

THE CHEMISTRY OF COMBUSTION

INTRODUCTION

Chemical reaction occurs continuously in the atmosphere, in factories, in vehicles, in the environment and in our bodies. In a chemical reaction, one or more kinds of matter are changed in a new kind – or several new kinds – of matter.

Life as we know it, could not exist without these processes: plants could not photosynthesize, cars could not move, pudding could thicken, muscles could not burn energy, glue could not stick and fire could not burn. With these few jesters in mind, we can define chemistry.

CHEMISTRY

This is said to be the (study) science of composition, structure and the properties of substances and how they react with other substances to form new substances with the addition or removal of energy in any of its forms.

There are two processes by which changes take place in the subject matter of chemistry:

- Physical
- Chemical

It is important to realize that many aspects of substance are not included in the subject matter of chemistry. For instance, water may be cooled, and at a certain temperature freezes and forms ice; the temperature at which this happens is (0°) which is an important fact about water, but this is physical rather than a chemical property. This is mainly because the process of freezing water is merely changing from the liquid state to the solid and is not changing into a new substance. Freezing is therefore regarded as a physical rather than a chemical process.

On the other hand, when magnesium ribbon is heated in a flame, it burns brilliantly and the white powder which is formed is a completely new substance; a chemical process has taken place in this case.

There are several important differences between physical and chemical processes:-

Figure i. PHYSICAL AND CHEMICAL PROCESSES	
PHYSICAL	CHEMICAL
1. No new substance is formed	1. A new substance is always formed
2. Usually easily reversible	2. Not easily reversible
3. Energy change involved is usually small	3. Large energy change may be involved

THE CLASSIFICATION OF SUBSTANCES

Matter is that which has weight and occupies space. Matter is the name given to all substances and can exist in any one of three states – **solid liquid or gas**. Some forms of matter eg. water may be found quite commonly in all three states, but many substances at normal temperature are found only in one or two of the states. Because the total number of substances is so large, running into millions, it is helpful to think about them grouped into different classes rather than as individuals.

Substances can be grouped into three classes:

- i. elements
- ii. mixtures
- iii. compounds

Elements

Element can be defined as substances that cannot be broken down by chemical treatment into any simpler substances. Elements consist of atom of the same type. Out of millions of substances that exist, this statement applies to about a hundred. Iron for example, is a familiar substance that part in many chemical processes. If it is left for some time in a moist atmosphere, it will change into a new substance, rust. Analysis of the rust shows that along with the iron, it also contains oxygen. Again, iron may be dissolved in sulphuric acid. If the resulting liquid is evaporated, green crystals are obtained. If these crystals are analyzed, they will be found to contain not only iron but sulphur and oxygen. In these two

reactions and in all other reactions in which iron takes part, the iron is converted into a more complicated substance. Apparently there is not chemical treatment which can convert iron into a simpler substance than it already is. Substances such as iron are placed into a class called **elements**. By using these simplest substances as building blocks and by putting them together in two different ways, all other substances known to exist can be made.

The group of elements may be divided into sub groups in several different ways – for example into solids (such as iron and sulphur), liquids (such as mercury and bromine), and gases (such as oxygen and nitrogen). Another division is into metals (such as iron and magnesium) and non-metal (such as sulphur and oxygen)

Mixtures and Compounds

A **mixture** is the product of mixing two or more substances in which these substances retain their properties. If iron powder and sulphur are put in a test tube and the content shaken, a mixture of iron and sulphur is produced.

The points listed in the left hand column of table ii. apply to this and other mixtures.

However, if the mixture is gently heated, after a time, the content of the tube begins to produce so much heat that they become red-hot. If the content is allowed to cool and then examine, it is found that the points listed in the right hand column of table ii apply. In fact, the material is no longer a mixture of iron and sulphur but a **compound** given the name *ferrus sulphide*.

Therefore, we can define compounds as being made up of elements, but looks and behave quite differently as a rule from any of its components or as a chemical combination of two or more substances which look and behave quite differently than any of its component element.

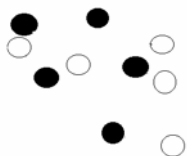
Thus, element can be placed together in two different ways, to make a mixture or a compound, many of which contains several elements, rather than only two, as in the above example. Also, compounds may themselves be mixed together. Sea water, many rocks and minerals, and on a purely chemical level, the human body are mixtures of compounds.

Figure ii. MIXTURES AND COMPOUNDS	
MIXTURES	COMPOUNDS
1. No large energy changes on formation	1. Often large energy changes on formation
2. Not usually homogeneous	2. Homogeneous
3. Separable by physical methods	3. Separable only by chemical methods
4. Variable composition	4. Fixed compositions
5. Properties are the sum of constituents	5. Properties differ from those constituents

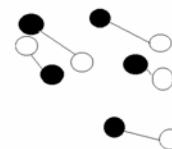
ATOMS AND MOLECULES

In order to properly explain the formation of compounds, it is necessary to refer to the atomic theory of matter. According to the theory, a sample of an element such as iron or sulphur is a collection of many millions of tiny iron or sulphur atoms and the chemical behaviour of these elements is a reflection of the behaviour of the individual atoms. When the iron and sulphur are mixed together, the iron and the sulphur atoms are not altered in any way so that no change in behaviour is observed. The iron atoms in the mixture go on behaving in the same manner as the iron atom in pure iron and the same applies to the sulphur atoms.

The compound of iron and sulphur however, behaves in a completely different way from either iron or sulphur, so we have to conclude that separate atoms of iron and sulphur no longer exist in the compound. A reasonable explanation for this is that the iron atoms and the sulphur atoms have joined to form larger particles called **molecules** in some ways such as this



Iron and sulphur atoms in the Mixture (the atoms are separate)



Ferrous sulphur molecules in the compound (bonds are formed between the atoms).

Since there are no longer any separate iron and sulphur atoms in the compound, the behaviour of these is no longer shown and instead we observe the different behaviour of the new ferrous sulphur molecules.

Molecules of some compounds contain many more than two atoms combined together. The molecules of substances such as wool and cotton and of many plastics, contain thousands of atom.

However, most elements like iron and sulphur can be regarded as an assembly of atoms but certain elements exist as assemblies of molecules. Examples such as nitrogen, oxygen, chlorine and hydrogen are all encountered in the form of molecules, each containing two atoms of the element combined.

COMBUSTION AND EXOTHERMIC REACTIONS

Combustion

There are many ways of defining the chemically complex process called combustion. Essentially it is **a chemical reaction or a series of reaction in which heat and light are evolved.**

All combustion or burning reactions involve the combination with oxygen or some other supporter of combustion. It could also be defined as **the rapid oxidation of a substance, liberating heat and light and combustion by-products (smoke, gases etc.)**

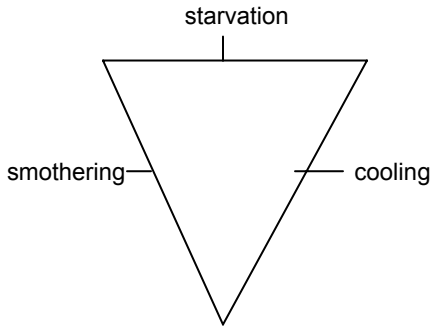
When the rate of reaction is very slow, only heat energy is evolved as in the case of iron rusting. Combustion represents a rapid rate of reaction in which light is emitted as well as heat. And if however the reaction is extremely rapid an explosion may be or is likely to be present.

Factors Involved in Combustion

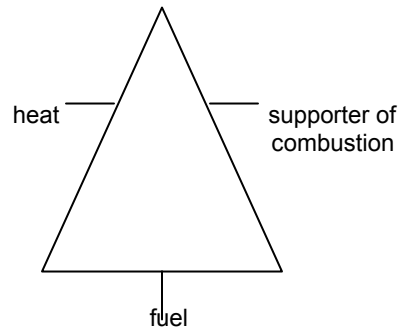
One way of discussing combustion is by using the triangle of combustion in figure iii which has evolved overtime into the fire tetrahedron. It is considered that for combustion to occur three factors are necessary: a fuel, heat and a supporter of combustion. The stable geometric form of the triangle suggests that combustion will continue as long as these three factors are present. The removal of any one of these factors will result in the collapse of the triangle and combustion will cease.

Figure iii.

TRIANGLE OF EXTINCTION



TRIANGLE OF COMBUSTION



The Fire Tetrahedron

Modern fire science has recognized that in order to support flaming combustion a fourth element must be added to what was previously known as the fire triangle. In addition to fuel, heat, and oxygen, a chemical chain reaction is required to continue flaming combustion. The addition of this fourth element graphically creates a pyramid structure that is called **The Fire Tetrahedron**.

Fuels

Fuels exist as solids, liquids or gases. In fact, material which can be oxidized may become fuel and the size and shape will influence the ease of combustion. The burning of most material produces flame. This occurs when gases or vapor given off by a liquid or solid material are ignited. There are however, instances of solid state burning in which surface burning occurs with little or no visible flame. Most of the substances that burn are of the class known as **organic chemicals** that is substances that contain carbon. There is a very large number of these including gases such as methane, liquids such as benzene and toluene and solids such as phenol and naphthalene. In addition to these, many metals burn particularly when in the form of dusts or powders and so do a few non-metals including hydrogen, carbon, sulphur and phosphorus. The physical properties of fuels including their size and shape will influence the ease of ignition and rate of burning. Some of the properties to be considered are:

- flash point
- fire point
- ignition temperature
- boiling point
- flammable or explosive limits
- specific gravity
- vapour gravity
- water solubility

- toxicity
- reactivity

The Supporter of Combustion

The supporter of combustion in the case of most fires is oxygen. This is the most uncontrollable leg of the triangle. However, in some situation, particularly in industry, there are several other possibilities of combustion. These include chlorine, a very common industrial chemical, and also fluorine, bromine, sulphur

and even nitrogen. Oxygen supports combustion but does not burn. There is normally 21% of oxygen in the air, however, the lower limits required for combustion is 6% - 10%, while 15% - 16% is the lower limits for free burning. If we should increase the oxygen level over 21%, the rate of burning would speed up significantly.

The amount of heat necessary to bring about combustion is that which is enough to raise the temperature of at least some of the fuel to its ignition temperature in the particular circumstance at the time. This will depend on such factors as the physical chemical nature of the fuel.

Most solids and liquids have to be heated above normal temperature before flammable vapours are emitted. In discussing combustion of such materials, several terms are used which are defined below:

Flash Point - is the lowest temperature at which there is sufficient vaporization of the substance to produce a vapour which will flash momentarily when a flame is applied. This temperature will be affected by atmospheric pressure and in some fire situations, will result in a reduction of flash-point temperature.

Fire Point - may be defined as the lowest temperature at which the heat from the combustion of a burning vapour is capable of producing sufficient vapour to enable combustion to continue. It will be seen that the difference between flash point and fire point is that the flash point temperature is only required to produce vapour to enable a momentary flash to take place, whereas the fire point temperature has to be high enough to produce sufficient vapour to sustain the reaction so that substance continues to burn independently of the ignition source.

Spontaneous Ignition Temperature - is the lowest temperature at which the substance will ignite spontaneously. That is the substance will burn

without the introduction of a flame or other ignition source. This is sometimes referred to as the **ignition temperature**. This implies that

under certain conditions, some materials undergo spontaneous combustion.

Spontaneous Combustion - certain materials, especially organic materials based on carbon may react with oxygen at room temperature. If the fuel is a good thermal insulator, the heat generated in such a reaction cannot escape. The temperature rises, which increases the rate of reaction and the situation escalates. Eventually the ignition temperature is reached and true combustion occurs. Compounds such as linseed oil contain carbon double bonds which are very prone to this type of reaction.

An **Exothermic Reaction** - is a chemical reaction in which heat is produced. Most chemical reactions that take place spontaneously are of this type. It follows from the definition of combustion that all combustion reactions are exothermic.

An **Endothermic Reaction** is a chemical reaction in which heat is absorbed.

Explosion is defined as a violent and rapid chemical change in which a substance, solid, liquid or gas, is converted into gases at a high temperature, the volume of gases being much greater than the bulk of the original substance.

SOURCES OF HEAT

The heat required for combustion can be generated from a number of different sources which fall under two broad headings:

Figure iv. Sources of Heat	
Chemical	Mechanical
a. Heat of combustion b. Spontaneous heating c. Heat of decomposition d. Heat of solution	a. Frictional heat b. Friction sparks c. Heat of compression

In addition to the chemical and mechanical sources, heat is also produced by electricity (including heat from arching and lighting), and nuclear fission and fusion.

TRANSMISSION OF HEAT

Heat travels from a high region of high temperature to a region of low temperature. This is true no matter how small the temperature difference. There are four methods by which heat travels. These are – **direct burning, conduction, convection and radiation.**

Conduction - may occur in solids, liquids and gases although it is most clearly present in solids. In this method, heat energy is passed on from one molecule to the next. The ability to conduct heat (thermal conductivity) varies between materials. Most metal conduct heat relatively easy and are therefore classed as good conductors. In fire situations, thermal conductivity is important in terms of the danger of fire spread of heat conducted along it.

Convection - occurs only in liquid gases. When a liquid or gas is heated, it expands and therefore becomes less dense. The lighter fluid rises, being displaced by colder and therefore denser fluid. This in turn becomes heated and so a circulation is set up. Heat energy is carried throughout the fluid by actual movement of molecules until a state uniform temperature is reached.

Radiation – this method of heat transmission does not involve any contact between bodies and is independent of any material in the intervening space but involve the transfer of heat through infrared rays and is one of the major sources of fire spread. This heat is transmitted in straight lines. Heat from the sun passes through empty space to warm the earth and the heat from a heater placed at a high level in a room can be felt underneath the heater where neither conduction nor convection can carry it.

FIRE

A rapid chemical combination of fuel and oxygen in the presence of heat, accompanied by the production of heat, light and combustion by-products (smoke, gases etc.)

PHASES OF A FIRE

First Phase – Incipient

Oxygen content 20% - 21% with ceiling temperatures of approximately 37° C°. At this stage the products of combustion are water vapour, carbon dioxide and sulphur dioxide, and hot gases rising. Smoldering fires may last for a few seconds to several hours before breaking into flames. A large volume of smoke will be present until flaming starts and then progress is rapid.

Second Phase – free burning, flame producing or steady state

At this stage the oxygen content is 15% - 19% and the ceiling temperatures are above 537°C and the products of combustion are water vapour, carbon dioxide, carbon monoxide and sulphur dioxide. There are large quantities of dark grey smoke and rapid destruction of combustible materials. It is at this point that **flash over** occurs. Flash over is when room and all its contents reach their ignition temperature and the area becomes fully involved in fire. Flame is now rapid.

Third Phase – smoldering

Oxygen content is less than 15% - 16% and ceiling temperature is above 815° C and soot is now added to the products of combustion. Dense, dark flammable smoke and toxic flammable gases are being emitted and a back draft or smoke explosion is now possible.

Some typical indications of a back draft are:

- a. little flame
- b. high temperature
- c. the smoke under pressure will “puff or breathe”
- d. smoke colour is very dark and dirty or yellow grey just prior to back draft
- e. smoked stained windows
- f. muffled sounds
- g. rapid inward movement of air when an opening is made

CLASSIFICATION OF FIRE BY TYPE

Fires are classified into four main groups mainly due to the type of material that is burning.

Class ‘A’

These are fire involving solid materials normally of organic nature (compounds of carbon), in which combustion generally occurs with the formation of glowing embers. Class 'A' fires are the most common and the most effective extinguishing agent is generally water in the form of a jet or spray.

Class 'B'

These are fire involving liquids or liquefiable solids. For the purpose of choosing effective extinguishing agents. Flammable liquids may be divided into two groups:

- i. Those that are miscible with water and
- ii. Those that are immiscible with water

Depending on i and ii, the extinguishing agents include water spray, foam, light water, vaporizing liquids, carbon dioxide and dry chemical powders. Examples of these materials are alcohol, kerosene, gasoline, beeswax, tar etc.

Class 'C'

These are fire involving gases or liquefiable gases in the form of a liquid spillage, or a liquid or gas leak and these include methane, propane, butane, etc. Foam or dry chemical powder can be used to control fires involving shallow liquid spills. (Water in the form of spray is generally used to cool the container).

Class 'D'

These are fires involving metals. Extinguishing agents containing water are ineffective and even dangerous. Carbon dioxide and the bicarbonate classes of dry chemical powders may also be hazardous if applied to most fires. Powered Talc, soda ash, limestone and dry sand are normally suitable for Class 'D' fires. Special fusing powders have been developed for fires involving some metals, especially the radioactive ones.

Electrical Fires

It is not considered that electrical fires constitute a class, since any fire involving or started by electrical equipment must in fact be a fire of Class A, B, C or D. The normal procedure in such circumstances is to cut off the electricity and use the extinguishing method appropriate to what is burning. Only when this cannot be done with certainty will special extinguishing agents be required which are

non-conductors of electricity and non-damaging to the equipment. These include vaporizing liquids, dry chemical powders and carbon dioxide.

EXTINGUISHING MEDIA

Water

Despite the many new techniques which have come to the assistance of firefighters, water is still the most efficient, cheapest and most readily available medium for extinguishing fires of a general nature. It is caused by fire brigades although the methods of application have undergone a number of improvements. Steam in large quantities can be used to smother a fire and in situations where it is available, eg. onboard ships or in factories, it can be used in fixed installations.

Foam

Some of the most dangerous substance so far as fire risk is concerned are liquids having a specific gravity lower than that of water. When water is applied to the burning surface of such liquids, it lowers the temperature briefly and then sinks below the surface where any further usefulness is lost. Except in the case of liquids such as mentholated spirits which mix freely with water and where dilation may occur to the point where combustion is halted. Foam which is relatively insoluble in most liquids and because of its light weight, floats on the surface of the liquid, forms a blanket capable of covering the surface of the burning liquid and so extinguishes the fire. It also forms a radiant heat barrier which is of importance in the extinction of oil and petrol fires.

Vaporizing Liquid

The halogenated hydrocarbons used for extinguishing fires have the property of vaporizing readily when heated and are therefore generally known as vaporizing liquids. They form a dense heavier than air cloud of non-flammable vapor which not only blankets a fire by the displacement of air, but also have the property of interfering with the chemical reactions within the flames of burning materials. This property is termed **inhibitory factor**.

If a certain portion of the extinguishing medium (eg. 16% chlorobromomethane is present), it interferes with the chemical reaction involving the oxygen and is stopped. The most common types are chlorobromomethane (CBM), bromochloridifluoromethane (BCF) and bromotrifluoromethane (BTM).

Carbon dioxide and Inert Gas

At normal temperatures, carbon dioxide is a gas 1.5 times as dense as air. It is easily liquefied and bottled where it is contained under a pressure of 51 bars (750lb/in). As a fire extinguisher, it acts in a manner similar to vaporizing liquids. When carbon dioxide is discharged, the liquid boils off rapidly as a gas, extracting heat from the surrounding atmosphere. The gas however extinguishes by smothering or reducing the oxygen content of the air. Materials which supply their own oxygen will continue to burn as well as those materials that tend to decompose carbon dioxide, eg. magnesium. Apart from these considerations, carbon dioxide is quick, clean, non-conductive of electricity non-toxic and does not harm most fabrics.

As an alternative to carbon dioxide, liquid nitrogen in bulk or in cylinders containing the gas will also produce the inert or smothering effect necessary for successful fire suppression.

Dry Chemical Powders

Water cannot be used on most fires involving burning metals. The chief method of extinction is by using dry chemicals which are stored in cylinders under pressure or can be ejected by the release of a gas under pressure (see extinguishers). The basis of most chemical powder is sodium bicarbonate. This, with the addition of a metallic stearate as waterproofing agent is widely used as an extinguishing agent.

Sand etc.

Dry earth sand, powdered graphite, talc, etc may be used on metal fire as a smothering agent.. Dry sand may also be used to prevent burning liquids, such as paints or oils from flowing down drains. Sand may also be used to confine shallow layers of such liquids so that foam or spray branches may be used. . on no account should sand be used for extinguishing fires in machinery, such as electric motors, since it may cause the entire machine to be dismantled for cleaning, even though the fire damage was small

Beating Out

Small fires in materials such as textiles etc. may often be extinguished by beating them out, or by rolling and screwing up the burning material tightly to exclude the air. Beating is also the method normally employed to extinguish heat, crop, grass and other similar fires in rural areas when water is not readily available.

Blanketing

Another method by which fires may be extinguished, especially for persons whose clothing may be on fire, is blanketing. The person should be laid down and covered or rolled in a rug, a coat, blanket etc. For dealing with fires in small utensils such as those containing cooking fats, the best method is to smother the fire with a **fire blanket** or a doormat which has been wetted first.