ion concentration at 25°C in a 1.3 x 10^{-2}MBa$(OH)_2$ solution. The pH of a solution is 9.55 at 25°C. What is the hydroxide-ion concentration in the solution?

7. Which is more acidic, a solution having a pH of 4 or one having a pH of 5?

8. Calculate the pH of a 0.01M HNO_3 solution?

9. Obtain the pH corresponding to the following hydroxide ion concentrations.
   a. 5.25 x 10^{-9}M **b.** 8.3 x 10^{-3}M
   c. 3.6 x10^{-12}M**d.** 2.1 x 10^{-8}M

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