HAZMAT Articles

Chemistry of Fire

Introduction

A fire is a chemical interaction involving heat, fuel and oxygen. One of the simplest examples of fire is one where methane is the fuel.

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

The methane molecule consists of a carbon atom and four hydrogen atoms, while the oxygen molecule consists of two oxygen atoms. For a complete reaction, two oxygen molecules must react with one methane molecule to form one carbon dioxide molecule and two water molecules. This reaction also takes place with the release of energy in the form of heat and light.

Molecular Collisions

And while the chemical formula gives an overall picture; the reality is quite different in a flame.

However to appreciate what is taking place in a flame, we first need to consider these two components, oxygen and methane before any reaction takes place.

Consider they are therefore mixed together in the correct proportions of 2:1. For every litre of this mixture there will be:

27,000,000,000,000,000,000,000 or
(27 sextillion) molecules.[1]

Every second they will be involved in about

10,000,000,000,000,000,000,000,000,000,000 or
(10 nonillion) collisions.[2]

Each molecule will collide with another molecule at about 370,000,000 (370 million) times[3] a second and will travel about 0.00001 cm between each collision.

These numbers indicate two things:

1. There are a phenomenal number of collisions taking place in each litre
2. From the number of collisions, there is an unlimited potential for a reaction

However in spite of all this they will continue bumping into each other indefinitely, and another factor has to be introduced to initiate the reaction.

Activation Energy

As already implied, all these molecules are in motion. At room temperature, the average velocity of the oxygen molecules is about 450 m/sec (1620 kms/hr), while the lighter methane molecules will be travelling at about 636 m/sec (2290 kms/hr).

This is because oxygen has a molecular weight of 32, compared with 16 for methane. As they collide and rebound off each other, so the big oxygen molecules send the lighter methane molecules flying.

As the temperature is raised, so the velocity of the molecules bumping into each other increases. This bumping increases in violence until a point is reached where they no longer bump, but crash.

The amount of energy required to raise the temperature from bump to crash is known as the activation energy.

It may take the form of only a tiny spark sufficient to energise just a few localised molecules; however the heat released from the initial reaction is sufficient for it to spread right throughout the mixture

The Reaction Mechanism

The term crash is apt, since the subsequent reaction involves fragmentation of the methane molecule to form transient highly reactive molecular fragments or free atoms known as free radicals.

These free radicals can continue to propagate the reaction by creating further fragments, which in turn begin to combine to form product molecules, and in the process, releasing energy. So instead of a simple overall equation, it is something more like this:

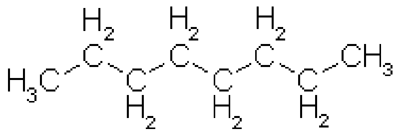
CH_4	+	O_2	→	CH_3*	+	H*	+	O_2
CH_4	+	OH*	→	CH_3*	+	H_2O		
CH_4	+	H*	→	CH_3*	+	H_2		
CH_4	+	O**	→	CH_3*	+	OH*		
O_2	+	H*	→	O**	+	OH*		
CH_3*	+	O_2	→	CH_2O*	+	OH*		
CH_2O	+	OH*	→	CHO*	+	H_2O		
CH_2O	+	H*	→	CHO*	+	H_2		
CHO*	+	H*	→	C	+	H_2O		
C	+	O**	→	CO				
H_2	+	O**	→	H*	+	OH*		
H_2	+	OH*	→	H*	+	H_2O		
CHO*	+	O**	→	CO	+	OH*		
CHO*	+	OH*	→	CO	+	H_2O		
CHO*	+	H*	→	CO	+	H_2		
CO	+	OH*	→	CO_2	+	H*		

Some of the molecules and radicals formed are:

CH_3*	Methyl radical
CHO*	Aldehyde radical
OH*	Hydroxyl radical
O**	Oxygen radical
H*	Hydrogen radical
H_2	Hydrogen molecule
CH_2O	Formaldehyde
CO	Carbon monoxide
C	Free carbon (soot)

These are few of the many possible reactions that may occur. In fact there are about 100 possible variations.

And if this is the simplest hydrocarbon, consider how many variations might be possible for a hydrocarbon such octane with 8 carbon atoms and 18 hydrogen atoms.



In other words the reaction process becomes extremely complex.

This reaction train however, illustrates what takes place in all flame reactions:

- Fragmentation from collisions
- Formation of free radicals
- Recombination to form reactions
- Release of heat energy.

This flame reaction can also explain several other factors about fires. They are:

1. Flame colour
2. Smoke formation
3. Irritant properties of smoke
4. Toxic gases

Flame Colour

A pale transparent blue flame is often seen in gas flames either fuel lean or mixed in the correct proportions. It may also be seen on certain parts of a candle or wood fire. This colour is associated with the energy release in that part of the reaction train where the hydroxyl radical (OH*) is formed and when carbon monoxide (CO) is being converted to carbon dioxide (CO_2).

The opaque yellow however, is far more common, in particular in oxygen deficient or fuel rich flames, in which free carbon atoms start to form. These carbon atoms come together to form microscopic soot particles of the order of 10-100 nm diameter (I nm = 0.000000001 metres), and they act exactly like burning charcoal which gives a yellow colour as it smoulders during combustion.

The nett effect of all these glowing particles, is to give the flame its characteristic yellow luminous colour.

Smoke Formation

Soot particles may be consumed in the region of the flame, or if there are sufficient numbers, they can escape from the burning zone where they continue to grow forming larger particles which we call "smoke".

It should be said here that smoke can also consist of tiny droplets, liquids in the form of tars or high molecular weight liquids which are distilled from smouldering combustion of solid materials such as cigarettes.

Irritant Properties of Smoke

One of the free radicals that form during combustion is aldehyde. They can either form free aldehyde molecules such as acrolein, or they can become absorbed onto soot particulates.

In either form they are extremely irritating to the nose, throat, lungs and eyes. It is the aldehydes which give smoke its particularly noxious properties.

Toxic Gases

Once again, from the chain reaction it can be seen that these are three reactions involved with the formation of carbon monoxide (CO), whereas there is only one involved in its consumption. At least for methane it can be seen why carbon monoxide can be easily formed in an oxygen deficient flame, and maybe this will explain why tragedies have occurred such as with unflued hot water gas heaters.

By way of final comment however, toxic gases such as hydrogen chloride, sulphur dioxide and nitrogen oxides, can be produced from the complete combustion of certain chemicals. This issue is another topic which we will deal with in a future article.

Man's Death Caused by Faulty Gas Heater

Thirteen people have died in Western Australia since 1973 due to a fault in a gas hot water system. One such fatality occurred in February, 1991, involving a 25 year old man.

The man died from acute carbon monoxide toxicity after having a shower at his Perth boarding house.

Hot water to the bathroom was supplied by a gas water heater which was fixed to a corner of the internal wall. The heater was connected to a flue which rose through the bathroom ceiling to the roof above.

Perth Coroner David McCann handed down a verdict of accidental death, but stressed the need to service gas hot water systems regularly.

He said advice should be sought if the flames in the burner were yellow, not blue.

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[1] The mathematical convention for writing such big numbers is to express them as multiples of 10. For example, $2.7x10^{22}$ becomes 2.7 multiplied by 10 with 21 noughts

[2] Or $1x\ 10^{31}$ or simply 10^{31}

[3] Or $3.7x10^{8}$

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