CHEMISTRY IN FIRE FIGHTING

There are three requirements for starting and maintaining a fire:

- Fuel - wood, paper, oil, textiles, flammable gases etc.
- An oxidant - usually oxygen fron the air, but may be a chemical in contact with the fuel
- Heat - the temperature must be greater than the ignition temperature of the fuel

There are three approaches to putting out a fire:

- Starvation - cutting off the fuel supply
- Smothering - separating the fuel from the oxidant
- Cooling - lower the temperature, usually with water

There are five main types of fire extinguishers: water, foam, carbon dioxide, BCF (or Halon 1211) and dry powder. The choice of extinguisher depends on the type of fuel, and the whether there is danger from live electrical equipment.

INTRODUCTION

In a fire a fuel, the material being burnt, is undergoing a rapid oxidation with the evolution of heat and light. The phenomenum is called combustion and oxygen from the air, O_2, is by far the most common oxidant, but oxidising chemical substances such as nitrates, chlorates and peroxides can also be the oxidant and should not be stored next to combustible materials. The chemistry occurring in a flame is very complex, and involves free radical chain reactions, and the overall reaction is very exothermic. When organic compounds undergo complete combustion the major products are carbon dioxide and water, but normally in fires complete combustion does not occur and fine solid material, smoke, and other gaseous material is given off.

Much common matter can burn, but fortunately a high temperature is required to initiate the reaction, the minimum required temperature being called the ignition temperature. However the oxidation reactions are highly exothermic and the heat given out can maintain or increase the temperature. The higher the temperature the faster the reactions. If heat is produced in the reaction faster than it can be dissipated to the surroundings a thermal explosion may take place.

The "flash point" of a fuel is the minimum temperature to which it must be heated for its vapour to ignite in the presence of air with a free flame; some examples - methanol, 11^oC; diethyl ether, -45^oC; *n*-hexane, -21^oC; benzene, -11^oC. The "ignition temperature" of a gas is the minimum temperature at which a combstible mixture of it and air ignites in the absence of a flame; some examples - hydrogen, 580^oC; petrol, 550^oC; town gas, 600-650^oC.

Heat from a fire can be transferred by three methods, conduction, convection and radiation. In conduction heat is transferred by passing kinetic energy down a temperature gradient through direct contact of material. This is not normally an important process by which fires spread. The most important is convection in which heat is transferred by the movement of matter itself, in a fire matter being in the gaseous state. However radiation is also important, this being the transfer of heat by emission of infra-red radiation from the material in the flames and conversion of this radiation back to heat on absorption by another body. Radiation as well as convection can prevent one from getting close to the seat of a fire. A fire can spread by both methods, raising the temperature of other matter to its ignition temperature.

Fires are classified according to the nature of the material being burnt (the fuel), and whether live electrical equipment is present. The method of fighting the fire depends on the fuel and on the electrical hazards. In general the methods involve removing the fuel (starvation), separating the fuel from the oxygen (smothering), or lowering the temperature (cooling).

CASSIFICATION OF FIRE

Fires are classified by the nature of the fuel and whether electrical equipment is involved.

New Zealand has adopted the British Standard Classification of Fires:

Class A:	Involving solids, usually organic. Wood, paper, textiles, hay, grain, plastics, sugar,coal leather, etc. come under this class.
Class B:	Involving flammable liquids or liquifiable solids. Petrol, oils, fats, kerosine, turpentine, wax, varnish, paint, alcohols, acetone, organic solvents, etc. come under this class.
Class C:	Involving flammable gases. CNG (methane), propane, butane (LPG), hydrogen. carbon monoxide come under this class.
Class D:	Involving combustible metals. Sodium, magnesium, lithium, aluminium come under this class.
Class E:	Electrical fires. Fires complicated by the presence of electricity.

In the American system, also adopted by Australia class C fires are those involving live electrical equipment.

The nature of the fuel and electrical hazards dictate the method of fighting the fire. **Table 1** summarises the different kinds of extinguishers. The rating of differnt kinds of extinguishers (ie what types of fires they should be used on) have come from extensive testing on real situations, taking into account possible undesirable side effects.

CHEMISTRY OF EXTINGUISHERS

Water

The function of water is simply to cool the burning fuel. Water is cheap, and can be directed on to the seat of a fire by a high pressure. Buildings are provided with sprinklers which operate automatically if the temperature rises above a certain value. Risers are verticle pipes in buildings to which a high pressure water supply may be attached at ground level. Many buildings have fire hose reels connected to the water supply ready for an emergency.

The cooling action of water is mainly due to its heat of vaporisation. The molar heat capacity of liqid water, $C_{p,m,}$ is 75 J K^{-1} mol^{-1} and its specific heat capacity, c_p, is 4.18 J K^{-1} g^{-1}. Thus a litre of water would absorb 313 kJ of heat in going from 25°C to 100°C. But its molar heat of vaporisation,$\Delta_{vap}H(H_2O,l)$, is 42 kJ mol^{-1}, or a litre of liquid water at 100°C would absorb 2300 kJ on completely vaporising.

Table 1 - Methods of fire extinction

Class	Extinguisher	Method	Remarks
A	Water Foam ABC dry powder	Cooling Smothering "	Lower temperature Blanket cuts off air from fuel
B	Dry powder foam, CO_2, BCF	Smothering "	Blanket cuts off air Possible reignition
C	Dry powder CO_2, BCF Water fog	Smothering " Cooling	Blanket cuts off air Possible reignition Special equipment
D	Special dry powders or sand	Smothering	Water would produce H_2 and an explosion
E	Dry powder CO_2, BCF	Smothering "	Blanket cuts off air Possible reignition

It is informative to consider how much heat is given out by burning wood. Wood is largely made up of celluose, a polymer of glucose. The molar heat of combustion of glucose, $\Delta_c H(C_6H_{12}O_6)$, is -2803 kJ mol^{-1}, and from this it is easily calculated that 1 kg of glucose would release 15 600 kJ of heat on complete combustion. Thus about seven litres of water would be needed to absorb the heat given out by a kilogram of burning wood.

Water should only be used on class A fires, solid fuel. Most organic liquids have a lower density than water and will float on top and keep burning. Spattering of drops of burning liquid can also occur. Where electrical equipment is involved water can cause shorting resulting in sparks which could ignite material, and in material becoming electricaly live. Reactive metals like sodium react vigorously with water at ambient temperature to produce combustible hydrogen, and less reactive metals such as aluminium also react in highly exothermic reactions at higher temperatures:

$$2Al(s) + 6H_2O(g) \rightarrow 2Al(OH)_3 + 3H_2(g)$$
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

The simplest water fire extinguisher is a hose connected to a high pressure water supply. Fire hoses must be able to deliver 14 litres per minute and the pressures required for this are 225 kPa for 13 mm hose and 150 kPa for 19 mm hose.

Water type portable extinguishers used to be activated by turning them upside down, this causing sulfuric acid to mix with sodium bicarbonate releasing carbon dioxide to provide the necessary pressure. These are now banned. Modern extinguishers are simply pressurised with enough nitrogen gas to drive out the water or have a cartridge containing a very volatile liquid, usually carbon dioxide. To activate the extinguisher the cartridge is opened in some way and the evaporating liquid provides the necessary pressure to drive out the water.

Foams

A foam is a stable mass of air filled bubbles and has a lower density than oil, gasoline or water. Surfactants which give water surface properties suitable for foam formation are dissolved in water, and when pressure is released on a mixture of the solution and air a foam is formed.

Foams work by:

- blanketing the fuel surface smothering the fire
- separating the surface of the fuel from the flames
- cooling the fuel and adjacent surroundings
- suppressing the release of flammable vapours that can mix with air

A variety of surfactants, based on fluorocarbons, hydrocarbons, hydrolysed protein and solvents are used, the particular formulation varying with the class of fire. They are used on both class A and class B fires.

Carbon dioxide

Carbon dioxide has a triple point (the pressure and temperature where gas, liquid and solid forms co-exist) of 5.11 atm and -57^{o}C compared that of water of 6 x10^{-3} atm and 0^{o}C. Thus while ice melts to liquid water at 0^{o}C at 1 atm pressure and then has to be heated to 100^{o}C for it to boil, solid carbon dioxide (dry ice) sublimes, that is goes directly from solid to gas at atmospheric pressure, and this occurs at -78^{o}C. However if carbon dioxide gas at 25^{o}C is compressed to a pressure above 67 atm it liquifies. This makes carbon dioxide an ideal material for fire fighting as it can be kept in liquid form in pressurised cylinders, and when the valve is opened rapid evaporation occurs giving a cloud of very cold carbon dioxide gas, the rapid expansion causing rapid cooling, due to the Joule-Thomson effect. Further as carbon dioxide is denser than air it can form a blanket over burning material. It is the smothering effect and not the cooling effect which is most important. And of course CO_2 cannot be further oxidised.

CO_2 extinguishers should not be used on class A fires as the blast can disperse fine burning solid particles or drops of liquid and thus spread the fire. Further they have insufficient cooling effect on burning solids.

BCF (Halon 1211)

BCF or Halon 1211is CF_2ClBr, the numbers being the number of carbon, fluorine, chlorine and bromine atoms respectively per molecule. Of course Halon 1211 does not undergo combustion itself. Its boiling point is -4^{o}C and thus it is easily liquified by pressure at room temperature and it has a vapour pressure of 2.3 atm at 20^{o}C Its vapour density is 16.5 g L^{-1} compared with 1.1 g L^{-1} of CO_2. Thus it has excellent properties for smothering a fire, and comes out from its container with much less pressure than CO_2 and is not so likely to disperse a fire. Smothering is not the only way in which they work. They act as scavengers of free radicals in the flame, terminating the propagating chain reactions. (In a sense they are anti-oxidants). It can be suitable for all classes of fire.

BCF are scheduled to be removed in light of the Montrial protocol on the ozone layer. However dispensations will probably be given for aeronautical, marine and shipping use until viable alternatives are found.

Dry powders

In addition to sand there are are two main dry powders used in fire fighting. These are regular dry chemical for classes B or C fire, the major constituent being sodium bicarbonate ($NaHCO_3$), and multi purpose dry chemical for A,B and C class fires, the major constituent being mono-ammonium phosphate ($NH_4H_2PO_4$). The latter has now almost completely (99%) replaced the former.

The powders are driven out of their containers by either a pressurised nitrogen or with a CO_2 cartridge as for water extinguishers.

Sodium bicarbonate melts and decomposes at 270°C on heating. The equilibrium reaction

$$2NaHCO_3 \ \_ \ H_2O + CO_2 + Na_2CO_3$$

is endothermic in the forward direction; $\Delta_r H = 91$ kJ mol^{-1}. Being endothermic the equilibrium constant increases with temperature. It changes from 1.8×10^{-5} at 25°C to 4×10^{8} at 427°C. Thus at the temperature of the fire heat is absorbed by the bicarbonate and carbon dioxide and water are produced. Thus sodium bicarbonate works by absorbing heat from the fire and giving products which would help smother it. Na_2CO_3 itself melts at 851°C.

Data books give the melting point of mono-ammonium phosphate ast 190°C, without mention of decomposition. To investigate further how this compound works the author of this article heated some $NH_4H_2PO_4$ in a crucible with a bunsen burner. As soon as it has melted it appeared to "boil", great blister-like bubbles formed and these are quite big when they burst. There was no smell of ammonia. The bubbling ceased after a short while and a viscous liquid forms. He next studied the compound in a differential scanning calorimeter (DSC), which records the amount of heat absorbed as the temperature is steadily increased. When a solid melts it shows a sharp peak at the melting point. The $NH_4H_2PO_4$ showed a large absorption of heat at the melting point, but a continuous absorption up to 350°C. Up to this stage

260 J g^{-1} of heat was absorbed. It showed two further small absorptions at 410-430 and 500-580°C, suggesting further chemical changes. On cooling to25°C a white solid formed, but on reheating this did not absorb heat or melt.

The most likely explanation of all this is that the anion of the salt undergoes a polymerisation driving off water, the first step being:

$$2(HO)_2PO_2^- \rightarrow (HO)PO\text{-}O\text{-}PO(OH)^{2-} + H_2O$$

Thus this compound also works by melting at a relatively low temperature, absorbing a large amount of heat and producing water, with the liquid smothering the fire efficiently.

Small home and vehicle fire extiguishers are dry powder. The smallest CO_2 extiguisher contains 2 kg of CO_2, and because the cylinders have to withstand much higher pressures than dry powder they are bulky and expensive. 1 kg of powder is as efficient as 4 kg of CO_2.

FIRE DETECTION AND PREVENTATION

Early detection of fire

Early detection of fires allows them to be fought before they gain in intensity and spread from their place of origin. Sprinklers which are automatically activated by heat can put out a fire in its early stages.

Fire detectors which raise an alarm can work on three principles- heat, light or smoke detection.

With heat there are several types. They can be activated by the melting of a metal component, by movement of a bimetallic strip, of by change in electrical conductance of a material above a certain temperature.

With light either infra-red or ultra-violet light is detected; they "see" the flame and activate an alarm.

Smoke detectors are of two types, ionisation chamber and optical. The former contain a very small radioactive source, usually Americium-241, a 5.5 MeV α-particle emitter. When smoke enters a chamber the emitted radiation from the source ionises the particles increasing the conductance of the gas and allowing a current to flow between electrodes, this current activating the alarm. In optical detectors smoke particles interrupt a continuous light beam by absorption or scattering of light.

Materials

Fire can be prevented by using non-combustible materials where possible. In silicate materials elements other than oxygen are already in their highest oxidation states. Thus they do not burn and of course are widely used in construction - concrete, tiles and glass.

Internal walls are often constructed of gypsum plaster board. With a fire in one room the plaster board absorbs heat, every kilogram of plaster releasing 200 g of water.

$$CaSO_4.2H_2O \rightarrow CaSO_4.\tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O$$

This water acts as a heat barrier, ensuring that the temperature behind the plaster board does not rise appreciably above the boiling point of water and thus preventing the fire from crossing over the board.

Written by John Packer with the help of Brett Neilsen of Actron Fire Services who provided advice and information. This included material of the NZ Fire Protection Association and advertising brochures of suppliers.